

Review Article

Polymeric Gas-Separation Membranes for Petroleum Refining

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Polymeric gas-separation membranes were commercialized 30 years ago. The interest on these systems is increasing because of the simplicity of concept and low-energy consumption. In the refinery, gas separation is needed in many processes such as natural gas treatment, carbon dioxide capture, hydrogen purification, and hydrocarbons separations. In these processes, the membranes have proven to be a potential candidate to replace the current conventional methods of amine scrubbing, pressure swing adsorption, and cryogenic distillation. In this paper, applications of polymeric membranes in the refinery are discussed by reviewing current materials and commercialized units. Economical evaluation of these membranes in comparison to traditional processes is also indicated.

1. Introduction

Implementation of membrane systems is growing in the industry because of the unique features that the membrane can provide [1]. Compared to other separation processes, the membrane is simple to install and requires minimum supervision [2]. Furthermore, it occupies less space and does not have moving parts; thus it needs almost no maintenance [3]. In addition, it operates with low energy and is considered as an environmentally friendly technology because it does not emit gases nor work with solvents [4]. The membrane is also easy to scale up for better commercialization [5].

Based on the material, the membranes are categorized into metallic, inorganic, and polymeric [6]. Metallic membranes made of platinum or palladium have excellent performance but the cost of precious metals greatly influences the membrane selection. Inorganic membranes are good alternatives and they have better chemical stability with lower fabrication cost [7]. Nevertheless, high temperature of 200 to 900°C is needed to operate inorganic membranes [2]. Nowadays, polymeric membranes dominate the industry because of the outstanding economy and competitive performance [8]. The membranes can be operated at ambient temperature and they have good mechanical and chemical properties [9].

Revolution of polymeric membranes started in 1960s when Loeb and Sourirajan developed a membrane made

from cellulose acetate for water desalination by reverse osmosis [10]. The thin membrane of 0.2 μm was supported on a porous substrate and it was capable of converting seawater to potable water. They found later that cellulose acetate membrane can be used for gas separation as well [11–13]. Afterwards, Stern et al. in 1969 studied the diffusion of different gases such as helium and nitrogen in polyethylene membrane at high temperatures and this opened the opportunity for more research in this area [14].

The first large scale membrane was developed by Permea (Air Products) in 1980 for separation of hydrogen. The hollow fiber membrane was made of polysulfone and it was designed to separate hydrogen from methane [15, 16]. In 1983, Cynara and Separex also manufactured a cellulose acetate membrane but for carbon dioxide separation from methane [16]. A few years later, nitrogen production from air using membranes was introduced [17]. The applications of membrane were expanded hereafter to cover removal of hydrogen sulfide from methane, removal of volatile organic compounds (VOCs) from air, oxygen enrichment, and air dehydration [2]. Today, the membrane is used in the refinery to purify natural gas by removing acid gases such as hydrogen sulfide and carbon dioxide from methane [17]. It is also implemented in many hydrotreatment processes to recover hydrogen from hydrogen sulfide [18]. Adjustment of hydrogen-to-carbon monoxide ratio in syngas to meet

TABLE 1: Processes where membrane technology is implemented [25–27].

Process	Gas to be separated from
Natural gas purification	H ₂ S/CH ₄
	CO ₂ /CH ₄
	H ₂ O/CH ₄
	C ₃₊ /CH ₄
Hydrocracker	H ₂ /light hydrocarbons
Hydrotreatment	H ₂ /H ₂ S
Steam-methane reforming	H ₂ /CO
Ammonia plant	H ₂ /N ₂
Polyolefin plant	VOCs/N ₂
	VOCs/Air
Refinery waste-gases	H ₂ from other gases
	CH ₄ from other gases
	CO ₂ from other gases

the requirement of petrochemical feedstock can be done using the membranes. Oxygen enrichment in furnaces for better oxidation is also practiced in many processes [19]. Applications of the membrane for petroleum industry and the corresponding separation gases are presented in Table 1. In this review, uses of these membranes are discussed in detail including the membrane materials, commercialized systems, and comparison with traditional separation methods. In the following section, transport mechanism of these membranes is given.

2. Transport Mechanism in Polymeric Membranes

For gas applications, the polymeric membranes are usually made from a thin, dense layer [17]. To enhance the mechanical properties, the dense layer is supported on a porous substrate [20]. The widely accepted theory for the transport mechanism is based on solution diffusion model [21]. This model consists mainly of three steps: (1) absorption of molecules on the polymer surface, (2) diffusion of molecules inside the polymer, and (3) desorption of molecules on the low-pressure side [9]. The driving force is the pressure gradient across the membranes, and each compound has different absorption and diffusion rate. The membrane performance can be evaluated by the measuring the permeability and selectivity of gases. The permeability is the product of absorption and diffusion coefficients as follows:

$$P = K_i D_i, \quad (1)$$

where K_i is the sorption coefficient and D_i is the diffusion coefficient. The unit of permeability is Barrer that equals 10^{-10} (cm³/cm·s·cmHg). Experimentally, the permeability can be calculated based on the flux [22]:

$$P = J \frac{\Delta l}{\Delta P}, \quad (2)$$

where J is the flux (volume flow rate per unit area), Δl is the membrane thickness, and ΔP is the pressure difference across

the membrane. On the other hand, selectivity (α_{ij}) refers to permeability ratio of two gases:

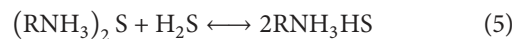
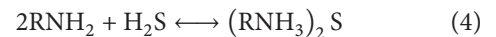
$$\alpha_{ij} = \frac{P_i}{P_j}. \quad (3)$$

The polymers are classified based on the structure to rubbery and glassy. Rubbery polymers have the ability to return to their original shape once stretched while glassy ones do not [23]. Furthermore, rubbery polymers tend to have higher permeation but lower selectivity and this is because the transport mechanism is controlled by absorption rather than diffusion [24]. Conversely, glassy membranes have higher selectivity but low permeation because they are diffusion limited. This indicates that there is a trade-off between permeability and selectivity and it is difficult to have a polymer having both characteristics. In the following section, uses of membranes for hydrogen sulfide separation, carbon dioxide recovery, hydrogen purification, air separation, gas dehydration, organic vapors recovery, and liquefied petroleum gas are discussed in detail.

3. Removal of Hydrogen Sulfide

Hydrogen sulfide is well known for its rotten-egg smell even in low concentration of parts per billion (ppb) [28]. The gas is emitted naturally from volcanoes and can be formed during the decomposition of organic matters [29]. The gas is also found in natural gas and it is called sour gas if hydrogen sulfide concentration is above 4 ppm [30]. Because the gas is corrosive and can cause damage to pipelines, the sale gas should not have more than 4 ppm of hydrogen sulfide and 2 mol% of carbon dioxide [31]. Hydrogen sulfide is a man-made gas too, and dehydrosulfurization process (to remove sulfur compounds from fuel) is considered as the main source [32].

3.1. Current Technologies. There are three methods for hydrogen sulfide removal: (1) physical/chemical absorption, (2) adsorption, and (3) membranes. Chemical absorption by amine scrubbing is the dominant process for hydrogen sulfide separation from natural gas [33]. The process can remove carbon dioxide as well and the treated stream can have lower than 4 ppm of hydrogen sulfide. The technology is based on the absorption of hydrogen sulfide and then the reaction with amine by [34]:



The solvent (mainly monoethanolamine, MEA) can be regenerated by increasing the temperature or reducing the pressure. In spite of the high efficiency of amine scrubbing, there are some drawbacks, which are (1) high capital investment, (2) massive energy required to regenerate the solvent, (3) oxidation of amines which can cause foaming or flooding, and (4) requirement of special alloys to withstand the solvent corrosivity [35–39].

Physical absorption by methanol is another way to remove hydrogen sulfide from natural gas. The process is called Rectisol (licensed by Linde Group and Air Liquide) and it can remove carbon dioxide, carbonyl sulfide, and mercaptans [40]. At lower temperature, the absorption capacity of methanol increases and that is why the process operates at -30 to -70°C [41]. It should be mentioned that methanol can be replaced with other solvents like polyethylene glycol (Selexol process) or potassium carbonate, but methanol has better absorption capacity and higher regeneration rate [35, 37, 42, 43]. Compared to amine scrubber, methanol absorption has better removal efficiency but at the expense of capital and operating costs [39].

Adsorption by carbon molecular sieve (CMS) is another technique to separate hydrogen sulfide from methane. The concept is based on adsorption of hydrogen sulfide on the carbon surface at high pressure [44]. Activated carbon has large surface area with high porosity, and the capacity can reach 150 mg of hydrogen sulfide to one gram of carbon [45]. The desorption (regeneration) step can be performed by reducing the pressure or increasing the temperature to 288 – 316°C [46]. Unfortunately, CMS cannot be used to remove high content of hydrogen sulfide of more than 1.5 mol% due to the lower adsorption capacity compared to amine scrubber [47]. Furthermore, carbon suffers from low mechanical properties making it unstable at high content of hydrogen sulfide [48].

The membrane technology can provide an alternative solution for removal of hydrogen sulfide. Unlike amine scrubbing or methanol absorption, the membrane does not require a solvent to operate, and this will cut down the cost of purchasing and disposing of the solvent. The membrane has also an advantage over CMS as it can operate with feeds containing up to 16 mol% of hydrogen sulfide [31]. In the following section, performances of different membrane materials are reviewed for removal of hydrogen sulfide from natural gas.

3.2. Membrane Materials. Cellulose acetate is widely used for hydrogen sulfide removal from natural gas [49]. This material is extracted from wood pulp and it has a hydrogen sulfide permeability of 2.13 Barrer with hydrogen sulfide to methane selectivity ($\alpha_{\text{H}_2\text{S}/\text{CH}_4}$) of 19.4 [50]. The material was tested with natural gas containing heavy hydrocarbons, and, unexpectedly, the selectivity dropped significantly due to the penetration of sorption sites [50, 51].

Polydimethylsiloxane (PDMS) gives a superior hydrogen sulfide permeability of 2750 Barrer, and this high permeability is related to the rubbery structure but at the expense of selectivity of 0.98 [17]. To enhance the membrane durability under the harsh environment of hydrogen sulfide, cross-linking was introduced [52]. It helps in reducing the polymeric chain mobility and this increases the glass transition temperature. As a result, resistance to plasticization and aging is improved [17]. In addition, cross-linking generally affects the segmental mobility of the polymer making the diffusion process rely more on the size and shape of the molecule to be separated and this improves the selectivity but reduces permeability [53]. In 1997, Chatterjee et al. developed

a copolymer consisting of ether, urethane, and urea and it was prepared by the two-step polycondensation technique. In the first step, methylene bis-(4-phenyl isocyanate) (MDI) is added to polyethylene glycol (PEG) with the use of dimethyl sulfoxide (DMSO) as a solvent. In the second step, a chain extender (1,2-diaminoethane) was added to the solution to form poly(ether-urethane-urea) (PUU) [50]. Unlike membranes made of single polymer, PUU consists of two segments: soft and hard. The hard segment has a glassy state and acts as a filler while the soft segment is rubbery giving the membrane elasticity and flexibility [54]. PUU was tested for hydrogen sulfide separation from methane, and the permeability was 199 Barrer with outstanding selectivity of 74 [55].

Pebax is another copolymer made of polyether and polyamide. The term “Pebax” stands for polyether-block-amide and it was manufactured by Arkema [56]. There are many grades of Pebax and each grade depends on the concentration of polyether and polyamide. For example, the popular Pebax 1074 is made from 73 wt% polyether and 27 wt% polyamide [57]. Hydrogen sulfide permeability of this material reached 888 Barrer with selectivity of 21 [50]. Permeability and selectivity of various membrane materials is given in Table 2. The choice of material depends strongly on the composition of the feed gas and whether permeability or selectivity is the first priority.

3.3. Case Studies and Economical Evaluation. Membrane Technology and Research (MTR) is one of the companies for manufacturing gas-separation membranes. SourSep (by MTR) is a membrane system to convert sour gas to sweet gas by the removal of hydrogen sulfide and it is expected to be based on Pebax. The unit was installed in an oil well in a remote area to treat wellhead gas so it can be used as a fuel [26]. Indeed, the system reduced hydrogen sulfide content from 3,400 ppm to less than 100 ppm. The feed pressure was at 51 bar and volume flow rate was $2001\text{ Nm}^3/\text{h}$. Compared to amine scrubber, the membrane system achieved lower capital and operating costs. The capital cost covers the membrane material, frame, heat exchanger, and vacuum pump while operating cost refers to energy used by compressors and pumps [17]. FuelSep is another system developed by MTR and designed to meet the quality of fuel gas by removing hydrogen sulfide and other impurities such as carbon dioxide, nitrogen, and heavy hydrocarbons [2].

Universal Oil Products (UOP) Separex membrane is based on cellulose acetate and designed to treat gases containing hydrogen sulfide up to 20 mol% [63]. The system was commercialized for nearly 30 years. The system was installed in an off-shore gas reservoir containing 15 mol% of hydrogen sulfide. The feed volume was $588,586\text{ Nm}^3/\text{h}$ of gas at 92 bar. The membrane was capable of reducing hydrogen sulfide content to 70 ppm in the treated gas.

An economical study was conducted by Bhide and Stern for natural gas treatment using membranes and amine scrubbing [64]. The membranes were based on cellulose acetate, and content of hydrogen sulfide varied from 0.1 to 1 mol%. The feed also contained carbon dioxide of 5 to 40 mol%. Feed flow rate was $41,201\text{ Nm}^3/\text{h}$ at 54 bar. The

TABLE 2: Permeability and selectivity of different polymeric membranes for removal of hydrogen sulfide from natural gas.

Material	$P_{\text{H}_2\text{S}}$ (Barrer)	$\alpha_{\text{H}_2\text{S}/\text{CH}_4}$	T ($^{\circ}\text{C}$)	P (bar)	Ref.
Polyamide (Torlon)	0.2	14.8	35	4.5	[58]
Cellulose acetate	2.1	19.4	35	10	[50]
Polyamide (6F-PAI-2)	2.7	12	35	4.4	[59]
Polyamide (6F-PAI-3)	4.6	11	35	4.4	[59]
Polyamide (6F-PAI-1)	6.4	8.5	35	4.4	[59]
Polyether-block-amide (Pebax 6333)	37.8	20	35	10	[50]
Polyether-urethane-urea (PUU4)	199	74	35	10	[50]
Polyether-urethane-urea (PUU1)	239	21	35	10	[50]
Polyether-block-amide (Pebax 1657)	248	50.6	35	10	[50]
Polyether-urethane-urea (PUU3)	271	58	35	10	[50]
Polyvinyltrimethylsilane (PVTMS)	350	1.59	35	$\Delta P = 1$	[60]
Polyether-urethane-urea (PUU2)	613	19	35	10	[50]
Polyether-block-amide (Pebax 3533)	888	21	35	10	[50]
Dimethyl silicone rubber	1000	10.5	25	1	[61]
Polydimethylsiloxane (PDMS)	2750	0.98	25	3	[62]

processing cost (defined as the capital and operating costs over production volume) was calculated to achieve less than 4 ppm of hydrogen sulfide and 2 mol% of carbon dioxide. It was found that the processing cost in a membrane system is a function of the concentration of hydrogen sulfide and carbon dioxide; the more the content, the higher the cost, but in amine scrubbing the processing cost was dependent on carbon dioxide content only. For a stream containing 1 mol% hydrogen sulfide and 30 mol% carbon dioxide, the processing cost for a membrane system was 4.87×10^{-7} $\$/(\text{Nm}^3/\text{h})$ compared to 6.34×10^{-7} $\$/(\text{Nm}^3/\text{h})$ for amine absorption. Therefore, the use of membrane resulted in 23% reduction in processing cost. However, if the feed was changed to 21 mol% carbon dioxide and 5000 ppm hydrogen sulfide, both systems had a processing cost of 4.87×10^{-7} $\$/(\text{Nm}^3/\text{h})$. Amine scrubbing showed lower processing cost of 1.99×10^{-7} $\$/(\text{m}^3/\text{h})$ if the feed contained 5% carbon dioxide and 1000 ppm hydrogen sulfide while the membrane gives 3.54×10^{-7} $\$/(\text{Nm}^3/\text{h})$.

4. Carbon Dioxide Capture

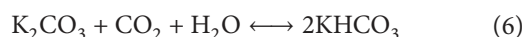
The atmosphere consists before of 315 ppm carbon dioxide (1955 reading), but because of the transportation and industrial activities, the content is increased to 390 ppm causing global warming and increase in the climate temperature [65]. The petroleum industry accounts for 8% of carbon dioxide emission and in order to reduce the impact, carbon capture from flue gases is necessary [66].

In the refinery, separation of carbon dioxide is required in the following processes: natural gas treatment, syngas production (hydrogen and carbon monoxide), and combustion. Today, wells are injected with a high-pressure carbon dioxide stream to enhance the oil recovery, and this results in production of natural gas with high amounts of carbon dioxide [67]. Removal of this carbon dioxide is essential because the gas is corrosive and can damage pipelines [68]. The maximum

content of carbon dioxide in commercial natural gas should not exceed 2 mol% [31]. Furthermore, the flue gases of most combustion processes (furnaces) have amounts of carbon dioxide and nitrogen. Carbon dioxide capture is necessarily before releasing this gas to the atmosphere [69].

4.1. Current Technologies. Most of the techniques for hydrogen sulfide removal work as well for carbon dioxide because both gases are polar. The dominant method for carbon dioxide removal from natural gas is still amine scrubbing [34]. The process can remove bulk quantities of carbon dioxide and the final stream can have as low as 50 ppm of carbon dioxide [39]. Physical absorption by water, polyethylene glycol, methanol, and potassium carbonate is possible to separate carbon dioxide. In water absorption, the gas enters a packed tower where carbon dioxide dissolves in water and the concentrated stream is stripped by air to generate carbon dioxide back and water is recycled. The process is cost effective because water is readily available; however the recirculated water can cause fouling; therefore special piping is needed [70]. Polyethylene glycol (PEG) on the other hand has better selectivity compared to water and is considered as a noncorrosive solvent [43]. The drawback of using PEG is the low regeneration rate [43].

Hot potassium carbonate is efficient for removing large amounts of carbon dioxide. The process can also remove small amounts of hydrogen sulfide. The mechanism is based on the reaction of carbon dioxide with potassium carbonate solution [35]:



The carbon dioxide-enriched stream enters an absorber where it flows in a counter-current with a hot potassium carbonate solution at 110°C [71]. The solution is then sent to a flash drum where most of the acid gas will be removed due to the reduction of the pressure. To regenerate the solvent, it is sent to a stripper that operates at 120°C and

TABLE 3: Current technologies for carbon dioxide separation.

Technology	Advantages	Disadvantages
Chemical and physical absorption	(i) No need for pretreatment. (ii) Can treat wider range of CO ₂ . (iii) High removal efficiency.	(i) High capital and operating costs. (ii) Regeneration of solvent.
PSA	(i) Does not involve a solvent. (ii) Better stability toward impurities in the feed.	(i) Low solid-to-gas capacity. (ii) Low regeneration rate. (iii) Pressure cycle is energy-intensive.
Cryogenic distillation	(i) Achieves >99% of CO ₂ capture. (ii) Produces liquefied CO ₂ for easier storage.	(i) Economical only if the feed contains 50–70% CO ₂ . (ii) Higher pressure is required to avoid CO ₂ sublimation.
Membranes	(i) Requires minimum supervision. (ii) Can remove H ₂ S and H ₂ O as well. (iii) Long-operating life (>5 years).	(i) High capital cost. (ii) Pretreatment is required to remove particulates and some inhibitors.

atmospheric pressure. Unfortunately, potassium carbonate has lower sorption properties compared to amine and it is highly corrosive [37, 42].

Methanol can also be used for physical absorption of carbon dioxide and it has the highest selectivity compared to other solvents [39]. The solvent can be regenerated by either reducing the pressure or increasing the temperature [40]. The final stream can have very low amounts of carbon dioxide of 10 ppm, which is more efficient than amine scrubbing. The only disadvantage of this process is the high capital investment [39].

Pressure swing adsorption (PSA) is another technique for carbon dioxide separation. Unlike previous methods, PSA does not require a solvent. The gas passes at a high pressure through a bed of activated carbon (also known as carbon molecular sieve), and due to the difference in polarity adsorption of carbon dioxide will take place [72]. The bed can be regenerated by reducing the pressure to vacuum. The technique has an excellent separation performance, and the gas can have more than 90% methane purity and it is expected to run for three years [73]. Other PSA materials are zeolite and alumina. Disadvantages of this system are the extensive energy for pressure cycle and low adsorption capacity compared to amine scrubbing [74].

Cryogenic distillation at very low temperature of -84°C is efficient for carbon dioxide removal. Because of the low triple point of carbon dioxide of -57°C at atmospheric pressure, carbon dioxide will not have a liquid state and will solidify directly [75]. Therefore, the distillation should take place at a pressure above 5 bar to overcome the triple point limitation; otherwise, carbon dioxide will cause blockage. The technology is used to liquify and produce high quality streams of carbon dioxide. For the process to be economical, the feed should contain 50 to 70% carbon dioxide, and this is because of the high capital and operating costs of cryogenic distillation [73]. Unfortunately, most of the refinery streams do not have that concentration of carbon dioxide [72].

In comparison with the above-mentioned, the membranes have a unique feature as they can remove carbon dioxide along hydrogen sulfide and water with one step [76, 77]. In addition to low operating energy, the membrane has a long life and it can be operated continuously for at least 5 years

[78]. However, the operating life is greatly affected if particulates were presented in the feed; therefore pretreatment is needed. Table 3 shows the advantages and disadvantages of different methods for carbon dioxide capture.

4.2. Membrane Materials. Removal of carbon dioxide started when Robb studied in 1968 the diffusion of gases in PDMS membrane [61]. The work was expanded in 1989 when Stern determined the permeability coefficient of gases at higher temperature [17]. CO₂-permeable membranes are similar to those that permeate hydrogen sulfide, but the permeability differs due to the difference in sorption and diffusion coefficients between carbon dioxide and hydrogen sulfide. The state-of-the-art materials for carbon dioxide separation are cellulose acetate, polyamide, polyimide, and Pebax. As shown in Table 4, cellulose acetate has the lowest permeability of 2.4 Barrer but yet the selectivity of carbon dioxide to methane ($\alpha_{\text{CO}_2/\text{CH}_4}$) reached 25 [25, 50]. Unfortunately, presence of heavy hydrocarbons in the feed caused a significant drop in the selectivity; therefore cellulose acetate was not suitable for fuel gas separation [50]. Polyimides on the other hand show better thermal and chemical stabilities compared to cellulose acetate [2]. These polymers are made from diacid with diamine in amic acid intermediate [79]. Matrimid 5218 is a polyimide containing phenylindane group and it gives carbon dioxide permeability of 8.5 Barrer [1, 80]. This polymer shows outstanding selectivity of 28 and 36.7 for carbon dioxide to methane ($\alpha_{\text{CO}_2/\text{CH}_4}$) and carbon dioxide to nitrogen ($\alpha_{\text{CO}_2/\text{N}_2}$), respectively [81, 82]. Carbon dioxide permeability of polyimide can be further enhanced by the introduction of fluoride. Fluorinated polyimides are made using 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanedianhydride (6FDA), and the permeability can be boosted to 456 Barrer [83, 84]. Copolymers like PUU and Pebax show also high permeability of 145 and 212 Barrer, respectively [85, 86]. The rubbery polymer PDMS has an excellent permeability of 4000 Barrer but the lowest carbon dioxide selectivity of 2.6, as given in Table 4.

4.3. Commercial Units and Economical Evaluation. The largest CO₂-removal unit is manufactured by Cynara

TABLE 4: Permeability and selectivity of different polymers for carbon dioxide removal.

Material	P_{CO_2} (Barrer)	α_{CO_2/CH_4}	α_{CO_2/N_2}	T ($^{\circ}C$)	P (bar)	Ref.
Cellulose acetate	2.4	22.1	20–25	35	10	[25, 50]
Polyamide (Nylon 11)	3.1	8.4	14.8	70	4–10	[87]
Polyimide (Matrimid 5218)	5.5	28	36.7	30–35	2–3	[81, 82]
Polysulfone (PSF)	5.6	22.4	22.4	35	10	[88]
Polycarbonate	6.5	22.4	24.1	35	10	[89]
Polyimide (6FDA-TBAPB)	42	25.7	21.5	30	3	[90]
Poly(2,6-dimethylphenylene oxide) (PPO)	61	14.2	14.9	35	—	[91]
Polyethylene glycol (PEG)	66	15.7	41.2	35	6	[86]
Polyether-urethane-urea (PUU)	145	7.8	29.6	25	10	[85]
Polyether-block-amide (Pebax 2533)	212	7.2	33	35	6	[86]
Dimethyl silicone rubber	325	3.4	11.6	25	1	[61]
Polyimide (6FDA-durene)	456	16	12.8	35	10	[83]
Polytetrafluoroethylene (Teflon AF 1600)	520	6.5	4.7	25	3.5	[25]
Polydimethylsiloxane (PDMS)	4000	2.6	6.6	35	1–15	[92]

(NATCO Group) for natural gas sweetening in an off-shore area in Thailand. The hollow fiber membrane is based on cellulose triacetate and capable of handling 830,000 Nm³/h [25]. Another system was installed to treat 120,000 Nm³/h of gas and it reduced carbon dioxide content from 80% to less than 10% [77, 93].

Polaris membrane (made by MTR) was installed after methane-reforming unit and it successfully increased carbon dioxide concentration from 20 mol% in the tail gas to more than 90 mol% [26]. The stream was used afterwards for well injection to enhance oil recovery. Polaris membrane can also treat flue gases with excellent selectivity (α_{CO_2/N_2}) of 50 [94].

UOP membranes are based on cellulose acetate and were installed in Pakistan in 1995. The system worked continuously for 12 years to cut down carbon dioxide concentration from 6.5 to 2 mol% [63]. The system was designed to process 311,950 Nm³/h of gas at 58 bar.

UBE on the other hand developed a robust membrane for better stability under feed impurities. The system is based on polyimide membrane and it can work without any drop in performance under the presence of 3 mol% hydrogen sulfide, full water saturation, and heavy hydrogen carbons of C₅₊ [95].

An economical study was done by Peters et al. to compare the membrane system with amine scrubbing for natural gas purification [96]. The feed gas contained 9.5 mol% CO₂, 20 ppm H₂S, 10 ppm H₂O and 72.4 mol% CH₄ and the remaining for C₂ to C₆. The operating conditions were 60 $^{\circ}$ C and 90 bar. Results show that both technologies achieved the sale gas specification of 4 ppm H₂S and 2 mol% CO₂; however, the treated gas by amine has better carbon dioxide purity compared to the membrane but this was at the expense of the capital investment. It was concluded that the membrane technology was still a better choice due to the environmental issue related to solvent disposal.

Another economical evaluation was performed by He et al., and it confirmed that the membrane can replace amine scrubbing for natural gas treatment containing 10 mol%

carbon dioxide and lower [97]. Natural gas processing cost by the membrane system was 0.00573 \$/Nm³, which was 10.4% less than amine scrubbing.

5. Hydrogen Recovery

Hydrogen is a key element for many processes in the refinery such as hydrocracking and hydrotreating. In hydrocracking, hydrogen is used to convert large hydrocarbons into smaller ones in presence of a catalyst, while in hydrotreating hydrogen is used to remove sulfur compounds from fuels in the form of hydrogen sulfide [98]. Furthermore, hydrogen is a feedstock for many industries like ammonia synthesis and methanol production [99].

Hydrogen is produced in the refinery by steam-methane reforming (SMR) where methane reacts with water to produce hydrogen and carbon monoxide. The produced gas is called syngas, and hydrogen yield can be further increased by the reaction of carbon monoxide with water to form hydrogen and carbon dioxide [100].

In petroleum industry, hydrogen separation can be practiced in the following processes: (1) to recover some hydrogen during natural gas production, (2) to adjust hydrogen-to-carbon monoxide ratio (H₂/CO) in syngas, (3) to recycle part of hydrogen from hydrocracker and hydrotreatment tail gases, (4) to separate hydrogen from nitrogen in ammonia plant, and (5) to purify hydrogen so it can be used as a feedstock for other industries [102–104]. Content of hydrogen in refinery off-gases is given in Table 5.

5.1. Current Technologies. Mainly, there are three methods to separate hydrogen from gas mixtures: (1) cryogenic distillation, (2) PSA, and (3) membrane system. The selection of technology depends on feed composition, product purity, product flow rate, reliability, turndown, and last but not least capital and operating costs. Comparison between the three technologies is given in Table 6. As indicated, the membrane has a better capability to treat a wider range of hydrogen from

TABLE 5: Hydrogen composition in refinery off-gases [101].

Process	Hydrogen content (vol%)
Catalytic reforming	40–85
Thermal hydrodealkylation	50–75
Hydrocracking	40–60
Hydrotreating	25–35
Catalytic cracking	10–30

30 to 90 mol%. PSA comes first for the product purity of over 99 mol% and cryogenic distillation is favorable to handle large volumes of 10,000 Nm³/h and above. Furthermore, the membrane provides the best reliability where unexpected shutdown occurs. This is because the membrane does not have mechanical parts whereas cryogenic distillation has the lowest reliability. Turndown refers to a small change in the operating condition and the membrane system is proven to be the most stable. For example, a change in the feed pressure can reduce the product purity in the membrane system by 10%, while PSA and cryogenic can be affected by 30 and 50%, respectively.

5.2. Membrane Materials. The first application of gas-separation membranes was for hydrogen removal. It was developed in 1970s by Monsanto (Air Products) to recover hydrogen from purge gas in ammonia plant [104–106]. The spiral-wound membrane was based on polysulfone and it has a permeability of 17 Barrer. Cellulose acetate membranes were introduced then by Separex and they showed a better permeability and stability; therefore they were employed for removal of hydrogen from natural gas [107]. The permeability was greatly improved from 14 to 24 Barrer when cellulose acetate was used instead of polysulfone. For adjustment of H₂/CO ratio in syngas, polyimide (made by UBE) gave a better permeation of 50 Barrer with superior selectivity of H₂/CH₄ (125), H₂/CO (50), and H₂/N₂ (83) [1]. Though PDMS gives maximum hydrogen permeability of 1500 Barrer, it has a low H₂/CH₄ selectivity of unity making it unsuitable for hydrogen separation from natural gas. Furthermore, it is reported that performance of PDMS membrane significantly drops if carbon monoxide was presented in the feedstock [108]. Table 7 shows hydrogen permeability and selectivity of different membrane materials.

5.3. Commercial Units and Economical Evaluation. The world-leading companies for hydrogen-permeable membranes are Air Products, MTR, UOP, GENERON, Praxair, and UBE. PRISM membrane (based on polysulfone and developed by Air Products) is able to recover 90 to 98 mol% of hydrogen from purge gas in ammonia plant [106]. The membrane can also upgrade hydrocracker off-gas stream containing 20–30 mol% hydrogen to 70–90 mol% in a single stage or to 95 mol% by two stages [114]. The system is expected to run for 7 years without any interruption.

VaporSep membrane manufactured by MTR can recover hydrogen from refinery waste gases. The system can also be used to adjust H₂/CO ratio in syngas to meet the feed requirement for different industries. The system can handle

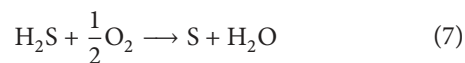
a feed pressure up to 170 bar with different concentrations of 30–95 mol% of hydrogen with a maximum volume of 235,434 Nm³/h. The permeate is estimated to have a hydrogen purity of 90–99 mol% [26]. The system was installed in a Korean refinery to recover hydrogen from a hydrocracker off-gas, and the unit improved the process economy and paid itself after only one month of operation.

UOP PolySep is another membrane for hydrogen production that can treat refinery off-gases. The membrane operates at temperatures of 60 to 82°C with feed pressures of 14 to 170 bar. Compared to VaporSep, PolySep can handle larger volume of 412,010 Nm³/h. The permeate pressure ranges from 4 to 84 bar with hydrogen recovery of 70–98% [63].

Hydrogen recovery is considered economical if the waste gas contains 50 mol% hydrogen or more [106]. Otherwise, production of hydrogen by SMR will be a better choice rather than separation. A study was performed by Mivechian and Pakizeh to evaluate the feasibility of using a membrane system to separate hydrogen from refinery off-gas containing 72 mol% hydrogen with light hydrocarbons (C₁–C₆). The membrane was based on polyimide and it showed a better recovery of 95% compared to 79% using PSA. The membrane also achieved a hydrogen purity of 98.3 mol%, which is close to PSA of 99.4 mol%. The capital cost was almost the same for both the membrane system and PSA [103].

6. Air Separation

Air contains 20.9 mol% of oxygen and 78.1 mol% of nitrogen, and the remaining is for other gases such as argon and carbon dioxide. An increase in oxygen content (>21 mol%) in the feed can improve the oxidation process due to the higher flame temperature. This raise in temperature is directly related to the reduction in nitrogen content in the feed [19]. Idea of using enriched oxygen for Claus process was initiated in 1970s and then fully commercialized in 1985 in Lake Charles Refinery (US) by Goar Allison and Air Products [31]. After hydrotreatment, the sulfur-enriched gas is sent to Claus process to recover hydrogen sulfide in the form of solid sulfur. The concept of Claus process is based on oxidizing hydrogen sulfide to sulfur and water:



Because air is used to oxidize hydrogen sulfide, presence of nitrogen lowers the flame temperature and this could result in the formation of ammonia salts too. These salts cause a pressure drop in the system. Use of enriched oxygen instead of air can greatly improve the capacity of sulfur removal and prevent salt formation. For example, use of 28 mol% oxygen can increase sulfur capacity up to 30% [115]. Furthermore, use of 45% oxygen nearly doubles the sulfur capacity.

Oxygen enrichment can be beneficial for fluid catalytic cracking (FCC) unit as well. This unit is used to break down large hydrocarbons (usually vacuum gas oil) to useful products such as gasoline and diesel. The feed is first heated to 315–427°C and then enters a reactor where it gets in contact with a catalyst [99]. The catalyst is then regenerated thermally (to remove coke) by burning it with air. However, studies

TABLE 6: Comparison between current technologies for hydrogen recovery [105].

Category	Cryogenic distillation	PSA	Membrane
Feed composition (H ₂ mol%)	30–75	75–90	30–90
Product purity (H ₂ mol%)	90–98	>99	90–98
Product volume (Nm ³ /h)	>10,000	1000–10,000	<30,000
Reliability (%)	Poor	95	100
Turndown (%)	10	30	30–50

TABLE 7: Hydrogen permeability and selectivity of various membrane materials.

Material	P_{H_2} (Barrer)	α_{H_2/CH_4}	$\alpha_{H_2/CO}$	α_{H_2/N_2}	T (°C)	P (bar)	Ref.
Polyimide (Matrimid 5218)	2.5	7	11	17	30	2	[81, 109]
Polysulfone	14	56	40–56	56	35	—	[1, 110]
Polyethylene	17	2.2	—	4.1	30	2	[111]
Polystyrene	24	30	—	40	30	2	[111]
Cellulose acetate	24	67	30–40	73	25	—	[1]
Polyetherimide	26	51	39	71	23	0.3–0.8	[112]
Polyimide (BPDA-based)	50	125	50	83	60	—	[1]
Dimethyl silicone rubber	65	0.8	0.7	2.2	25	1	[61]
Poly(2,6-dimethylphenylene oxide) (PPO)	80	30	—	31	22	—	[113]
Polydimethylsiloxane (PDMS)	1500	1	—	2.5	35	1–15	[92]

show that when 27 mol% of oxygen is used, the capacity of regenerating the catalyst increases by 10 to 15%. In addition, use of enriched oxygen in furnaces can reduce nitrogen compounds (NO_x) and this will reduce the emissions [116].

6.1. Current Technologies. Idea of using enriched oxygen in furnaces was practiced since 1930s for iron production by cryogenic distillation [19]. The process gives ultra-pure oxygen (>99.9 mol%) by compressing air and then cooling it to a very low temperature below -187°C using a refrigeration cycle to liquify air. After that, it is sent to a distillation tower where oxygen leaves in the form of liquid and nitrogen in the form of gas due to the difference in boiling point [117].

PSA by zeolite can produce enriched oxygen within the range of 25 to 50 mol% oxygen [72]. Actually, both oxygen and nitrogen will be adsorbed on zeolite but nitrogen has a higher adsorption rate; thus the gas passing through zeolite will have a higher content of oxygen. Unfortunately, due to low adsorption rate of 0.02–0.08 mol oxygen per one mol of sorbent, the process is not widely used [118].

Polymeric membrane is an alternative technology for air separation. The technology has an advantage over cryogenic distillation as it does not require cold temperatures. Furthermore, the membrane does not need a regeneration step same as PSA. It is worthwhile to mention that ceramic membranes made of ionic-electronic conducting materials are capable of producing oxygen with 100% purity [119]. The mechanism is based on oxygen vacancies that are created at temperature of 800°C and above [120]. Unfortunately, the technology is not yet commercialized due to many issues related to sealing and instability due to presence of impurities in the feedstock making the polymeric membrane a solid choice at the moment [121–123].

6.2. Membrane Materials. Use of polymeric membranes for oxygen enrichment started in 1980s and it showed promising results compared to cryogenic distillation and PSA [124]. The selection of membrane material relies on the selectivity toward nitrogen (α_{O_2/N_2}). It is stated that a selectivity of at least 4 is needed for the membrane to compete with other technologies [125]. List of materials meeting these criteria is cellulose acetate, polysulfone, polyamide, polyimide, polyetherimide, and poly(4-methyl-1-pentene) (TPX) [1, 82, 91, 126, 127]. As given in Table 8, polyetherimide shows the highest selectivity of 8.2 yet lowest oxygen permeability of 0.41 Barrer. Polysulfone (PSF) has a better permeability of 1.5 Barrer with very good selectivity of 5.8 and it is used in fabrication of many commercial units [128]. Poly(4-methyl-1-pentene) (TPX) is also used commercially and it has a permeability of 30 Barrer and good selectivity of 4 [128].

6.3. Commercial Units and Economical Evaluation. UOP developed a membrane called SPIRAGAS that produces a stream containing 30 mol% of oxygen from air [128]. The membrane is based on a porous polysulfone coated with silicone and it has a spiral-wound module. It operates at 21°C , and the product flow rate can reach up to $10.6\text{ Nm}^3/\text{h}$ with feed pressure varying from 1 to 1.4 bar. GENERON on the other hand fabricated a membrane based on TPX and it gives a higher oxygen content up to 35 mol% [129].

Moreover, AVIR membrane (manufactured by A/G Technology Corporation) can produce 37 to 60 mol% of oxygen-enriched air [130]. It should be mentioned that the membranes in Table 8 also produce a nitrogen-enriched stream in the retentate. For example, PRISM hollow fiber membrane (based on PDMS and made by Air Products) produces not

TABLE 8: Oxygen and nitrogen permeabilities of different polymeric materials.

Material	P_{O_2} (Barrer)	P_{N_2} (Barrer)	α_{O_2/N_2}	T ($^{\circ}C$)	P (bar)	Ref.
Polyetherimide	0.4	0.05	8.2	35	—	[91]
Polysulfone (PSF)	1.5	0.26	5.8	—	2	[126]
Polycarbonate	1.5	0.26	5.8	35	—	[91]
Cellulose acetate	1.6	0.33	4.8	25	—	[1]
Polystyrene	1.7	0.8	2.1	30	2	[111]
Polyimide (Matrimid 5218)	2.1	0.32	6.6	35	2	[82]
Polyvinyl acetate (PVA)	2.3	1.3	1.8	30	2	[111]
Polyamide	3.1	0.46	6.7	30	3	[127]
Polyimide (6FDA-based)	10.1	2	5	30	3	[90]
Polyphenylene oxide (PPO)	16.8	3.8	4.4	—	—	[1]
Natural rubber	17.7	6.12	3	25	—	[133]
Poly(4-methyl-1-pentene) (TPX)	30	7.1	4.2	—	—	[1]
Dimethyl silicone rubber	60	28	2.1	25	1	[61]
Polydimethylsiloxane (PDMS)	1000	600	1.7	35	1–15	[92]
Poly(1-trimethylsilyl-1-propyne) (PTMSP)	7600	5400	1.4	—	—	[1]

TABLE 9: Economical study for the production of 20 tons of enriched oxygen (35 mol%) with different technologies [132].

Technology	Power requirement (kWh/tons O_2)	Capital cost (\$/tons O_2)	Operating cost (\$/tons O_2)
Cryogenic distillation	350	>70,000	39
Pressure swing adsorption (PSA)	285	25,000–70,000	26
Membrane	177	16,000–27,000	23

only enriched oxygen but also nitrogen with purity of 95–99 mol%. The membrane operates at feed pressure of 5.5 to 10 bar with volume flow rate up to 708 Nm³/h [131].

An economical analysis was done for the production of 20 tons of enriched oxygen with 35 mol% purity using various technologies [132]. The comparison was based on power requirement, capital cost, and operating cost and the data is given in Table 9. As expected, the membrane comes first in power requirement and it can save energy up to 49% and 38% compared to cryogenic distillation and PSA, respectively. The membrane also has the lowest capital cost of 16,000 to 27,000 \$ per tons of oxygen compared to cryogenic distillation and PSA. Moreover, the membrane still has the lowest operating cost of 23 \$/ton O_2 whereas cryogenic distillation needs 39 \$/tons O_2 , which is nearly double.

7. Gas Dehydration

One of the issues in natural gas transport is the formation of solid hydrates. These solids are formed due to the presence of water and hydrocarbons at high pressure and low temperature [134]. An example is methane hydrate with chemical formula of CH_4nH_2O where n is hydration number. This parameter is used to determine hydrates in methane storages and natural gas reserves [135]. To prevent hydrate formation, the water content in natural gas should not exceed 104 mg per m³ of natural gas [136].

7.1. Current Technologies. Physical absorption by triethylene glycol can be used to dehydrate natural gas. However, volatile organic compounds (VOCs) will be formed during solvent regeneration [137]. Water removal by silica gel or activated alumina is another technique where the wet gas enters a desiccant bed and water will be adsorbed [138]. The bed is simply regenerated by heating, and the adsorption process is more effective compared to ethylene glycol.

Molecular sieve by zeolite is widely used for removal of water from natural gas. Compared to other desiccants, zeolite (3A) can treat streams with wider range of relative humidity [139]. Furthermore, zeolite has a better chemical stability and is capable of adsorbing hydrogen sulfide and carbon dioxide, making it a good choice for treating sour gas [140]. Also, zeolite shows the highest adsorption capacities of 20 g H_2O /g zeolite for streams having a relative humidity of 10% at 25 $^{\circ}C$ [141]. With time, zeolite will be saturated with water, and the bed can be regenerated by thermal regeneration (heating to 200–300 $^{\circ}C$) or reducing the pressure to vacuum [142]. The drawback of zeolite is the higher energy requirement for regeneration, which is 16% more compared to silica and alumina [141].

Polymeric membrane not only removes water but also separates hydrogen sulfide, carbon dioxide, and heavy hydrocarbons, all in one step [63]. The membrane is also expected to run without interruption for many years. However, pre-treatment may be necessary to remove particulates from the feed gas. Unfortunately, the technology is not suitable for

TABLE 10: Current technologies for dehydration of natural gas [141, 150].

Technology	Advantages	Disadvantages
Glycol absorption	(i) Continuous process. (ii) Lower pressure drop compared to solid desiccants. (iii) Better chemical stability.	(i) Difficult to achieve water dew point below -32°C . (ii) Harmful VOCs are formed during the regeneration of solvent.
Alumina desiccant	(i) Ability to adsorb heavy hydrocarbons. (ii) Performance is nearly independent of the feed operating condition.	(i) High pressure drop. (ii) Regeneration is needed.
Zeolite molecular sieving	(i) Ability to achieve dew point of -101 to 149°C . (ii) Stable under sour gas.	(i) More energy is needed for regeneration.
Polymeric membranes	(i) Ability to separate hydrogen sulfide, carbon dioxide, and heavy hydrocarbons (C_{3+}) in one step. (ii) Long life (7 years). (iii) No need for regeneration.	(i) Pretreatment may be required. (ii) Energy requirement for compressors. (iii) Not suitable for large volume.

TABLE 11: Water permeability of hydrophilic and hydrophobic membranes.

Polymer	$P_{\text{H}_2\text{O}}$ (Barrer)	$\alpha_{\text{H}_2\text{O}/\text{CH}_4}$	T ($^{\circ}\text{C}$)	Ref.
<i>Hydrophobic membranes</i>				
Polyethylene (PE)	90	31	25	[151]
Polyimide (Kapton)	640	14,000	30	[152]
Polycarbonate (PC)	1,100	3,100	25	[152]
Polystyrene	1200	1500	30	[111, 153]
Dimethyl silicone rubber	3600	39	25	[61]
Poly(phenylene oxide) (PPO)	4060	780	30	[143]
Polydimethylsiloxane (PDMS)	45,000	38	30	[143, 144]
<i>Hydrophilic membranes</i>				
Poly(2,6-dimethylphenylene oxide) (PPO)	4060	944	30	[91, 153]
Polysulfone	8000	44,444	30	[91, 153]
Cellulose acetate	10,000	190,000	30	[143]
Ethyl cellulose	20,000	2500	30	[143, 152]
Polyether-block-amide (Pebax) 1074	50,000	6,060	30	[145, 146]
Nafion 117	450,000	4,100,000	30	[147, 154]

treating large volume of natural gas due to economical issues [141]. Table 10 shows the advantages and disadvantages of each process for water removal from natural gas.

7.2. Membrane Materials. Water separation membranes are divided into two groups: hydrophobic and hydrophilic materials. In hydrophobic membranes, natural gas permeates while water is rejected. Examples are polyimides and silicone rubbers particularly PDMS. The latter have a water permeability of 45,000 Barrer with water-to-methane selectivity ($\alpha_{\text{H}_2\text{O}/\text{CH}_4}$) of 38 [143, 144]. On the other hand, hydrophilic membranes are water permeable and some examples are polysulfone and cellulose acetate. As shown in Table 11, hydrophilic membranes have higher water permeability and selectivity compared to hydrophobic membranes. For example, the water-permeable Pebax has a permeability of 50,000 Barrer, which is 11% higher than PDMS [145, 146]. Nafion gives an outstanding permeability of 450,000 Barrer and $\text{H}_2\text{O}/\text{CH}_4$ selectivity of 4,100,000. It is a copolymer developed by DuPont and made by the copolymerization of tetrafluoroethylene and perfluorovinyl with sulfonyl fluoride

termination step [147, 148]. Actually, Nafion consists of a hydrophobic backbone (based on Polytetrafluoroethylene, PTFE) and a hydrophilic sulfonated group that provides the transport path for water [149].

7.3. Commercial Units and Economical Evaluation. PRISM (Air Products) developed a water-permeable membrane for removal of water from natural gas. A unit was successfully installed in Shell Nigeria to process $600,000 \text{ Nm}^3/\text{h}$ of natural gas [77]. The membrane is expected to be based on PDMS. As discussed previously, FuelSep (MTR) is designed to remove hydrogen sulfide from natural gas but it can also permeate carbon dioxide and water. GENERON also provides dehydration membranes, and, similar to FuelSep, the membrane permeates hydrogen sulfide and carbon dioxide. The system can work at operating condition up to 95 bar, 71°C , and flow rate of $588,586 \text{ Nm}^3/\text{h}$ [155].

Comparing the membrane with other separation methods, glycol absorption has the lowest capital cost followed by alumina adsorption, zeolite molecular sieve, and the membrane [141, 150]. On the other hand, the membrane shows

TABLE 12: Comparison with different technologies for VOCs removal [27, 159, 160].

Technology	VOC content	Efficiency (%)	Temperature (°C)	Remarks
Thermal oxidation	20 ppm–20% LEL	95–99	371	(i) Energy recovery up to 85%. (ii) Chlorinated compounds can form toxic gases.
Catalytic oxidation	100–1000	90–98	149	(i) Energy recovery up to 70%. (ii) Efficiency is dependent on operating conditions. (iii) Certain impurities can poison the catalyst.
Activated carbon	700–10,000	80–90	<54	(i) Performance is greatly affected by moistures. (ii) Unstable in ketones, aldehydes, and esters.
Membranes	<20 ppm–25% LEL	90–99	Ambient	(i) Treated gas does not require further processing.

the lowest operating cost. For more details, an economical study was made by Binci et al. to evaluate the membrane system (PRISM) for natural gas dehydration [150]. The study also included the implantation of glycol system. The feed volume varied from 20,083 to 187,500 Nm³/h and life span was 20 years. The feed was at 30 bar and 30°C. The membrane lifetime was assumed to be 10 years and accordingly it was changed twice. It was concluded that the membrane was cost effective for treating 20,083 to 41,667 Nm³/h of gas. The system was considered uneconomical for treating more than 41,667 Nm³/h of natural gas.

8. Removal of VOC

Volatile organic compounds are liquids having a boiling point of 50 to 260°C [156]. VOCs are carbon compounds that react with nitrogen oxides in the presence of sunlight to form harmful ozone in the atmosphere [157]. Therefore, from environmental point of view, VOCs need to be removed from air and industrial off-gases. Some VOCs are valuable solvents, and recovery of these compounds is necessary. Examples of VOCs are acetone, benzene, formaldehyde, chlorofluorocarbons (CFCs), and hydrochlorofluorocarbons (HCFCs) [158].

8.1. Current Technologies. Activated carbon, thermal oxidation, and catalytic oxidation are widely used to remove VOCs from gases. Activated carbon is favorable to treat streams containing 700–10,000 ppm VOCs and it is based on physical adsorption [27]. At high pressure, VOCs will be adsorbed and carbon can be regenerated by reducing the pressure to vacuum. On the other hand, thermal oxidation is more suitable for removing VOCs with higher concentration of 20 ppm up to 20% of lower explosion limit (LEL) of the gas. LEL is defined as the lowest concentration in which the gas will produce fire in the presence of an ignition. Going higher than 20% LEL will generate excessive heat, which may result in an explosion [159].

In thermal oxidation, the gas containing VOCs will be heated to a very high temperature of 760–871°C where VOCs will be oxidized to carbon dioxide and water. A catalyst can be used to reduce the temperature to 316–538°C and this process is called catalytic oxidation [160]. The thermal/catalytic oxidation has an advantage over activated carbon as it can withstand streams with high humidity. However, the system

is not suitable if chlorinated compounds were presented. This is because chlorinated compounds will be incompletely combusted and this leads to formation of toxic gases [161]. The membrane technology overcomes this issue due to the high chemical stability [27, 160]. In addition, the membrane can be operated under heavy moistures where activated carbon cannot be used [159]. Furthermore, the membrane works at ambient temperature where other processes need elevated temperatures. Table 12 compares current methods for VOCs removal.

8.2. Membrane Materials. Silicone rubbers like PDMS are widely studied for removal of organic vapors from air. These rubbery polymers were tested for many VOCs like acetone, benzene, toluene, and xylene. For acetone removal from air, PDMS has a selectivity of 11 to 25 while, for removal of toluene, PDMS has a higher selectivity of 83, as given in Table 13.

Glassy polymers like polyimide were also evaluated for VOCs recovery. Polyimide type PI 2080 (developed by Upjohn and based on condensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride, BDTA) was tested for different VOCs such as methanol, ethanol, hexane, toluene, and xylene [162]. PI 2080 has a toluene-to-air selectivity more than double compared to PDMS. Furthermore, xylene-to-air selectivity is 9 times more in PI 2080 in comparison with PDMS.

8.3. Commercial Units and Economical Evaluation. MTR started installing VOC-recovery membranes for refineries and petrochemical industries in 1992. The process was feasible for removal of VOCs in the range of 200 to 1000 ppm containing carbon tetrachloride. First, air containing VOCs is compressed to 13 bar to condense water and some of VOCs. After that, the stream enters two-stage membrane system, and VOCs permeate in the liquid form due to the use of vacuum pump [27]. Content of VOCs in the treated air will have less than 10 ppm. GKSS also developed a spiral-wound membrane for VOCs removal and it is based on PDMS with polyetherimide support [128].

Unfortunately, there are some economical issues for selecting the membrane system for VOCs recovery and this is related to high capital and operating costs. A study was done on the removal of 1000 ppm VOCs from air with capacity of 850 Nm³/h, and it showed that the membrane

TABLE 13: Selectivity of various membranes from VOC separation from air (or N₂ if stated).

Membrane	VOC	Selectivity	Ref.
Silicone	Acetone/N ₂	53	[163]
	Ethylbenzene/N ₂	28	[163]
	Toluene/N ₂	39	[163]
	Xylene/N ₂	50	[163]
	Freon-113/N ₂	32	[163]
PDMS	Acetone	11–25	[164]
	Toluene	83	[165]
	p-Xylene	68	[165]
	1,2-Dichloromethane	142	[165]
	1,2-Dichloroethane	103	[165]
Polyimide (PI 2080)	Methanol	221	[166]
	Ethanol	297	[166]
	Hexane	32	[166]
	Benzene	51	[166]
	Toluene	180	[166]
	p-Xylene	460	[166]

requires a capital cost of 660,000 \$ whereas thermal/catalytic oxidation needs only 280,000 \$ [27]. The activated carbon is also expected to have a capital cost less than 280,000 \$. Thermal/catalytic oxidation achieved the lowest operating cost of 15,700 \$/month, and it increased to 41,000 \$/month when the membrane system was used. The activated carbon has slightly higher operating cost of 45,000 \$/month. The study is given in Table 14.

Despite the excellent capital and operating costs of thermal/catalytic oxidation, the technology is not suitable to treat gases with volume less than 1699 Nm³/h. In this case, activated carbon or membrane system should be selected. Activated carbon is a better choice for treating low quantity of VOCs (e.g., 1000 ppm), but if the stream contains higher than 10,000 ppm VOCs, the membrane is the winner because activated carbon cannot be operated at these concentrations.

9. LPG Recovery

Liquefied petroleum gas (LPG) contains mainly propane (C₃) and butane (C₄). The mixture is in the gas state at normal pressure but it becomes a liquid at moderate pressures [167]. LPG is generally used as a source of heating and cooking and a fuel for vehicles [168]. It is found in natural gas or produced from crude oil. LPG can also be recovered from refinery off-gases such as FCC overhead gas and PSA tail gas [26]. Furthermore, flare gases can have valuable amounts of LPG.

9.1. Current Technologies. The dominant method to recover LPG is by the combination of cryogenic cooling and gas expansion (also known as turbo-expander) of natural gas. First, the gas is compressed and cooled to a very low temperature of -51°C resulting in a partial condensation (cold box process). The gas stream is then sent to a turbo-expander in which the pressure is reduced and the temperature is

further decreased to -91°C. The liquid stream (from the cold box process) passes through a throttle valve to decrease the temperature to -81°C. After that, both streams are sent to a demethanizer unit to produce natural gas liquids (C₂₊) and recover methane by distillation [33, 169].

Before the invention of turbo-expander method in 1970s, LPG was separated from natural gas by an absorption plant. The process uses a hydrocarbon solvent to physically remove LPG at low temperature of -25°C. Due to the intensive manpower and complexity of the technology, the process was replaced with turbo-expander [169].

The membrane technology is recently applied for LPG recovery. Unlike turbo-expander, the membrane is more energy-efficient because it operates at ambient temperature. In addition, it does not need the distillation step, especially if the feedstock does not contain significant amount of heavier hydrocarbon (C₅₊).

9.2. Membrane Materials. The concept of using the membrane for LPG recovery from refinery off-gases was introduced by ExxonMobil in 2006 [170]. The membrane was based on a rubbery polymer, which permeates propane and heavier hydrocarbons (C₃₊) but rejects hydrogen, methane, and ethane [170]. Polymers like polysiloxane and polybutadiene are suitable for LPG separation due to the high sorption of C₃₊ compounds [170]. Unfortunately, few materials were tested for LPG removal and some of them are given in Table 15. PDMS membrane gives propane and butane permeabilities of 7400 and 14,000 Barrer, respectively [171, 172]. On the other hand, poly[1-(trimethylsilyl)-1-propyne] (PTMSP) shows interesting permeabilities of 33,800 and 53,500 Barrer for propane and butane [173, 174].

9.3. Commercial Units and Economical Evaluation. MTR developed a membrane system called LPG-SEP to recover

TABLE 14: Economical study for removal of VOCs (1000 ppm) from air to treat 850 Nm³/h by different technologies [27].

Technology	Capacity (Nm ³ /h)	Capital cost (\$)	Operating costs (per month, \$)
Thermal/catalytic oxidation	1699–849,505	280,000	15,700
Activated carbon	170–10,194	<280,000	45,000
Membranes	340–2548	660,000	41,000

TABLE 15: Performance of polymeric membranes for LPG removal.

Polymer	$P_{C_3H_8}$ (Barrer)	$P_{C_4H_{10}}$ (Barrer)	$\alpha_{C_3H_8/CH_4}$	$\alpha_{C_4H_{10}/CH_4}$	T (°C)	Ref.
Polyvinyl-allyl-dimethylsilane (PVADMS)	11.2	41.3	2.7	10.1	35	[175]
Dimethyl silicon rubber	410	900	4.3	9.5	25	[61]
Poly(4-methyl-2-pentyne) (PMP)	4700	40,300	1.6	13.9	25	[176]
Polydimethylsiloxane (PDMS)	7400	14,000	5.7	10.8	35	[171, 172]
Poly[1-(trimethylsilyl)-1-propyne] (PTMSP)	33,800	53,500	5.2	8.2	25	[173, 174]

LPG from natural gas containing heavy hydrocarbons (associated petroleum gas) [26, 177]. This stream sometimes needs to be flared thus wasting valuable products and causing increase in carbon dioxide emissions. In LPG-SEP process, associated gas is compressed to 24 bar and then cooled to 16°C to condense hydrocarbons of propane and above (C₃₊). These hydrocarbons are then sent to a fractionator (distillation column) to separate LPG. The compressed associated gas will enter a membrane that permeates methane to recover natural gas. This membrane system can handle 2354–58,858 Nm³/h of gas with natural gas content of 5 to 50 mol%. LPG recovery can reach 95% with payback of 6 to 18 months [26].

MTR also developed a membrane called VaporSep, which can be used to separate LPG from flare gas, FCC overhead gas, and PSA tail gas [26]. As a case study, a Texas refinery had an issue with excess flare gas that contains valuable amounts of hydrogen and LPG. The problem was evaluated by the installation of a compression-condensation-membrane combination system. The flare gas was first compressed and condensed to recover some of LPG. After that, the gas enters a membrane system to separate LPG from hydrogen. The unit was designed to handle 9.3 Nm³/h of LPG, and payback was less than a year [26].

As discussed, the membrane technology needs to be integrated with conventional methods if the stream contains significant amounts of C₅₊. This is because the membrane permeates C₃ and above and the permeability increases with carbon number. Therefore, it is not possible to produce LPG from a stream containing C₃ to C₅₊, and therefore a distillation column will be required to separate C₃ and C₄ from C₅₊. However, the membrane will be a good separation technique if the stream contains LPG only with other gases such as hydrogen or carbon dioxide.

10. Conclusion

In this paper, applications of polymeric membranes in the refinery were discussed. The membranes are currently implemented for hydrogen sulfide separation, carbon dioxide capture, hydrogen recovery, air separation, gas dehydration, VOCs removal, and LPG recovery. For hydrogen sulfide

separation, cellulose acetate is widely used as a membrane material, and the processing cost for natural gas treatment was lower compared to amine scrubbing to treat natural gas with 1 mol% of hydrogen sulfide. For carbon dioxide capture, polyimide membrane has an advantage over other technologies as it can remove hydrogen sulfide and water in one step. The membrane also shows lower capital costs compared to conventional methods. For hydrogen recovery, polyimide membrane can be used to recover hydrogen from natural gas and refinery off-gases. However, the process is considered economical only if hydrogen content is higher than 50 mol% in the waste gas. In air separation, use of enriched oxygen can improve the capacity of Claus and FCC units. Polysulfone membranes were used to produce 35 mol% oxygen, and the technology has reduced the power requirement by 49% compared to cryogenic distillation. For gas dehydration, water needs to be removed from natural gas to avoid solid hydrates formation. This is usually done by glycol absorption but the process results in formation of toxic VOC. The membrane not only eliminates this issue but also removes other natural gas impurities. Furthermore, PDMS membrane was proven to be cost effective compared to glycol absorption for treating 20,083 to 41,667 Nm³/h of natural gas. VOCs are usually found in waste gases and some of VOCs are expensive solvents. Recovery of these VOCs is a must due to environmental and economical issues. The membrane technology is unique for that application as it can deal with feeds containing halogens and moistures. However, high capital and operating costs negatively affect the selection of this technology compared to thermal/catalytic oxidation. In the refinery, LPG is recovered from natural gas and waste gases. Combination of cryogenic distillation and gas expansion is widely used to separate LPG. The membrane still cannot substitute the current technology but it can be integrated to eliminate the cryogenic step as it operates at ambient temperature and this will greatly reduce the energy requirement.

One issue of the membrane technology is the sensitivity to impurities in the feedstock. Cellulose acetate can be used for many applications such as acid gas removal, hydrogen recovery, and air separation, but presence of water and

TABLE 16: Summary of gas separation processes in the refinery and advantages of using membranes.

Process	Separation	Applications	Current technologies	Advantages of membranes	Membrane materials
Hydrogen sulfide separation	CH ₄ /H ₂ S	NG sweetening	Amine scrubbing K ₂ CO ₃ absorption Methanol absorption PSA	(i) Does not need a solvent. (ii) Can treat feeds with wider range of H ₂ S. (iii) Low NG processing cost for feeds with <1 mol% H ₂ S.	Cellulose acetate (UOP) Polyether-block-amide Polyamide Polyether-urethane-urea
Carbon dioxide capture	CO ₂ /CH ₄ CO ₂ /N ₂	NG sweetening Treatment of off-gases	Amine scrubbing Water absorption PEG absorption K ₂ CO ₃ absorption Methanol absorption PSA Cryogenic distillation	(i) Can separate CO ₂ with other impurities such as H ₂ S and H ₂ O. (ii) Can be operated continuously for more than 5 years. (iii) Low NG processing cost for feed with <10 mol% CO ₂ .	Cellulose triacetate (Cynara) Cellulose acetate (UOP) Polyimide (UBE) Polyether-block-amide Polysulfone Polyamide Polyether-urethane-urea
Hydrogen recovery	H ₂ /CH ₄ H ₂ /CO H ₂ /N ₂	H ₂ recovery from NG Syngas adjustment Ammonia purge gas	Cryogenic distillation PSA	(i) Ability to treat feeds with wider range of H ₂ . (ii) Better turndown. (iii) Higher reliability.	Cellulose acetate (Separex) Polysulfone (PRISM) Polyimide (UBE) Polyetherimide
Air separation	O ₂ /N ₂	Oxygen enrichment	Cryogenic distillation PSA	(i) Can be operated at ambient temperature. (ii) Does not need regeneration. (iii) Low capital and operating costs.	Cellulose acetate Polysulfone (UOP) Poly(4-methyl-1-pentene) (GENERON) Polydimethylsiloxane (PRISM) Polyimide Polyamide Polyetherimide
Water removal	H ₂ O/CH ₄	NG dehydration	TEG absorption Silica bed Activated alumina Zeolite molecular sieve	(i) Can be run for more than 7 years without interruption. (ii) Ability to remove H ₂ S, CO ₂ , and C ₃₊ compounds.	Polydimethylsiloxane (PRISM) Cellulose acetate Polysulfone Polyether-block-amide Polyimide
VOC recovery	VOC/air VOC/N ₂	Treatment of off-gases Recovery of solvents	Thermal oxidation Catalytic oxidation Activated carbon	(i) Works at ambient temperature. (ii) Better chemical stability.	Polydimethylsiloxane (GKSS) Polyimide (Upjohn)
LPG	(C ₃ -C ₄)/CH ₄	Recovery of LPG from NG	Cryogenic distillation and gas expansion	(i) Process integration to reduce energy requirement.	Polydimethylsiloxane Poly[1-(trimethylsilyl)-1-propyne]

NG: natural gas.

hydrocarbons can negatively affect the membrane performance. Therefore, the membrane should be tested under real feeds to insure the membrane stability for long-term operation. Summary of this paper is given in Table 16.

Competing Interests

The authors declare that they have no competing interests.

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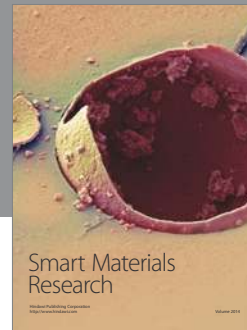
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