RECENT PROGRESS OF OXYGEN/NITROGEN SEPARATION USING MEMBRANE TECHNOLOGY

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Abstract

The oxygen-enriched air is highly demanded for various industrial applications such as medical, chemical and enhanced combustion processes. The conventional oxygen/nitrogen production is either cryogenic distillation or pressure swing adsorption (PSA). Both of these techniques possess the production capability of 20 to 300 tonnes of oxygen per day and oxygen purity of more than 95%. However, these techniques are energy intensive. Alternatively, membrane technology is an emerging technology in gas separation as it requires low energy consumption and relatively moderate production volume, if compared to the conventional gas production techniques. These advantages have spurred much interest from industries and academics to speed up the commercial viability of the O_2/N_2 separation via membrane technology. In this review, the conventional and membrane technologies in O_2/N_2 separation, as well as recent development of membrane fabrication techniques and materials are reviewed. The latest membrane performance in O_2/N_2 separation is also tabulated and discussed.

Keywords: Membrane, Nitrogen, Oxygen, Gas Separation, Selectivity.

1. Introduction

The mass transport across the non-porous membrane from the higher concentration to lower concentration region was mathematically modelled by Adolf Ficks in 1855 through Fick's laws of diffusion [1]. The commonly used membrane materials during that period of time for separation were leather and cotton. About one hundred years later, Loeb and Sourirajan invented asymmetric cellulose acetate membrane fabricated by phase inversion technique and applied in water separation process by reverse osmosis. With the great breakthrough in the past 30 years, membrane technology is

yet to be adopted in industrial scale gas production, although membrane technology has been widely used in the water separation today [2].

The oxygen-enriched air is commonly used for medical, chemical and industrial applications, for example, combustion enhancement for furnace and oxygen gas improvement in sewerage treatment plant [3]. Recently, the interest was also arisen in the oxygen enrichment of natural gas and coal fired combustion engine by inducing oxygen gas into the combustion process to reduce the fuel consumption and the indoor oxygen gas enhancement for a better indoor air quality [4]. Conventionally, oxygen enriched air is produced by two techniques, i.e., cryogenic distillation and pressure swing adsorption (PSA). Cryogenic distillation is a large-scale production technique with daily production volume more than 100 tonnes of high purity oxygen gas, whereas PSA is a medium scale production technique with high purity oxygen gas production capacity of 20 to 100 tonnes per day [5]. Even though these techniques have been available in the industry for more than 70 years, they still encounter some drawbacks, such as high capital cost and intensive energy requirement. With the advancement of membrane technology, it is believed that membrane technology is able to cater for small oxygen gas production volume at the range of 10 to 25 tonnes per day with an oxygen purity of 25 to 40% [6].

Up till now, there are no commercially feasible membranes that have high permeability and selectivity for large-scale commercial gas production. In principle, the commercially viable membrane shall posses the characteristics of superior permeability and selectivity as well as the chemical and mechanical stability under the long-term operation condition [6]. Previous review articles emphasized the chronology of the development of membranes in gas separation and the progress of separation of various binary pairs of gases. However, this paper was aimed to review the recent progress of the conventional methods and membrane technology used in the O_2/N_2 separation, the membrane fabrication and polymer materials used as well as to provide a brief overview of the recent advancement of the O_2/N_2 separation via membrane technology in the fulfilment of industrial and medical needs.

2. Governing equations in membrane gas separation

Gas separation such as O_2/N_2 separation is a pressure driven process, where the driving force is induced by the difference in pressure between downstream and upstream sides. The membrane used in the gas separation process is generally non-porous layer, so there will be no severe leakage of gas across the membrane due to the membrane porosity [7].

The gas separation performance of a membrane can be described by the solution-diffusion mechanism which is governed by the permeability and selectivity. Under this model, the gas permeability is defined as the product of gas solubility, S_A (cm^3 STP/cm^3 polymer atm or cm^3 STP/cm^3 polymer cm Hg) and effective diffusion coefficient, D_A (cm^2/s) as shown in Eq. (1):

$$P_A = S_A D_A \tag{1}$$

The diffusion coefficient is generally affected by the penetrant size, where the larger gases having a lower diffusion coefficient attributed to the mass transfer mechanism. Additionally, the polymer chain flexibility and free volume in the

polymer depict the positive effect on the diffusion coefficient as the rise in the openings within the polymer is large enough for the gas molecules to diffuse across. The solubility is expressed as the ratio of the concentration of gas in a polymer, C, to the pressure of the gas, P, adjacent to the polymer as shown in Eq. (2).

$$S_A = \frac{C}{p} \qquad (2)$$

The permeability describes the ability of a membrane to allow the permeating gas to diffuse through as a result of transmembrane pressure difference. The permeability can be calculated by the product of permeate flux and membrane thickness divided by the transmembrane pressure difference as shown in Eq. (3) [8].

$$P_A = \frac{N_A l}{(p_2 - p_1)} \qquad (3)$$

where P_A is the membrane permeability, N_A is the permeate gas flux, p_1 is the downstream pressure and p_2 is the upstream pressure. The unit of the permeability is usually represented as Barrer (1 Barrer = 10^{-10} cm^3 (STP)-cm/cm^2-s-cm Hg = 3.35×10^{-16} mol m / m^{2}s Pa). In the case where the membrane is in asymmetric form, causing the difficulty in determining the exact value of membrane skin thickness, membrane permeance will be determined to estimate the membrane performance. Membrane permeance (P_A/l) can be expressed as the ratio of membrane permeability to the membrane thickness and represented in unit of gas permeation unit (GPU) (1 GPU = 10^{-6} cm^3 (STP) /cm^2-s-cm Hg = 3.35×10^{-16} mol m / m^{2}s Pa). (Eq. (4)).

$$\frac{P_A}{l} = \frac{N_A}{(p_2 - p_1)} \qquad (4)$$

Apart from the permeability and permeance, the selectivity of the membrane, $\alpha_{A/B}$ plays a vital role as it illustrates the permeation ability of binary gas separation (e.g., gas A and gas B) in the membrane [9]. The selectivity can be calculated based on the ratio of the permeability of respective gases in binary separation as expressed in Eq. (5):

$$\alpha_{A/B} = \frac{P_A}{P_B} \qquad (5)$$

where P_A and P_B are the membrane permeability of gas A and B, respectively.

3. Oxygen/Nitrogen Separation Techniques

Up to date, membrane technology is still not commercially popular in O_2/N_2 separation and other gas separation applications. The techniques that are widely used in the current industries for O_2/N_2 separation are cryogenic distillation and pressure swing adsorption [4, 5]. These two techniques that dominate the O_2/N_2 separation in industries will be briefly described in the sub-sections with the use of suitable schematic diagram.

3.1. Cryogenic distillation

Cryogenic distillation (Fig. 1), or also known as cryogenic liquefaction process, is similar to the conventional air distillation. The ambient air will be drawn and

compressed by multistage air compressor and purified by air filter to remove the impurities [10]. Then, the temperature of the compressed air will be reduced to remove carbon dioxide, trace hydrocarbon and water vapour prior to the liquefaction. The liquefied air will be transferred into the distillation column where the nitrogen will be extracted from the top of the column due to its relatively lower boiling point compared to oxygen which will be removed from the bottom of the column. The excessive feed gas in the column will be re-circulated to the distillation column for several stages for further purification until the desired concentration of oxygen is achieved. Cryogenic distillation has the advantages of high daily gas production volume (> 100 tonnes per day) and excellent oxygen purity (> 99%) [6]. To date, the well-known global gas producers like Air Products and Linde have commissioned more than 5,000 oxygen product plants in the world using cryogenic distillation to produce oxygen and nitrogen for industrial use [11, 12].
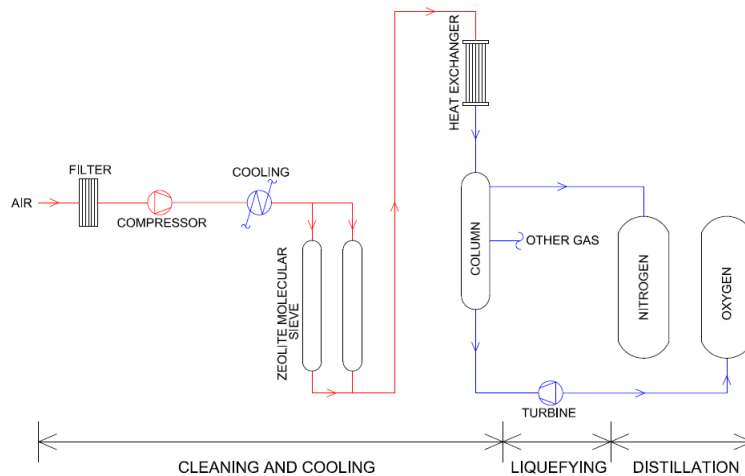

Fig. 1. Schematic diagram of cryogenic distillation process.

3.2. Pressure swing adsorption

Pressure swing adsorption (PSA) (Fig. 2) is a non-cryogenics air separation process which is commonly used in the commercial practice. This process involves the adsorption of the gas by adsorbent such as zeolite and silica in a high pressure gas column. In the PSA process, the air is drawn from the ambient and compressed into high pressure gas [13]. The gas will be transferred into a column which is filled with desired adsorbent materials depending on the required gas. The system will be pressurized for a predetermined period and depressurized to atmospheric pressure, where the low sorbing gas will be slowly leaving out from the column first and followed by the other gases [14]. If the adsorption process occurs under vacuum condition instead of pressurized environment, the process will be known as vacuum swing adsorption (VSA) [14]. Generally, there are two or more adsorbent columns in the PSA process to avoid system down time, so that gas production will not be interrupted during the pressurized and depressurized processes. The PSA is appropriate to be utilized at a relatively lower daily

production volume of 20 to 100 tonnes of oxygen and the oxygen purity of more than 90% [15]. Up to the present, the industrial gas production company Praxair has pushed the production limit to 218 tonnes of oxygen per day with the purity up to 95% by integrating the PSA and VSA into one process, namely vacuum pressure swing adsorption (VPSA) [16].
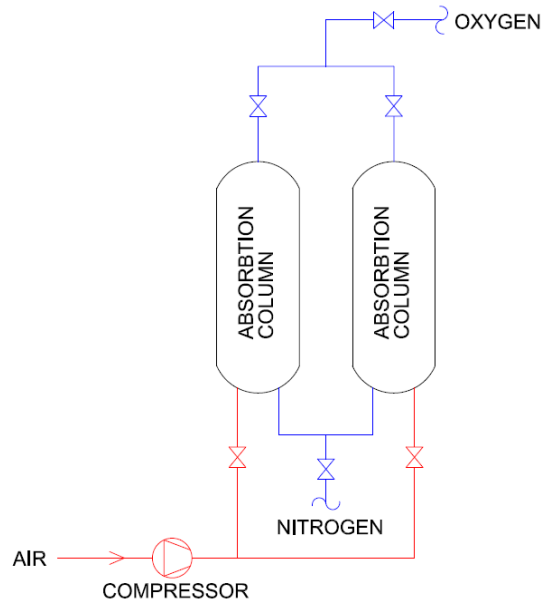

Fig. 2. Schematic diagram of pressure swing adsorption process.

3.3. Membrane technology

Membrane technology is regarded as an emerging gas separation technique in the industry due to the lower cost in both initial capital and energy consumption, if compared to cryogenic distillation and pressure swing adsorption [17]. The typical design of the membrane gas separation technique is that the air is drawn from the ambient into the membrane module and the targeted gases are separated based on the difference in diffusivity and solubility. In the membrane module, oxygen will be separated from the ambient air and collected at the upstream due to the high diffusivity, whereas nitrogen will be collected at the downstream of the module. To date, membrane technology has been reported to produce 10 tonnes to 25 tonnes of oxygen per day with the purity of 25 to 40% [6].

4. Membrane Fabrication Methods and Materials

There are several methods to fabricate membrane such as phase inversion, electrospinning, stretching, interfacial polymerization, and track etching. The selection of the fabrication method is mainly based on the polymer used and the membrane structure requirement [18]. Phase inversion and electrospinning are the most commonly studied membrane fabrication methods in the literature for water

and gas separation processes, whereas interfacial polymerization and stretching are often used to fabricate the membrane used in water filtration [18]. Typically, the membrane fabrication process can be summarized in Fig. 3. Polymer pellets are heated in an oven for 24 hours to remove moisture content. Then, the polymer pellets are added into solvent and stirred for at least 24 hours to prepare dope solution, or the dope solution becomes homogeneous. The dope solution is then degassed in the ultrasonic cleaner to remove any bubble that can be trapped during the membrane fabrication. Subsequently, the dope solution can be used for membrane fabrication by either phase inversion method, electrospinning or other membrane fabrication method. The fabricated membrane will undergo drying process for moisture removal, followed by other post treatment process such as coating or surface modification.
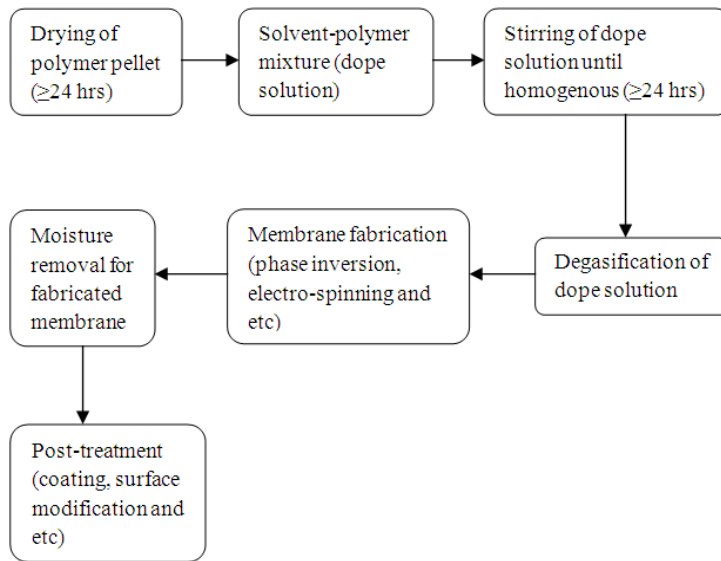
Fig. 3. Flow chart of membrane fabrication.

4.1. Phase inversion

Phase inversion method is a demixing process where the polymer dope solution is transformed into a solid state through solvent-nonsolvent exchange. This method can be used for the fabrication of both flat sheet and hollow fiber membranes depending on the setup of the fabrication equipment. The process usually starts with the immersion of polymer dope solution into nonsolvent coagulation bath for the solvent-nonsolvent exchange during the demixing process [18]. Then, the phase separation will occur where the solvent is evaporated in the coagulation bath, leading to the solidification of the polymer. There are many works have reported the use of the phase inversion technique in producing dense-structured membrane for the use in gas separation [19-23]. Figures 4 and 5 illustrate the system setups that can be used to produce hollow fiber membrane [21] and nanofiber membrane mat [24], respectively.
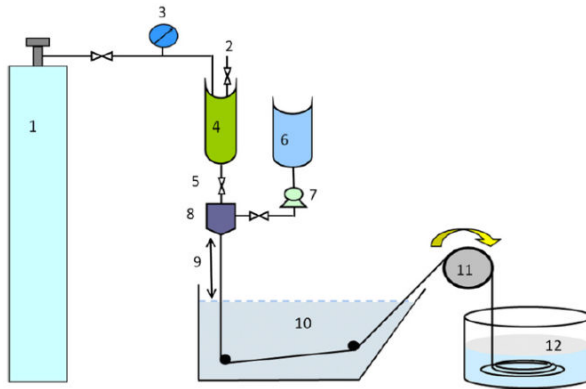
Fig. 4. Schematic diagram of hollow fiber spinning system:
(1) spinning dope tank, (2) regulating pressure valve, (3) pressure gauge,
(4) dope vessel, (5) dope valve, (6) bore liquid vessel, (7) dope liquid pump,
(8) spinneret, (9) air gap, (10) coagulation bath, (11) wind-up drum,
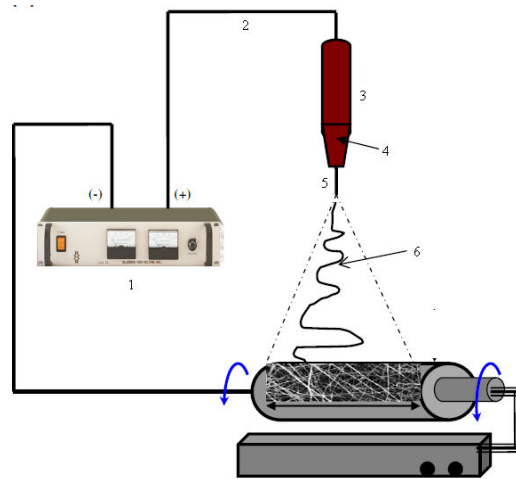**(12) fibre collecting reservoir [21].**

Fig. 5. Schematic diagram of electrospinning system:
(1) high voltage power supply, (2) metal electrode, (3) electrospinning nozzle,
(4) polymer solution, (5) needle tip and (6) polymer liquid jet [24].

4.3. Membrane materials

4.3.1. Polysulfone

Polysulfone (PSU) is a type of thermoplastic which contains subunit of aryl-SO_2-aryl, defining the sulfone group and widely used in the membrane fabrication. PSU was first introduced by Union Carbide in 1965 as replacement for polycarbonates due to the high mechanical strength in nature [25]. Later in 1970,

PSU gained attention by Monsanto Co. as the first polymeric material employed in the large scale membrane gas separation [25]. However, the interest of PSU is diminishing due to the lower permeate flux performance in the gas separation relative to other polymeric materials. Recently, with the advancement of membrane technology, PSU regained the attention in both water and gas separation processes through membrane modification or additive. The commonly used commercial PSU pellets in the literature studies are Vitrex PES, Udel PSF and Radel R where the chemical structures of these polymers are shown in Fig. 6. As illustrated in the Robeson upper bound published in 1991 and 2008 (where the later was the revision of upper bound due to the discovery of better performance membrane with the advancement of membrane technology), PSU recorded a slightly lower performance in terms of permeability and selectivity compared to polyimide. Nevertheless, it still possesses a high potential to be commercially viable membrane [26].
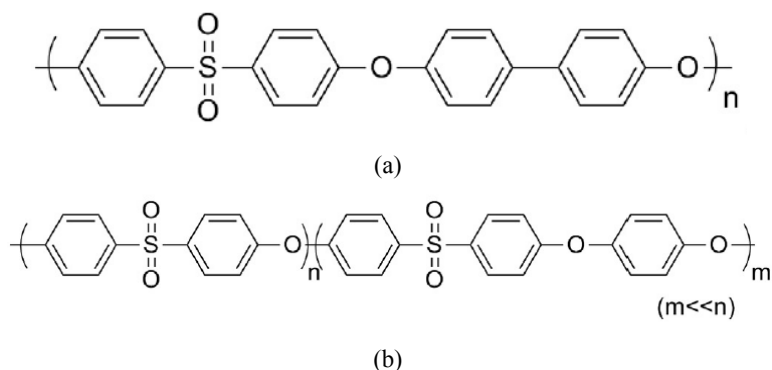

(a)

(m<<n)

(b)

**Fig. 6. Chemical structure of (a) polysulfone (Radel R)
and (b) polysulfone (Radel A).**

4.3.2. Polyimide

Polyimide (PI) is one of the polymers that garners the interests from the academics due to the superior permeate flux and selectivity reported by various researchers in the Robeson 2008 upper bound [27]. Several industrial gas producers such as Air Liquide and Praxair have recently revealed the usage of commercial polyimide pellet (Matrimid®) as polymeric materials in their membrane fabrication for commercial gas separation [6]. The chemical structure of PI consists of 3,3'-4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and diaminophenylindane (DAPI) as shown in Fig. 7 [28]. PI was initially developed for microelectronics and thin film for plastic extrusion due to its excellent mechanical strength and high glass transition temperature, t_g. The combination of these properties enables PI to be used in the more rigorous environment such as high temperature N_2/O_2 gas separation process and oxygen gas in combustion engine [5]. To date, there are no commercial applications of PI owing to the high material cost, despite its above-mentioned advantages on the gas separation.

4.3.3. Poly(2,6-dimethyl-1,4-phenylene oxide)

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an aromatic polyether that is synthesized from oxidized coupling polymerization of phenol with the presence of stoichiometric amount of oxygen under the room temperature as shown in Fig. 8 [29]. PPO is a superior engineering thermoplastic which possesses stable properties against oxidation under high temperature and relatively good mechanical strength compared to PSU due to the stale aromatic ether bond from the phenol. PPO exhibits a relatively good permeability, but moderate selectivity in the 2008 Robeson upper bound [25]. In this regard, it was recently targeted to chemically modify PPO molecular structure or blend PPO with additive to produce modified PPO membrane with superior selectivity [30].
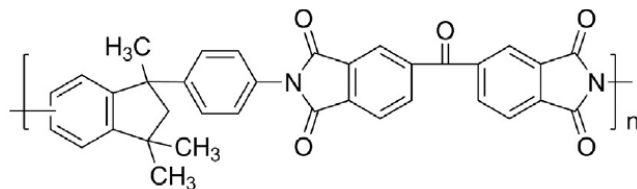

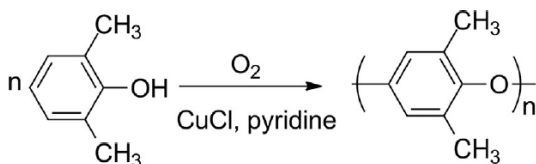**Fig. 7. Chemical structure of polyimide (Matrimid®).**

Fig. 8. Chemical structure of poly(2,6-dimethyl-1,4-phenylene oxide).

4.4. Configurations of membrane module

Typically, there are three different membrane module configurations, namely flat sheet, spiral wound and hollow fiber membrane as depicted in Fig. 9. The ultimate goal of design principle in the membrane module is to achieve high surface to volume ratio, low pressure drop and facilitate high separation efficiency. As gas diffuses through the membrane surface by relatively high pressure driving force, flat sheet membrane module is not a desired configuration in the gas separation process due to poor gaseous flow pattern and low packing density [31].

Generally, the more desired membrane module design is spiral wound and hollow fiber membrane module. In spiral wound membrane module, the flat sheet membrane will be rolled to form the envelope layer separated by spacer, whereas hollow fiber membrane will be packed into the hollow fiber membrane module. These two configurations can maximize the surface to volume ratio as well as accommodate for high pressure applications. For instance, Ma et al. (2015) fabricated the polyimide hollow fiber membrane in O_2/N_2 separation and recorded a promising performance with an oxygen permeability of 63 ± 7 GPU (average $\pm$ standard deviation) and selectivity of 4.6 ± 0.1 [32].
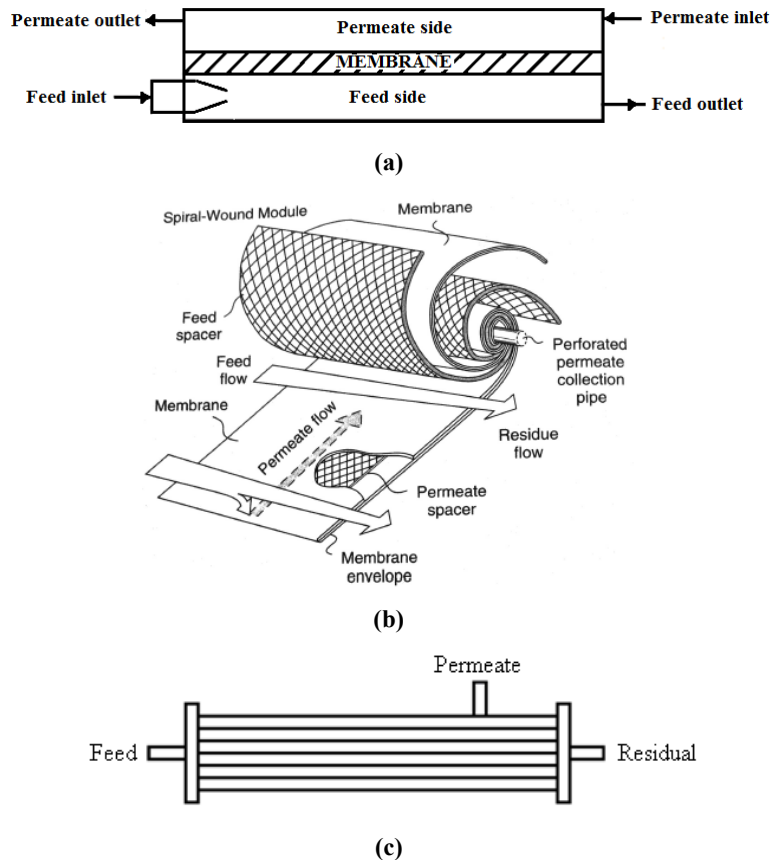
(a)

(b)

(c)

**Fig. 9. Membrane module configurations: (a) flat sheet [33],
(b) spiral wound [34] and (c) hollow fiber [35].**

5. Membrane Performance

The O_2/N_2 separation performance is determined by the permeance, permeability and selectivity as illustrated in Section 2. A commercially viable membrane should exhibit good gas permeability and high selectivity, while maintaining superior chemical and mechanical characteristics under prolonged operating period. The factors contributing to the separation performance of a membrane in terms of permeability and selectivity are the membrane morphology and thickness. In principle, the desired membrane morphology in the gas separation is spongy structure with considerably low membrane thickness (Fig. 10). Besides, the selectivity of a membrane is determined by the type of polymeric material used in the membrane fabrication. It has been reported that the polymeric materials with good selectivity in O_2/N_2 separation are PI, PSU and PPO [6, 26, 28].

Robeson realized the importance of the trade off between membrane permeability and selectivity in determining the potential of the membrane to be commercially feasible (Fig. 11). In 1980, Robeson compiled numerous membrane

gas separation findings in binary pair (O_2/N_2, O_2/CO_2, O_2/CH_4, and etc.) into a correlation which today is commonly known as Robeson upper bound or gas separation trade off limit [37]. The Robeson upper bound is widely used as the benchmark for the novel high performance membrane development for gas separation process. It was subsequently revisited in 1991 and 2008 [26] (Fig. 11) as a result of the improvement of membrane permeability and selectivity. The upper bound is believed to be revisited in the near future with the increase of the research works from various industries, the discovery of novel polymeric materials and the advancement of the technologies [26, 37].

Recently, several literature studies reported that the polymeric materials such as PSU, PI and PPO showed the performance was close to or slightly above the 2008 upper bound (Table 1). For instance, PI carbon membrane recorded the O_2/N_2 permeability and selectivity in the range of 200 to 800 Barrer and 7.5 to 15, respectively. The advancement of the membrane materials indeed indicates the potential of the membrane technology to be commercially feasible in the O_2/N_2 separation process. However, there is still large improvement required to compete with the current available O_2/N_2 separation techniques [6, 37].
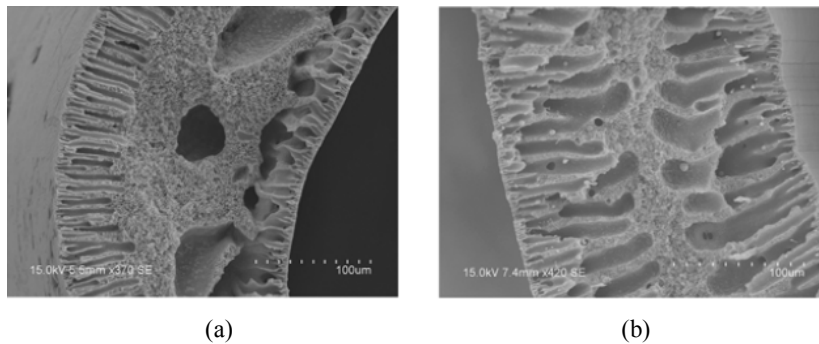

(a)   (b)

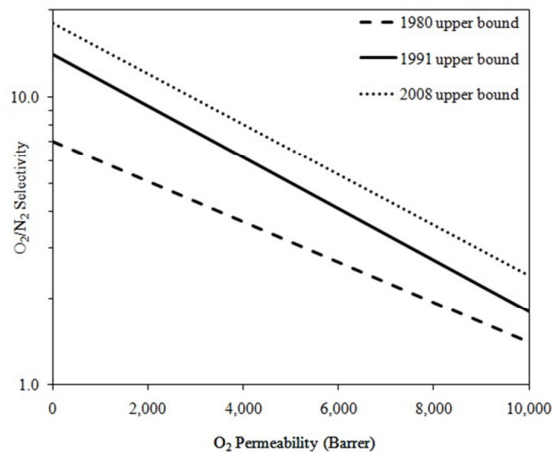**Fig. 10. Membrane morphology, (a) spongy-like structure and (b) finger-like structure [36].**

Fig. 11. Robeson upper bound in 1980, 1991 and 2008.

Table 1. O_2/N_2 separation performance of selected membrane materials.

Membrane	O_2 permeability (Barrer)	O_2/N_2 selectivity	Reference
PSU/CNF mixed matrix	2.2	3.86	[19]
PSU with 20% silica nanoparticles	5.0	4.50	[38]
PPO with SBA15/CMS/Al_2O_3	10.2	8.30	[39]
PSU with 5% µCX	15.3	7.03	[40]
PPO, pristine	16.8	4.41	[41]
PSU with 5% CX	17.8	5.95	[39]
PPO with 20% SBS	18.5	3.80	[42]
PI with 6FDA/BATFM	27.1	3.80	[43]
PI with 6FDA/PPDA/CF_3	30	4.30	[44]
PPO with 1.0% H40	32.2	14.60	[45]
PI/Glucose TLU at $400^{o}C$	135.0	4.00	[46]
PI/PVP blend (b) carbon membrane	200.0	15.0	[47]
PI/Glucose TLU at $425^{o}C$	254.0	3.80	[46]
PI/PVP blend (a) carbon membrane	600.0	10.00	[47]
PI carbon membrane	812.0	7.50	[48]

6. Conclusions

Membrane technology experienced a significant improvement and emerged as an important separation process since asymmetric reverse osmosis membranes were developed by Loeb-Sourirajan in the early 1960s. Throughout these 60 years of evolution and advancement of membrane fabrication techniques, researchers from the industries and academics are in the midst of developing novel membranes that are technically and economically feasible to be applied in gas separation. With the development of current promising polymeric membrane materials such as PSU, PI and PPO, it is important to further explore the possibility of producing mixed matrix, cross-linked and selective layer membranes in order to significantly improve the permeability and selectivity in the O_2/N_2 separation. It is therefore expected that the membrane technology will demonstrate a huge potential to compete with the currently available separation techniques such as PSA and cryogenic distillation to massively produce oxygen for the fulfilment of industrial and medical needs.

Acknowledgement

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