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REVIEW ARTICLE

Carbon membrane for gas separation: A short review

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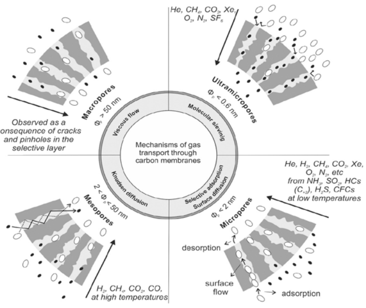

Abstract

For the past 30 years, membrane technology has been prominently used for various gas purifications to obtain a high purity gas. Membrane acts as semipermeable wall, which the separation occurs by controlling the rate of movement of various molecules between two liquid phases or two gas phases or a liquid and a gas phase that passing through the membranes. Then, the advantages offered by membrane process such as simple operation with low energy consumption, low operating and capital cost, continuous process and unnecessary regeneration process compared to absorption and adsorption processes, have attracted considerable attentions by researchers. Besides, traditional methods such as pressure swing adsorption, cryogenic distillation and amine absorption which experienced with high energy consumption, expensive and lead to adverse impact on the environment has even made membrane process as preferable method for gas separation. Polymeric materials were used to develop a membrane that can attain high selectivity and permeability with high chemical and thermal resistance.

Keywords: Membrane, permeability, selectivity, carbon dioxide

INTRODUCTION

In early 1950's, the feasibility of membrane process for gas separations was not widely explored and studied. Until in the late of 1970's, membrane technology has became available for general utilization (Luis *et al.*, 2012). Then, hydrogen separation has became the first industrial application that used membrane technology in large scale production. To date, more than 200 membrane-based plants have been installed in worldwide. In addition, the growing interest in membrane technology also leads to the establishment of few vendors that offering the gas separation process for CO_2 from natural gas, such as Universal Oil Products (cellulose acetate (CA) spiral wound module), Natco (CA hollow fiber membrane modules), Ubi, Air Liquide, Air Products (polyimide (PI) hollow fiber membrane modules) and MTR (perfluoropolymer membranes in spiral wound modules) (Luo *et al.*, 2016). Currently, membrane technology has been used in various gas separation processes such as H_2 recovery, O_2 and N_2 enrichment, natural gas sweetening and the removal of volatile organic compounds from effluent stream. Even though membrane technology has been extensively applied for gas separation, the durability and the performance have been issued comparing with the conventional process. Aforementioned study has reported that membranes tended to have low permeability and selectivity and suffered from severe deformation in corrosive and rigorous operating conditions (Abedini and Nezhadmoghadam, 2010).

Furthermore, membranes used for gas separation are only capable of operating small volume of gas as well as having some other limitations including chemical and physical stability, plasticization at higher pressure and the tendency of swelling by CO_2 (Scholes *et al.*, 2012). However, these limitations are usually associated when dealing with polymeric membrane, as their performances have reached maximum level and became stagnant. Thus, inorganic membrane for gas separation is introduced to overcome the limitation possess by polymeric membrane with better gas separation properties and can withstand at harsh operating conditions. However, inorganic membrane is also suffered with issues on fragility and high cost. Referring at the limitations possessed by both polymeric and inorganic membranes, studies have explored the feasibility of carbon membrane as an alternative solution to provide excellent permeability and selectivity with simple fabrication process by using the flexible polymeric materials. In fabrication of carbon membrane, the utilization of polymeric precursor must be in perfect form in order to prevent the problem occurs during fabrication process (Saufi and Ismail, 2004). Thus, the process condition need to be considered and measured in order to produce an excellent carbon membrane. Producing of low quality carbon membrane may cause the carbonization process conditions that take place to be not sufficient for the selectivity of the membrane itself (Sazali *et al*., 2015; 2017).

Membrane for CO_2 separation

Membrane technology used for CO_2 separation has brought a new revolution in gas separation industries due to the simple separation process and its energy conserved (Fernández-Barquín *et al*., 2016; Sazali *et al.,* 2017). Today, using membrane technology for CO_2 separation has been proven to be a promising substitute to the conventional processes. However, the characteristics of the membrane used for CO_2 removal, such as high permeability and selectivity, thermal and chemical stabilities, plasticization resistance, aging resistance, cost effective and modularity, playing an important role to achieve the desired separation performance (Carapellucci *et al.*, 2015, Waqas Anjum *et al*., 2015; Adewole *et al*., 2013). Several conventional methods of removing CO_2 from refinery gas stream have been applied, such as chemical absorption, physical absorption, physical-chemical absorption and adsorption method (Rufford *et al*., 2012; Sazali *et al.,* 2018). Although most of the processes are commercialized technology and widely used, they are still suffered from some drawbacks. For example, the enrichment of CH_4 in natural gas by using chemical and/or physical separations has required the engineering aspect of large, thick-walled and heavy vessels for absorber stripper with an expensive budget. In addition, with low efficiency of adsorption process, membrane-based separation has emerged as a promising approach to the conventional methods (Scholes *et al*., 2012). There are various factors need to be considered in chemical adsorption system, including low CO_2 loading capacity, high equipment corrosion and abundant energy consumption during solvent regeneration. Moreover, the degradation of amine by SO_2, NO_2 and O_2 in flue gas, high solution circulates rate and degradation, the toxicity of the amine, presence of contaminants and cost-ineffectiveness are other factors need to take into account (Zhao *et al*., 2016; Sun *et al*., 2015).

Current status in carbon membrane technology

At the beginning of the emergence of membrane technology in early 60's, synthetic-type membrane has been introduced and applied for various applications. Then, polymeric synthetic-type membrane was mostly developed and used for gas separation as it could provide with a good efficiency. However, this polymeric membrane faced problems in selectivity and tended to wear out in high pressure operation. Besides, it also possessed low thermal and chemical resistances. Hence, chemical and/or physical modifications such as the synthesis of new polymer materials has been performed to improve the properties and performances of polymeric membrane (Banerjee *et al*., 2004). Furthermore, carbon membrane that produced as the end result of thermal decomposition (carbonization process) of polymeric membrane (as precursor) has became another promising type of membranes for gas separation. Besides, carbon membrane has also a better separation capability (sieving effect) as compared to polymeric membrane. Other than that, introducing an inorganic membrane for gas separation can diminish challenges faced by polymeric membrane such as swelling and plasticization, due to the properties of inorganic membrane that can withstand at high temperature and pressure, as well as in harsh environment (Dalane *et al*., 2017). Apart from the inorganic membrane, carbon membrane, zeolite membrane and metallic membrane also have been mostly studied (Rungta *et al*., 2015; Sazali *et al.,* 2018), in which carbon membrane can achieve a superior performance by selecting a material with high thermal and mechanical stabilities (George *et al*., 2016). Thus, carbon membranes offer as the best candidates for the development of new type of membrane in membrane technology, due to their stability and molecular sieving capabilities. The most notable advantages of carbon membranes over polymeric membranes have been recently reviewed to emphasize the influences that make the carbon membranes very appealing and beneficial as separation tools (Lin and Yavari, 2015; He and Hägg, 2012; Khalilpour *et al*., 2015). For gas separation, the energy intensity required is low or comparable with the absorption (0.5-0.6 MJ/kg CO_2). However, the limited use of the membrane separation is mainly related to the low selectivity of membrane materials which induces an indirect energy requirement (Wang *et al.*, 2012).

Aforementioned studies have reported on the separation of mixture gases by using polymeric membranes (Lin and Yavari, 2015; Brunetti *et al.*, 2010). However, some difficulties are occurred, involving the low perm-selectivities and the deficiency of thermal and chemical stabilities of the polymeric membranes. These difficulties have motivated most researchers to fabricate thermally and chemically stable non-polymeric membranes that possessed various enhanced characteristics to improve the gas separation performance. According to Noro *et al.* (2015), the selection of carbon membranes is distinctive and proficient in distinguishing size changes among alkane and alkene molecules. In addition, it is possible to retain carbon membranes in separating isomers of hydrocarbons into standard and separated sections (Lee *et al*., 2013; Yusuf *et al*., 2015). Nevertheless, the main issue in the fabrication of carbon membranes is the high production cost. According to Mannan *et al.* (2013), the comparison of carbon membrane's cost per unit area is described to be within one and three orders of magnitude bigger than usual polymeric membranes. Therefore, carbon membranes need to accomplish better performance compared to polymeric membranes in order to repay on behalf of their higher expenses.

Carbon membranes

Carbon membranes have received huge interest for gas separation process as efforts to develop new membrane materials that can show excellent permeability and selectivity. Carbon membrane is formed from the carbonization of polymeric precursors under thermal treatment. The presence of benzene ring and other functional groups in the polymeric precursor will result in amorphous materials after undergoing carbonization process. These resultant carbon membranes are consisted of disordered sp2 hybridized, condensed hexagonal sheets that serve as an idealized pore structure, with pores formed due to packing imperfections (Bhuwania *et al*., 2014). The idealized pore structure serves as channels for gas permeation while providing good selective features through molecular sieving. As compared to the polymeric membrane, carbon membrane possesses higher thermal and chemical resistances that can prevent over membrane contamination, physical aging and plasticization (Adewole *et al*., 2013). In addition, the great pore volume of carbon membrane has improved the performance of carbon membrane with higher selectivity and permeability, especially in the separation of similar size of gas molecules such as O_2/N_2, CO_2/CH_4 and CO_2/N_2 (Koresh and Soffer, 1986; Jones and Koros, 1994; Tanihara *et al*., 1999; Hunt *et al*., 2010). In addition, carbon membrane also offers a great performance without increasing energy consumption and operational cost as the cooling process can be omitted from the system (Hosseini and Chung, 2009; Sazali *et al.,* 2018). Previous study also has reported that carbon membrane is an ideal candidate for gas separation as it exhibits an excellent permeability and selectivity (Ismail and Li, 2008; Song *et al*., 2008). Based on Xiao *et al.* (2009) findings, the orientation dislocations of aromatic micro domains in glass-like matrix are able to increase the free volume and ultra-micro porosity. The microspores are usually considered to be nearly slit-shaped and the pore mouth dimensions are similar to the diameters of the small molecules.

Type of carbon membranes

In general, carbon membranes can be divided into two groups based on their effective pore size and separation mechanism towards gas separation; which are adsorption-selective carbon membrane (ASCM) and carbon molecular sieve membrane (CMSM) (Xiao *et al.*, 2010). The modification on micropore size of the carbon membrane produced can influence the permeation rate as well as the selectivity (Ismail and Li, 2008). Therefore, two types of carbon membrane are distinguished in this study. The idealized arrangement of a pore in a carbon material is shown in Fig. 1 (Merritt *et al*., 2007). Furthermore, based on density and selectivity, membrane can be divided into two classes which are porous and non-porous. Porous membrane has rigid and extremely voided structure with inter-connected pores. According to Barsema *et al.* (2002), separation by porous membrane can be obviously affected by permeation characteristics and membrane properties, including the molecular size of the membrane polymers, pore sizes and pore-size distributions. If molecules have greatly differed in size, it can divide efficiently by microporous membranes. Interestingly, porous membrane configuration is suitable to be functioned as common filter. For gas separation application, porous membrane is able to perform at excessive level of density; nonetheless it still able to obtain small selectivity values. Microporous membranes are characterized based on the average pore diameter, the porosity of the membrane and asymmetry of the membrane. They demonstrate unique permeability properties for $CO_{2,}$ as well as high selectivity towards CH_4, CO_2 and N_2 (Ismail and David, 2001).

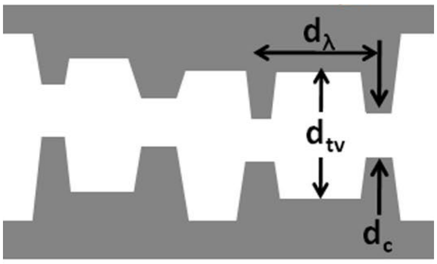

Fig. 1 Idealized arrangement of a pore in a carbon material (Merritt *et al.*, 2007).

In 2000, Fuertes had studied on carbon membrane which mainly focused on the preparation of CMSM. There are numerous precursors that can be used for fabrication of CMSM such as phenolic resins (Centeno and Fuertes, 1999; Teixeira *et al.*, 2011), polyimide (Jones and Koros, 1994; Xiao *et al.*, 2009; Chua *et al.*, 2013), phenol formaldehyde resin (Zhang *et al.*, 2007; Zhang *et al.*, 2006), and polyetherimide (Bakeri *et al.*, 2012; Tseng *et al.*, 2012). It is reported that CMSM has pore sizes ranging from 3 to 5 Å (Fuertes, 2000). Thus, CMSM is capable to separate the mixtures of permanent gases (<4) such as O_2/N_2, CO_2/N_2, CO_2/CH_4 (Centeno *et al.*, 2004) based on its molecular sieving mechanisms. The separation properties of CMSM can change abruptly depending on the kinetic diameter and the shape of penetrating gases (Kiyono *et al.*, 2010).

Configuration of carbon membranes

Carbon membrane can be divided into two main configurations: unsupported and supported carbon membranes (Zhang *et al.*, 2013). Then, unsupported membranes can be splitted into three different configurations: flat (film), hollow fiber and capillary while, while supported membranes can exist in two configurations: flat and tubular. Fig. 2 shows the classification of carbon membrane configuration (Ismail and David, 2001). Furthermore, the unsupported carbon membranes are more brittle than the supported carbon membranes. On the other hand, the supported carbon membranes require the polymer deposition-carbonization steps to be conducted for several times in order to produce almost crack-free membranes (Briceño *et al.*, 2012). The selection of a carbon membrane configuration depends on several factors including the nature of the polymer, the straightforwardness of shape and structure formation, the reproducibility of the given structure, the membranes performance characteristics and structural strength, the nature of the separation, the extent of use and the separation economics.

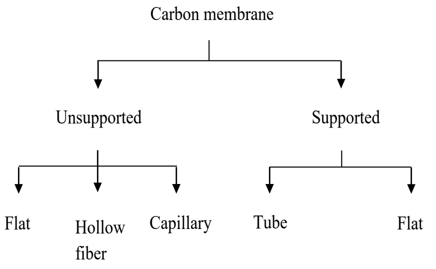

Fig. 2 Configurations of carbon membranes (Ismail and David, 2001).

With an aim to produce a high-quality carbon membrane, the conditions during fabricating process must be optimized. As low-quality carbon membrane will interfere with the carbonization process that eventually may not achieve the selectivity target of the desired membrane. According to the previous researches, improvement in the sorptivity (capacity of the medium to absorb and desorb) and diffusivity of penetrants in carbonized membrane is measured. It is reported that at high temperature, the micropore volume (free space) and segmental stiffness of carbon membranes are increased and optimized the selectivity of the penetrants. The results are in line with the statement stated that carbonized membranes possess a micropore structure which is able to recognize the sizes of different molecules (Ismail and David, 2001). Due to the brittleness of unsupported carbon membranes, an extra careful handling is required (Tin *et al.*, 2004). Besides, it faces challenges to be fabricated especially for larger surface area of membrane. However, this problem can be overcomed by producing supported carbon membranes either in tube or flat sheet configuration. In addition, with aim to produce and achieve the best quality carbon membrane, several ideal specifications need to be highlighted. For instance, low quality of carbon membrane may form due to the incomplete selectivity of certain membranes during the carbonization process. Therefore, the precursor or polymeric membranes used to fabricate carbon membranes should be prepared with defect free form to reduce the issues that might be happened during fabrication process of carbon membranes (Saufi & Ismail, 2004).

Advantages of carbon membranes

In general, carbon membranes are produced by thermal decomposition of polymer precursor membrane. These materials can sustain high temperature due to their highly aromatic structure comprised of disordered sp2 hybridized carbon sheet and disorientation angle. Moreover, a study has reported that carbon membranes can produce high permeability and selectivity without sacrificing their productivity compared to those typically found with polymeric membranes (Maab *et al.*, 2009). This is due to the well-defined and disordered structures of carbon materials that distinguishing them from zeolites. Previous researchers have critically reviewed the advantages and the potential of carbon membrane for gas separation in the last decade (Ismail and David, 2003). Carbon membranes are proven to exhibit higher selectivity than polymeric membranes especially in the separation of similar gas molecules such as O_2/N_2, CO_2/CH_4 and CO_2/N_2 (Salleh and Ismail, 2012, Yong *et al.*, 2013; Wang *et al.*, 2007). Surprisingly, higher selectivity achieved by carbon membrane does not sacrify the permeability and/or productivity that usually occurred in polymeric membrane (Lie and Hägg, 2006). In often, carbon membranes are capable to provide excellent shape selectivity and high chemical stability as required in gas separation processes (Brunetti *et al.*, 2010; Luis *et al.*, 2012; Sazali *et al.,* 2018). Besides, carbon membranes also have an interesting feature of separating a gas mixture at various temperatures (normally up to the temperature where carbon membrane begins to deteriorate). While, separation of non-oxidizing gases, this temperature can be up to $1000^{o}C$ (Ismail and David, 2001). A continuous test of carbon membrane at operational temperature of 400 ^{o}C for one month by Koresh and groups (Koresh and Soffer, 1986) have reported that no deterioration is measured. Another study also found that carbon membranes are able to work at sub-ambient temperature, leading to great increase in selectivity with little or no loss in permeability, especially in separating O_2 from Ar to produce pure Ar (Fu *et al.*, 2011).

Carbon membranes also provide the advantage in term of operation environment such as in the presence of organic vapor or solvent and non-oxidizing acids or bases environments which is prohibitive to polymeric membrane (Tang *et al.*, 2013; Sazali *et al.,* 2018). Furthermore, carbon membrane can resist towards radiation, chemicals and microbiological attack. CMSM can be used for a long period under an environment that contains low levels of oxidants in air (Yamamoto *et al.*, 1997). This is to make sure that this type of membranes possess longer life time compared to polymeric membranes. The membranes become more attractive as their pores characteristic can be controlled based on the preferable separation applications. Besides, the same material can be used during fabrication process to develop a carbon membrane with different permeation properties for different gas mixtures (Kargari *et al.*, 2014; Centeno and Fuertes, 1999). This is completed by conducting simple thermos-chemical treatment to meet different separation requirements and objectives. Due to those features, it attracts more researches in carbon membrane in order to tailor its separation performance in different applications.

CONCLUSION

The application of membrane in gas separation is a dynamic and rapidly growing field. It has drawn much attention by offering a number of advantages including ease of operation (no moving parts), low energy requirements and the overall economics of low-scale operation. Gas separation is one of the premier applications of membrane technology. Membrane for gas separation technology can be marked as a competing industrial gas separation technique. Carbon membrane is one of the potential methods to remove CO_2 from natural gas. A wide interest received on this membrane for gas separation is strongly due to its molecular sieving properties that possess a high selectivity as well as its high thermal and chemical resistance. Thus, the advantages offered by carbon membrane has provided it with ideal characteristics to be fabricated for gas separation in industrial application.

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