

carbonization process conditions that take place to be not sufficient for the selectivity of the membrane itself (Sazali et al., 2015; 2017).

Membrane for CO₂ separation

Membrane technology used for CO₂ 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 CO₂ separation has been proven to be a promising substitute to the conventional processes. However, the characteristics of the membrane used for CO₂ 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 CO₂ 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 CH₄ 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 CO₂ loading capacity, high equipment corrosion and abundant energy consumption during solvent regeneration. Moreover, the degradation of amine by SO₂, NO₂ and O₂ 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 become 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 CO₂). 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 O₂/N₂, CO₂/CH₄ and CO₂/N₂ (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

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