

A Mini Review on Carbon Molecular Sieve Membrane for Oxygen Separation

Fatin Nurwahdah Ahmad¹, Norazlianie Sazali^{1,2,*} and Mohd Hafiz Dzafran Othman³

*Correspondence
azlianie@ump.edu.my

+This author contributes
equally to this work

¹ Faculty of Mechanical
Engineering, Universiti
Malaysia Pahang, 26600,
Pekan, Pahang, Malaysia

² Centre of Excellence for
Advanced Research in Fluid
Flow (CARIFF), Universiti
Malaysia Pahang, Lebuhraya
Tun Razak, 26300 Gambang,
Kuantan, Pahang, Malaysia.

³ Advanced Membrane
Technology Research Centre
(AMTEC), Universiti
Teknologi Malaysia, 81310
Skudai, Johor Bahru,
Malaysia.

Articles Info:
Received **28 January 2020**
Received in revised form
20 March 2020
Accepted **27 March 2020**
Available online
31 March 2020

Keywords:

Oxygen
Carbon membrane
Gas separation
Carbonization
Polymeric precursor

ABSTRACT

Membrane-based technology has proved its practicality in gas separation through its performance. Various type of membranes has been explored, showing that each type of them have their own advantages and disadvantages. Polymeric membranes have been widely used to separate O₂/N₂, however, its drawbacks lead to the development of carbon molecular sieve membrane. Carbon molecular sieve membranes have demonstrated excellent separation performance for almost similar kinetic diameter molecules such as O₂/N₂. Many polymer precursors can be used to produce carbon molecular sieve membranes through a carbonization process. This paper discusses the variety of precursors and carbonization parameters to produce high quality and performance of carbon molecular sieve membranes. This paper covers the evaluation in advancement and status of high-performance carbon membrane implemented for separating gas, comprising the variety of precursor materials and the fabrication process that involve many different parameters, also analysis of carbon membranes properties in separating various type of gas having high demand in the industries. The issues regarding the current challenges in developing carbon membranes and approaches with the purpose of solving and improving the performance and applications of carbon membranes are included in this paper. Also, the advantages of the carbon membrane compared to other types of membranes are highlighted. Observation and understanding the variables affecting the quality of the membrane encourage the optimization of conditions and techniques in producing high-performance membranes.

INTRODUCTION

The word membrane comes from the membrana, which is a Latin word with a definition of skin (A.G. (Tony) Fane *et al.*, 2011). Presently, this word of membrane represents a thin flexible sheet or film that acts as a barrier that allows particular substances to pass through (Paola Bernardo & Clarizia, 2013). Membrane technology has been studied and become one of interest in the industry in the past 60 years. The gas separation membrane's market was expected to reach 350 million USD in 2010, however, it is reported that the real market value achieved is in the range of 500 million USD which is 30% more than expected value (W.Baker, 2002; Yampolskii, 2012). The increase of market value for the gas separation membrane shows that its demand is growing and expanding. The gas separation technology begins from the year 1850 when the law of diffusion was first discovered by Graham. Since the world is heading to the target of optimizing the use of clean source energy, gas separation mainly hydrogen from carbon dioxide (H₂/CO₂) has received extensive attention and interest. Of late, gas-product (flue gas) from power plants

such as CO₂ and nitrogen (N₂) are reported to be major contributors to the emissions of man-made CO₂ (Rufford, 2012). The arising concern of global warming causes a lot of studies and researches have been done to develop and improve separation and capture methods of CO₂ from flue gas. Commercial gasification facilities are being built on larger scales, and as a result, they have enormous oxygen (O₂) requirements, which continue to push the technology requirements to economically produce oxygen to meet such large-scale demand. Gas separation of nitrogen from oxygen has been marketed in the industry since 1985. Researches on membranes involving a variety of polymeric precursors and separation of various gas are currently continuing.

The slight difference between the kinetic diameters of oxygen and nitrogen causes the process of gas separation to become very difficult. Membrane gas separation is currently accepted as a cost-effective process for the production of moderately pure streams oxygen of 60% up to 80%. The streams can be further processed to achieve the desired purity percentage depending on the applications. Membrane-based gas separation has demonstrated its potential to be better alternatives compared to conventional separation techniques. The two main conventional technologies used for gas separation before membrane technology is introduced are sorption technology and cryogenic distillation. Limitations of these technologies inducing the consideration in developing membrane as a convincing technology for gas separation. The practicality of membrane-based technology for separating oxygen is strongly dependent on the performance enhancement of the membrane. Polymeric membrane materials are known as a dominator in gas separation for current industrial use.

Polymeric membranes are widely used in the gas separation process due to their properties such as high mechanical strength, high flexibility, and cost-effective processing capacity. However, there are several disadvantages of polymer membranes that limit their industrial implementation especially in terms of their quality where they will depreciate over time if being used in harsh environments (Zhang & Way, 2017). The polymeric membranes studies give results that their limitations of physical aging (Murphy *et al.*, 2011), poor stability of chemical and thermal as well as plasticization performance make it not good enough for gas separation (M.Wessling *et al.*, 1991). An extremely small number of polymers have successfully surpassed the upper bound limit because the selectivity of those polymers is small. These disadvantages of polymeric membranes in the separation process encourage the study of carbon membrane primarily due to their higher mechanical strength, pore-volume, chemical and thermal resistance with high separation factors compared to the polymeric membrane.

The carbon molecular sieve membrane is produced through the carbonization of the polymeric precursor. Carbon molecular sieve membranes have been reported to have great separation performance for gases having a slight difference in molecular size (Gilron, 2002; Li-HuaCheng *et al.*, 2014). The pore dimension in this type of membrane can be modified depending on the selection of precursor material, fabrication procedure, as well as the parameters used during the carbonization process. In the early 1980s, Koresh and Soffer (1983) followed by Kapoor and Yang (1989) proved the carbon membranes produced from carbonization of polymeric materials is effective for separating gas (Kiyono *et al.*, 2010). The pore dimensions of the carbon membrane can be modified by manipulating carbonization conditions. The carbon membrane has been recognized as a solution to the current membrane technology problems (Koros & Mahajan, 2000). The carbon membrane seems to have a successful trade-off combination of permeability-selectivity, also it is capable of separation performance in a condition where impractical for other polymer membranes. Different carbon molecular sieve membrane structure and gas permeation performance will be produced through differentiating the experimental parameters. The development of carbon molecular sieve membrane with improved permeability and selectivity using various precursors can be found in past researches. So far, there is not yet to be found that carbon membrane performance tends to be a trade-off between permeability and selectivity, for example, highly selective membrane appearing to have low permeability (Geiszler & Koros, 1996). Also, the implementation of carbon molecular sieve membrane in industrial scale is still unavailable due to its high cost, aging issues, poor mechanical stability and gas separation performance for various gas are still needed to be studied (W. Salleh, 2017).

ADVANTAGES OF MEMBRANE TECHNOLOGY

Membrane technology has several advantages compared to traditional technologies such as sorption technology and cryogenic distillation. Membrane technology is an energy-efficient technology and it does not harm the environment. Also, the low capital cost is required since this technology involves only simple equipment design. This technology comprises a completely enclosed system that minimizes direct gas-product emissions. Other than that, this method involves a compact and modular system, thus it can be easily transported. This technology is favorable for industrial applications since it requires small operating cost and its scale is adjustable. Only a small amount of energy is required due to the only vaporization

process need to be done is the vaporization of the liquid. Besides this process allows to recover the concentrated products, its asymmetric structure can be prepared easily.

POLYMERIC MEMBRANE FOR OXYGEN SEPARATION

Oxygen constitutes 21% of the air. Oxygen is used as industrial oxygen (enhanced combustion during cement and glassmaking operations, melting and smelting operations in steel, and aluminium and copper production), an oxidizing agent during the production of many chemicals, fuels, as a safer and environmentally friendly alternative in pulp-and-paper operations for bleaching compared to chlorine, as well as an agent for delignification. Besides, oxygen is used to support fermentation processes in biotechnology and pharmaceutical applications, and to provide biological oxygen demand during aerobic wastewater treatment. More recently, strong demand for very large quantities of oxygen (tonnage quantities) has been spurred by steady growth in chemical process operations, for instance, that rely on oxygen-blown gasification to convert coal, petroleum coke, biomass, municipal solid waste, and other feedstocks into an intermediate synthesis gas, which can then be further processed to yield electricity, chemicals or transportation fuels.

Polymer have been explored for gas separation as they have low coefficients of permeability, high selectivity and good thermal stability. Various polymeric materials have been studied to alter their chemical and physical characteristics to obtain excellent separation performance for separating O₂/N₂ as shown in Table 1 (*1GPU = 1 × 10⁻⁶ (cm³ (STP). cm)/(cm². sec. cmHg)) (R. S. Murali *et al.*, 2013).

Table 1 Previous polymeric membranes studies for O₂/N₂ separation

Polymer	P _{O₂} (Barrer)	PO ₂ /PN ₂
PMP	37.2	4.2
PP	1.6	5.4
PDD-TFE	908 (GPU)	2.63
PSF-PEO	0.4	5.8
ABS	0.7	6.8
Hyflon®AD60	180 (GPU)*	3.5
Hyflon®AD80	574 (GPU)	3.1
Cytop®	130 (GPU)	3.8
Teflon®1600	1175 (GPU)	2.3
6FDA/TAPOB	2.3	6.2
6FDA-TPEQ	2.2	6.0
6FDA-TPER	1.1	6.6
6F-BAPB	1.1	4.9
6F-DBAPB	1.5	5.1
6F-TBAPS	2.7	5.3
TMBPS-BTDA	1.0	9.3
BATB-6FDA	4.5	6.6
BATB-BPDA	0.9	7.9
BATB-BTDA	0.9	8.8
TMBPS-6FDA	5.2	6.8
TMBPS-ODPA	1.6	7.8
TMBPS-BTDA	1.0	9.3
PIM-1	370	4.0
PIM-7	190	4.5
BTDA-ODA/pPDA	0.05	5.5
6FDA/BTDA-ODA	0.6	7.8
BTDA-ODA/DAM	0.4	6.0
6FDA-TMPDA	110.3	3.66
6FDA-DAT	8.8	5.76
6F-HPI	3.73	6.8
P-HPI	2.58	7.1

B-HPI	0.72	7.7
Bt-HPI	0.6	6.6
O-HPI	0.54	9.3
PEEKWC	13.9	6.4
Torlon 4000TF	0.12	8
TM-NPSF	1.2	7.6
HF-NPSF	1.2	6.4
TMHF-NPSF	1.4	6.1
6FDA-2,6-DAT	8.8	5.8
6FDA-2,6-DAT/mPDA(3:1)	5.2	6.1
6FDA-2,6-DAT/mPDA(1:1)	3.7	6.3
6FDA-2,6-DAT/mPDA(1:3)	2.5	6.5
6FDA-mPDA	2.1	6.8
Extem	0.81	6.2
HFA/TERT	5.8	5.0
HFA/TERT-b-DBF/ISO 18	4.7	6.4
HFA/TERT-b-DBF/ISO 12	3.3	7.4
HFS/TERT-b-DBF/ISO 9	4.1	7.4
PA	5.23	8.05
PMDA-ODA	0.61	436
PMDA-(ODA:DABA)(4:1)	1.03	5.17
PMDA-(ODA:DABA)(9:1)	0.84	4.97
PMDA-[ODA:(DABA/PTMS)](4:1)	1.35	6.42
PMDA-[ODA:(DABA/PTMS)](9:1)	0.96	5.64
TR- α -PBO	148	4.35
TR- β -PBO	15	5

CONFIGURATION OF CARBON MOLECULAR SIEVE MEMBRANE

Generally, membrane configurations can be categorized into two, which are supported (flat and tube) and unsupported (flat sheet, capillary, and hollow fiber membrane). Flat sheet membranes are the earliest and the most produced membrane until early 1990, then followed by the fabrication of other membrane configurations in the middle of 1990 which are carbon hollow fiber membranes, carbon capillary membranes and carbon-supported tubes membranes (A.F. Ismail & David, 2001). L.M Robeson has stated in 1991 that the limitation of membrane performances is the upper bound trade-off, and in the year of 2008, it has been updated for gas pairs such as H_2/N_2 , H_2/CH_4 , H_2/CO_2 and O_2/N_2 (M.Robeson, 1991, 2008). The plot of Robeson's upper bound for O_2/N_2 separation is shown in Figure 1, where permeability (P) on the x-axis and selectivity (α) on the y-axis. The points on the plots indicate data for various types of membranes.

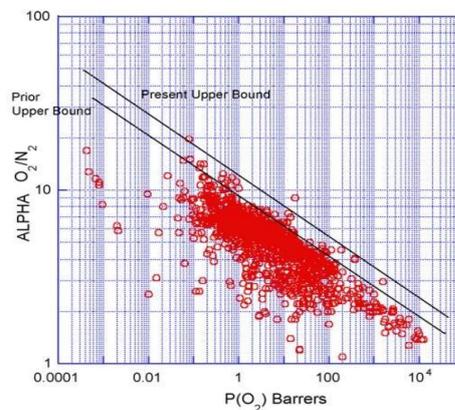


Figure 1: Robeson's upper bound.

Configurations of carbon molecular sieve membranes can be divided into two main groups, which are supported and unsupported (Centeno *et al.*, 2004). As stated earlier, unsupported membranes are further divided into three: hollow fiber, capillary while, and flat (film) configurations, whereas supported membranes are divided into two: flat sheet and tube. The supported carbon membrane is produced by coating a support, commonly metallic or ceramic and it is stronger than the unsupported carbon membrane. Supported carbon membrane involves a couple of cycles of polymer deposition-carbonization steps to produce an almost crack-free membrane. The selection of membrane configuration is determined by various factors such as the nature of the material, the desired structure and specification, the reproducibility of a structure, the characteristics and structural strength of the membrane, the separation performance as well as economic aspect. A high-quality carbon molecular sieve membrane can be produced by certain optimized parameters. The selectivity of a membrane may not be satisfying at the carbonization stage if low quality carbon membranes are used. The brittle characteristics of the carbon membrane require careful handling which causes difficulties in manufacturing especially for larger surface membranes (Xiao & Chung, 2006). The implementation of supported carbon membranes either a flat sheet or tube can solve this problem.

The carbon membrane is further categorized into two classes based on its pore size and gas separation mechanism (Stern *et al.*, 1989). Slight changes in the microspore size of the carbon membranes could greatly alter its permeation and separation rate (Menendez & Fuertes, 2001). Fuertes, A.B. says research on carbon membrane is primarily focused on the fabrication of carbon molecular sieve membrane (Antonio B. Fuertes, 2000). Polyimide (Ahmadizadegan *et al.*, 2018), phenolic resin (Teixeira *et al.*, 2011), polyetherimide (Zainal *et al.*, 2017) and phenol-formaldehyde resin (Abd Jalil *et al.*, 2017) is the common precursors used in fabricating carbon molecular sieve membrane. It is assumed that the pore size of the carbon molecular sieve membrane is 3 to 5 Å (Antonio B Fuertes, 2000). The carbon molecular sieve membrane has the ability to separate permanent gas mixtures depending on molecular sieving mechanisms, such as CO₂/N₂, O₂/N₂, and CO₂/CH₄ (Menendez & Fuertes, 2001). The pores of the carbon molecular sieve membrane change depending on the kinetic diameter as well as the shape and molecular size of the penetrating gases.

ADVANTAGES AND DISADVANTAGES OF CARBON MOLECULAR SIEVE MEMBRANE

Researchers have reviewed comprehensively the advantages of carbon molecular sieve membrane and its potential in separating gas (A. F. Ismail & David, 2001). Noticeable progress has been done in the development of carbon membrane specifically for separation of gas. It has been shown that the carbon molecular sieve membrane exhibits superior selectivity compared to the polymer membrane for a similar size of gas molecules such as CO₂/N₂, CO₂/CH₄, and O₂/N₂ (N. Sazali *et al.*, 2018). High selectivity is achieved without losing its efficiency and permeability. Carbon membranes are capable to change its pore shape, selectivity and have high chemical stability that is important in gas separation processes (Zito *et al.*, 2017). Another desirable feature of the carbon molecular sieve membrane is its ability to separate gas mixture at different temperatures up to its deteriorating temperatures. No deterioration occurs for non-oxidizing gasses in which the temperature could be about 1000°C, and various tests performed repeatedly on the carbon membrane at 400°C (Haider *et al.*, 2018). Another study found that carbon membrane can also work under sub-ambient temperature, resulting in remarkably increased selectivity with only a slight or no loss of permeability in producing pure argon (Ar) by separating from oxygen. Carbon molecular sieve membrane benefits by its ability to work in conditions that are prohibitive for polymer membrane, for example, in the presence of organic solvent and vapor, or non-oxidizing bases and acids. It also has high radiation, microbiological and chemical resistance. The carbon molecular sieve membrane can be used in atmospheric conditions containing low levels of oxidants for an extended period of time (Hayashi *et al.*, 1997). Hence, this independent time factor increases the operating life span of the carbon membrane relative to the polymer membranes.

Carbon molecular sieve membranes being more useful with its ability to modify and control their size of pores to separate different pairs of gases. Similar material can be used in fabricating carbon molecular sieve membranes to separate different gas mixtures with diverse permeation properties. This will draw numerous carbon membrane-related research to enhance its separation capability for a particular implementation. Whereas, the major disadvantage of carbon molecular sieve membrane is being delicate and breakable (Hamm *et al.*, 2017). The practical use of an unsupported carbon membrane requires careful handling. This problem can be reduced by using a supported carbon membrane. However, polymer deposition-carbonization needs to be repeated to produce defect-free supported carbon membrane (Wollbrink *et al.*, 2016). The brittleness causes membrane with broader surface area difficult to be produced. Therefore, the presence of supported carbon membranes of flat or tube configuration can solve this problem (Mahdyarfar *et al.*, 2013).

At room temperature, the carbon membrane outermost layer has a high oxygen affinity. When exposed to air, the complex oxygen-containing surface is created as a result of the oxygen chemisorbed by carbon membrane which will later act as the main site of water sorption (Grewe *et al.*, 2016). Additional water molecules will be attracted by those water molecules formed through the clusters of hydrogen bonding that will expand combined forming pores filling. This causes a negative impact on the carbon molecular sieve membrane in which it will separate gases according to their narrow microporosity. At room temperature, micropores are gradually filled with water that causes a reduction in the permeability of non-polar gases. Changing the surface properties of the carbon molecular sieve membrane is, therefore, a critical technique for separating desired gas. Comparable to the polymeric membrane, carbon membrane also prone to fouling in many hydrocarbon compounds occur due to the presence of impurities (vapors of toluene and n-hexane). This will reduce the gas selectivity (Bae *et al.*, 2007). Therefore, the carbon membrane must be fitted with a pre-purifier to eliminate highly adsorbent impurities and vapors trace through various extraction, separation and filtration techniques. However, the advantages of the carbon molecular sieve membrane are more significant than these drawbacks as carbon molecular sieve membrane has shown to be efficient in multiple applications, for example, fine chemical products dehydration and, gases blend purification for energy and cost saving.

OXYGEN SEPARATION OF CARBON MOLECULAR SIEVE MEMBRANE

Over recent years, membranes are used in various separation processes such as water separation and gas separation. The carbon molecular sieve membrane has high stability of chemical and thermal, high selectivity without reducing its productivity, as well as stable pore structure. These carbon molecular sieve membrane characteristics are reported to be useful for nanofiltration, microfiltration, pervaporation as well as in fabricating high-quality gas separation membranes. The carbon membrane for oxygen separation applications are tabulated in Table 2 (W. Salleh, 2017).

Table 2 Precursors have been used by researchers for oxygen separation.

Precursor/configuration	O ₂ /N ₂
Phenolic resin/plate circular	3.3
PFA/disk	1.2
Zeolite ZSM-5/PEI/flat sheet	4.2
Novolac resin/tubular	15
6FDA/DETDA/flat sheet	7
6FDA:BPDA(1:1)/DETDA/flat sheet	4
6FDA/DETDA:DABA(3:2)/flat sheet	4
6FDA/1,5-ND:ODA(1:1)/flat sheet	6
Phenolic resin/disk	15

PROCEDURES IN FABRICATING CARBON MOLECULAR SIEVE MEMBRANE

Commonly, aromatic polymers carbonization is used in carbon membrane fabrication (Yoshimune & Haraya, 2013). Carbonization is the most important process in fabricating carbon molecular sieve membranes. The procedures to improve the quality of carbon molecular sieve membrane involves precursor selection, membrane preparation, and carbonization conditions as shown in Figure 2. Further developments in separation and technology specifications and implementation lead to the need for a new membrane to satisfy separation efficiency and productivity. Carbon membrane fabrication is done to overcome the limitations of polymer membranes.

The precursor material is the most significant element in starting the fabrication process to ensure the production of high-quality carbon molecular sieve membrane. The selection of a precursor determines the properties of the membrane, in which the same carbonization conditions applied to two different precursors will produce different properties of the carbon membrane. Various materials such as coal, graphite, resin, and polymers are used in preparing carbon membranes with good gas separation properties. Some requirements should be meet by a polymer to undergo the carbonization process.

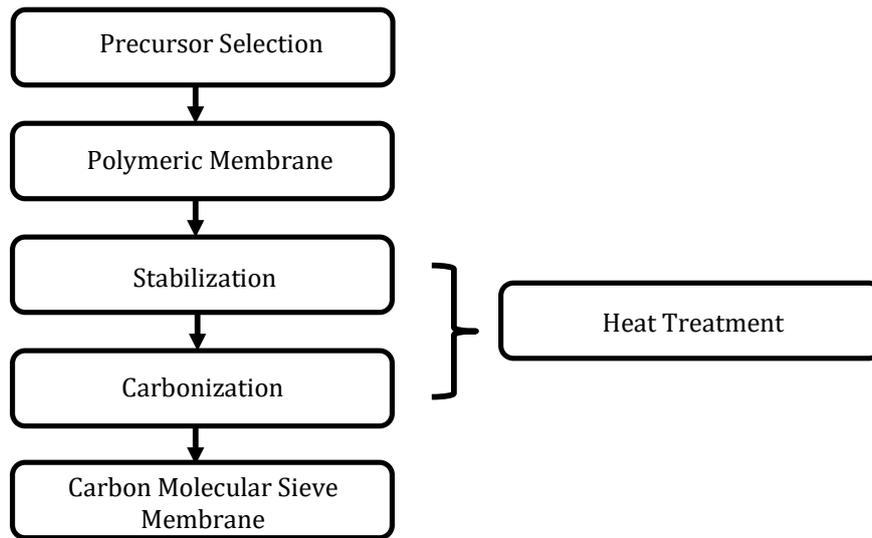


Figure 2: Carbon molecular sieve membrane fabrication procedure

In tubular polymeric membrane fabrication, the coating procedure is frequently repeated until a defect-free carbon molecular sieve is obtained. Generally, the surface coating technique enhances the membrane selectivity. Implementation of coating repeatedly results in better surface defect coverage, at the same time, reducing unselective surface pinholes permeance. Various coating techniques, such as dip coating (Zainal *et al.*, 2017), gel coating (Nisticò *et al.*, 2017), film casting (Lee *et al.*, 2017), spray coating (N. H. Ismail *et al.*, 2018), and spin coating (Nisticò *et al.*, 2017) have been introduced. Although these coating techniques are intended for commercial applications to prepare various types of membranes, a small number of studies have been carried out to compare all of these techniques. It is believed that the selectivity and permeability of membranes are influenced differently by different coating techniques. Generally, selectivity enhancement is influenced by an increasing number of sequential coatings as the coating solution penetrates the pinholes on the surface. Dip-coating will increase the membrane selectivity compared to other coating methods because Matrimid can have better penetration into the membrane surface pinholes. After three times of dip-coating, the selectivity of the membrane becomes almost constant, whereas the film casting technique requires four times coating. The increases number of repeated coatings allows for sealing or plugging the exposed defects or pores on the membrane surface to achieve better performance.

The full potential of the dip-coating technique is currently not yet completely explored. Pinhole defects facilitate the intolerable weakening of the membranes with losses in the separation performance. Polyimides have excellent thermal stability and high glass transition temperature, for example, Matrimid possesses a glass transition temperature of 300 °C. It is a glassy polymer at both fabrication and application temperatures. Dip-coating is a simple and cost-effective technique that has been optimized by various researchers to increase the mechanical strength of highly porous material (N.Sazali *et al.*, 2018). Dip-coating technique is used to prepare supported polymer membranes in which resulting in excellent gas separation results (N. Sazali *et al.*, 2018).

Depending on the precursor material, high-performance carbon membrane stabilization is effective under atmospheric air at a reasonable temperature ranging from 200 to 300°C. The stabilization process contributes to preventing fusion and melting of polymer membranes. Other than that, this process avoids the occurrence of excessive volatilization of carbon elements during the carbonization cycle. Kelly *et al.*, (2012) conducted a study focusing on the stabilization temperature of Matrimid polymer ranging from 32 to 150 °C (Briceño *et al.*, 2012). The last procedure which is carbonization process will be further discussed in the following topic.

PARAMETERS IN CARBONIZATION PROCESS

The separation performance of carbon molecular sieve membrane is mainly controlled by carbonization parameters. Carbonization or also known as pyrolysis is a heating process at a specific heating rate of a chosen precursor up to a temperature in a controlled environment. This process is done

after the stabilization phase. The result of this process is a significant reduction of membrane weight because of volatile by-products are being discharged (Geiszler & Koros, 1996). The emission of gas causing the formation of the pores in the polymer membrane. For the separation process, the carbonization temperature should be aligned with the type of gas desired, which also can be achieved via thermal soaking (Hiroyuki Suda & Haraya, 1997). Parameters such as the duration of thermal soaking, carbonization condition, temperature, rate of heating and other factors can change the pore structure and performance of the membrane. The carbon molecular sieve membranes must be protected and kept in airtight bags to avoid physical aging after the carbonization process (Lagorsse *et al.*, 2008; Xu *et al.*, 2014). After sometimes being exposed to the ambient atmosphere, the regeneration step is necessary for resetting the properties of the membrane (Cheryl W. Jones & Koros, 1994; MAY-BRITT HÄGG *et al.*, 2006). Table 3 tabulates several polyimides that have been described in the literature for the carbonization.

Table 3 Carbonization conditions used in previous researches.

Precursor/configuration	Temperature (°C)	Heating rate (°C/min)	Thermal soak time (h)	Atmosphere
FFA/tubular	800	1		N ₂
Phenolic resin/plate circular	400	2	3	N ₂
	600	1	6	
PFA/disk	550	0.5	2	N ₂
Zeolite ZSM-5/PEI/flat-sheet	400	2		
	650	1		
Novolac resin/tubular	100	1	½	N ₂
	450-1000	1	2	
PAN/hollow fiber	250	5	0.5	Air
	500-800	3	0.5	N ₂
PAN/flat sheet	450-950	1	2	N ₂ /Ar
BTDA-TDI/MDI (P84) copolyimide/hollow fiber	900	5	1	Ar
Cellulose acetate/hollow fiber	550	4	2	CO ₂
Matrimid/disk	550-700		1	Helium or a N ₂ /O ₂ mixture (99.95% N ₂ and 0.05% O ₂)
Phenolic resin/disk	150-300	1		Air
	600-900	1		Vacuum
Phenolic resin/tubular	700-1000	10	1-8	Vacuum
	PEI/PVP/hollow fiber	300	3	0.5
PEI/PEG/disk	650	3	0.5	N ₂
	300	1		Air
BPDA-ODA/tubular	550-700	1		N ₂
	600-900	5		Deoxygenated nitrogen
PFA/tubular	100	5	1	Argon
	400-600	5	2	
Novolac resin/tubular	150	0.5	1	Air
	850	0.5	1	Argon
PPO/tubular	700	5		Argon

The final temperature, heating rate, and conditions are the carbonization parameter that gives the most significant effects. Matrimid is the most widely used in fabricating carbon membrane (Ba *et al.*, 2009). Carbonization of the Matrimid membrane at temperatures of up to 800 °C leads to the production of carbon membrane with larger-sized micropores and ultramicropores (less than 7 Å).

Carbonization Temperature

Carbonization temperature or also called pyrolysis temperature is the allowable maximum temperature for the precursor during the carbonization process. The carbonization temperature usually lies in the range of the graphitization temperature to the decomposition temperature of the polymer precursor (Y.-J. FU *et al.*, 2011). Some parameters that affect the perm-selectivity of the membrane such as by-products degradation, structure compactness, and polymer kinetics can be modified by regulating the carbonization temperature (Geiszler & Koros, 1996). As shown in Table 3, the range of carbonization temperature lies between 100 to 1000 °C. It has been reported that the most of heteroatoms which originally exist in the precursor macromolecules are eliminated with the rise in carbonization temperature. The result is a matrix consisting rigid, amorphous and porous carbon. Carbonization temperature is a major factor in carbonization as it directly affects the properties such as separation performance, gas separation transport mechanism as well as structure (B.S.H. Janice *et al.*, 2017).

Research that has been conducted by Islam *et al.*, shows that when sulfonated polyimides are carbonized at 450 °C which is lower than carbonization temperature, their flexibility and selectivity is as good as polymeric membranes and carbon molecular sieve membranes respectively (Islam *et al.*, 2005). Besides, carbon molecular sieve membrane has been tested using carbonization temperature in the range between 500 and 800 °C resulting that all carbonization temperature used produced permeability and selectivity exceeding the upper bound line of C₂H₄/C₂H₆. It is reported that the permeability drops at 500 to 550 °C whereas the selectivity increases. The selectivity increases at 550 to 675 °C with a very small drop of permeability and beyond 675 °C, the selectivity is not increases with permeability drop (R. Muha *et al.*, 2015).

The selectivity of the membrane can be increased if a high carbonization temperature is used because the pore size distribution will be altered to become smaller. At higher temperature which is around 800 °C, most of the membranes that analyzed via differential scanning calorimetry (DSC) still containing almost 95% carbon content (Hosseini *et al.*, 2014). Besides increased density and compactness, employing higher carbonization temperature will also increase the crystallinity of the membrane, nevertheless, the interplanar spacing of the carbon layers will decrease (Clare J. Anderson *et al.*, 2008; Lua & Su, 2006).

Carbonization Environment and Flow Rate

For carbonization environment, vacuum or inert purge gas functions in removing volatile gases and preventing the membrane from any damage throughout the carbonization process. Research shows that a highly selective and low permeable membrane is produced if the degree of vacuum is increased at a constant temperature, depending on the precursor material, inert gas and degree of vacuum used (Geiszler & Koros, 1996; Hosseini *et al.*, 2014). By using either low degree of vacuum or inert gas, highly permeable membrane can be produced while the selective properties of the membrane is determined by the precursor materials used which can be proved by the researches carried out by Kinoyo *et al.*, and Geiszler *et al.* Kinoyo and co-workers used two degrees of vacuum which are 0.005 torr and 0.042 torr to carbonize a polyimide 6FDA/BPDA-DAM. The result shows that the usage of a lower degree of vacuum produces a high oxygen permeability (630 barrers) with low selectivity (8.8) membrane, while the usage of a higher degree of vacuum produces low oxygen permeability (52 barrers) membrane having relatively high selectivity (10) (Kiyono *et al.*, 2010).

The research on carbonized membranes using different environments such as argon, vacuum, carbon dioxide and helium conducted by Geiszler *et al.*, shows that the membrane carbonized in a vacuum environment has a higher selectivity for oxygen-nitrogen separation. The similar conditions are applied in separating carbon dioxide. Other research has been conducted using Matrimid polymer as precursor, and it is carbonized under two different environments which are nitrogen and argon. Under both environments, the polymer precursors converted themselves into carbon membrane. The results show that their functional group is very similar which proven by the similar peaks in FTIR analysis (N. Sazali *et al.*, 2015) Besides, it has been published that carbon membrane carbonized under vacuum environment causes the selectivity to be significantly increases, however, the permeability drops (C.P. Hu *et al.*, 2019). Pirouzfard *et al.*, observed the effect of carbonization environment in which the vacuum degree is let to be decreased from 0.01 torr to 10⁻⁷ torr, on carbon membrane performance, resulting that the selectivity increases by 1.4 times with permeability drops. They concluded that the optimum conditions is 10⁻⁷ torr at 620 °C.

The process of carbonization in the inert gas atmosphere improves the permeability of the membrane due to increased porous structure on the membrane. The inert purge intensifies the precursor degradation because of increasing heat transfer and gas phase mass. W.J Koros *et al.*, carbonized a membrane in an inert purge of increased oxygen content, resulting in the weight loss of the carbonized membrane to decrease (Kiyono *et al.*, 2010). For thin carbon molecular sieve membranes, they possess

relatively lower permeability if the gas flow rate is low ($2 \text{ cm}^3(\text{STP})/\text{min}$) compared to when higher gas flow rate ($200 \text{ cm}^3(\text{STP})/\text{min}$) is used (Geiszler & Koros, 1996). Whereas for dense carbon molecular sieve membranes, flow rate shows no significant impact on their separation performance (Kiyono *et al.*, 2010). Commonly, this parameter is not highlighted and discussed in detail in the literature review.

Soaking Time

Thermal soaking time is defined as the duration of time required to hold the precursor at the carbonization temperature. This parameter dependent on the thickness of film, type of precursor as well as the composition of final product (B.S.H. Janice *et al.*, 2017). Besides, this parameter can modify the separation performances and characteristics of the carbon molecular sieve membranes. If the soaking time during the carbonization process is lengthened, rearrangement of microstructures will occur. Therefore, the pore size distribution of the membrane, also its average porosity will be tuned. A PAN hollow fiber membrane is pyrolyzed by David *et al.*, in a lengthen soaking time, and it is reported that the permeability of the membrane increases only at the early stage which is about 2 hours. After 2 hours, its permeability starts to decrease (David & Ismail, 2003). Other than permeability reduction, increased soaking time reduces the size of pore because of the sintering effect (K. Steel & Koros, 2005; Campo *et al.*, 2010; David Scott Lafyatisa *et al.*, 1991; Hiroyuki Suda & Haraya, 1997). The effect of soaking time on carbon membrane has been studied using soaking time of 60 minutes (E.P. Favvas *et al.*, 2015). The results show that the gas permeance is low. Besides, it is stated that carbonization process using a longer soaking time and higher temperature will produce carbon membrane with effective pore having smaller size (X. Ma *et al.*, 2016).

Heating Rate

Generally, the gas transport properties of carbon molecular sieve membrane fabricated at low temperatures are not affected by the heating rate, however, there is a change of permeation properties in the case that involves higher carbonization temperature where the permeation properties are improved with the implementation of different procedures (Shao *et al.*, 2005). As the heating rate increases, the pore size will become smaller resulting in a higher selective membrane (Teresa A. Centeno *et al.*, 2004). On the other hand, if the heating rate is decreased, the emission rate of the by-product becomes slower. Suda and Haraya use Kapton in preparing the carbon molecular sieve membrane at two different heating rates which are 13.3 K/min and 1.33 K/min. It is found that at a lower heating rate, the permeability of the membrane decreases (Hiroyuki Suda & Haraya, 1997). Based on the research done by Centeno *et al.*, where the phenolic resin is pyrolyzed at five different heating rates in the range between $0.5 \text{ }^\circ\text{C}/\text{min}$ up to $10 \text{ }^\circ\text{C}/\text{min}$, the result shows that the selectivity of the membrane increases as the heating rate increases (Teresa A. Centeno *et al.*, 2004). A research carried out by Kim *et al.*, used three different heating rates which are 0.8, 2.4 and $9.6 \text{ }^\circ\text{C}/\text{min}$. They found out that higher ramping rate lead to abruption between substrate and carbon membrane producing a significant crack. Similar to the parameter of flow rate, heating rate is rarely highlighted. However, most of researchers use low heating rate as shown in Table 3.

CONCLUSIONS

The fundamental matter in producing carbon membranes is the selection of precursors. The usage of polymer precursor has been acknowledged by many researchers for gas separation. The variety of polymer precursors and carbonization conditions was discussed in this paper which focuses on gas separation application. As reviewed, the performance of the carbon molecular sieve membrane can be modified and improved by altering its pore structure. This paper explains that the carbon molecular sieve membrane that undergoes different carbonization conditions will produce different molecular sieving behaviour and pore structure. The five carbonization parameters were discussed to provide insights into the elements that control gas separation characteristics in the carbon membrane. This research is recommended to be extended to new precursor materials with optimization of their gas separation characteristics. The limitations of carbon membranes need a suitable method during the fabrication process. A study on the carbonization conditions on performance is significant to improve the quality of carbon molecular sieve membrane to meet industrial needs as the carbon membrane is capable of working in extreme pressure and temperature. The carbon membrane may be the favourable alternative for various mixtures of gas and to be further used in other applications.

ACKNOWLEDGEMENT

Authors would like to extend their gratitude to Ministry of Higher Education Malaysia and Universiti Malaysia Pahang (UMP) with grant number RDU192703.

REFERENCES

- [1] A.F. Ismail, & David, L. I. B. (2001). A review on the latest development of carbon membranes for gas separation. *Journal of Membrane Science*, 193(1), 1-18
- [2] A.G. (Tony) Fane, Rong Wang, & Jia, Y. (2011). Membrane Technology: Past, Present and Future. *Membrane and Desalination Technologies*: Humana Press.
- [3] Ahmadizadegan, H., Tahriri, M., Tahriri, M., Padam, M., & Ranjbar, M. (2018). Polyimide-TiO₂ nanocomposites and their corresponding membranes: Synthesis, characterization, and gas separation applications. *Solid State Sciences*.
- [4] Bae, S. D., Lee, C. W., Kang, L. S., & Sakoda, A. (2007). Preparation, characterization, and application of activated carbon membrane with carbon whiskers. *Desalination*, 202(1), 247-252.
- [5] Briceño, K., Iulianelli, A., Montané, D., Garcia-Valls, R., & Basile, A. (2012). Carbon molecular sieve membranes supported on non-modified ceramic tubes for hydrogen separation in membrane reactors. *International Journal of Hydrogen Energy*, 37(18), 13536-13544.
- [6] Briceño, K., Montané, D., Garcia-Valls, R., Iulianelli, A., & Basile, A. (2012). Fabrication variables affecting the structure and properties of supported carbon molecular sieve membranes for hydrogen separation. *Journal of Membrane Science*, 415-416(Supplement C), 288-297.
- [7] Burdyny, T., & Struchtrup, H. (2010). Hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process. *Energy*, 35, 1884-1897.
- [8] Campo, M., Fernão D. Magalhães, & Mendes, A. (2010). Carbon molecular sieve membranes from cellophane paper. *Journal of Membrane Science*, 350(1), 180-188.
- [9] Centeno, T. A., Vilas, J. L., & Fuertes, A. B. (2004). Effects of phenolic resin pyrolysis conditions on carbon membrane performance for gas separation. *Journal of Membrane Science*, 228(1), 45-54.
- [10] Cheryl W. Jones, & Koros, W. J. (1994). Carbon molecular sieve gas separation membranes-II. Regeneration following organic exposure.
- [11] Clare J. Anderson, Steven J. Pas, Gaurav Arora, Sandra E. Kentish, Anita J. Hill, Stanley I. Sandler, & Stevens, G. W. (2008). Effect of pyrolysis temperature and operating temperature on the performance of nanoporous carbon membranes. *Journal of Membrane Science*, 322, 19-27.
- [12] Daniel Ferreira, P. B., Roger D. Whitley, Adelio Mendes. (2015). Single-Stage Vacuum Pressure Swing Adsorption for Producing High-Purity Oxygen from Air. *Industrial & Engineering Chemistry Research*, 54(39), 9591-9604.
- [13] David, L. I. B., & Ismail, A. (2003). Influence of the thermastabilization process and soak time during pyrolysis process on the polyacrylonitrile carbon membranes for O₂/N₂ separation. *Journal of Membrane Science*, 213(1), 285-291.
- [14] David Scott Lafyatis, Jeannie Tung, & Foley, H. C. (1991). Poly(furfuryl alcohol)-derived carbon molecular sieves: dependence of adsorptive properties on carbonization temperature, time, and poly(ethylene glycol) additives.
- [15] Eriksson. Tore, K. Y. (2014). Temperature Swing Adsorption Device for Oxygen-enriched Air. *Journal of Cleaner Production*, 76, 174-179.
- [16] FU, Y.-J., LIAO, K.-S., HU, C.-C., LEE, K.-R., & LAI, J.-Y. (2011). Development and characterization of micropores in carbon molecular sieve membrane for gas separation. *Microporous and Mesoporous Materials*, 143(1), 78-86.
- [17] Fuertes, A. B. (2000). Adsorption-selective carbon membrane for gas separation. *Journal of Membrane Science*, 177(1), 9-16.
- [18] Gary T. Rochelle, e. a. (2009). Amine Scrubbing for CO₂ Capture. *Science*, 325, 1625.
- [19] Geiszler, V. C., & Koros, W. J. (1996). Effects of Polyimide Pyrolysis Conditions on Carbon Molecular Sieve Membrane Properties. *Industrial & Engineering Chemistry Research*, 35(9), 2999-3003.
- [20] Gilron, J. S., A. (2002). Knudsen diffusion in microporous carbon membranes with molecular sieving character. *Journal of Membrane Science*, 209, 339-352.
- [21] Grewe, T., Meggouh, M., & Tüysüz, H. (2016). Nanocatalysts for Solar Water Splitting and a Perspective on Hydrogen Economy. *Chemistry – An Asian Journal*, 11(1), 22-42.

- [22] Haider, S., Lindbråthen, A., Lie, J. A., Andersen, I. C. T., & Hägg, M.-B. (2018). CO₂ separation with carbon membranes in high pressure and elevated temperature applications. *Separation and Purification Technology*, 190(Supplement C), 177-189.
- [23] Hamm, J. B. S., Muniz, A. R., Pollo, L. D., Marcilio, N. R., & Tessaro, I. C. (2017). Experimental and computational analysis of carbon molecular sieve membrane formation upon polyetherimide pyrolysis. *Carbon*, 119, 21-29.
- [24] Hayashi, J.-i., Mizuta, H., Yamamoto, M., Kusakabe, K., & Morooka, S. (1997). Pore size control of carbonized BPDA-pp' ODA polyimide membrane by chemical vapor deposition of carbon. *Journal of Membrane Science*, 124(2), 243-251.
- [25] Hiroyuki Suda, & Haraya, K. (1997). Gas Permeation through Micropores of Carbon Molecular Sieve Membranes Derived from Kapton Polyimide. *Journal of Physical Chemistry*, 101(20), 3988-3994.
- [26] Hosseini, S., Omidkhak, M., Moghaddam, A., Pirouzfaz, V., Krant, W., & Tan, N. (2014). Enhancing the properties and gas separation performance of PBI-polyimides blend carbon molecular sieve membranes via optimization of the pyrolysis process. *Separation and Purification Technology*, 122, 278-289.
- [27] Islam, M., Zhou, W., Honda, T., Tanaka, K., Kita, H., & Okamoto, K.-i. (2005). Preparation and gas separation performance of flexible pyrolytic membranes by low-temperature pyrolysis of sulfonated polyimides. *Journal of Membrane Science*, 261(1), 17-26.
- [28] Ismail, A. F., & David, L. I. B. (2001). A review on the latest development of carbon membranes for gas separation. *Journal of Membrane Science*, 193(1), 1-18.
- [29] Ismail, N. H., Salleh, W. N. W., Sazali, N., & Ismail, A. F. (2018). Development and characterization of disk supported carbon membrane prepared by one-step coating-carbonization cycle. *Journal of Industrial and Engineering Chemistry*, 57(Supplement C), 313-321.
- [30] J. Allam, R. (2009). Improved oxygen production technologies. *Energy Procedia*, 1(1), 461-470.
- [31] Kiyono, M., Williams, P. J., & Koros, W. J. (2010). Effect of pyrolysis atmosphere on separation performance of carbon molecular sieve membranes. *Journal of Membrane Science*, 359(1), 2-10.
- [32] Koros, W. J., & Mahajan, R. (2000). Pushing the limits on possibilities for large scale gas separation: which strategies? *Journal of Membrane Science*, 175(2), 181-196.
- [33] Lee, R. J., Jawad, Z. A., Ahmad, A. L., Ngo, J. Q., & Chua, H. B. (2017). Improvement of CO₂ /N₂ separation performance by polymer matrix cellulose acetate butyrate. IOP Conference Series: *Materials Science and Engineering*, 206(1), 012072.
- [34] Lua, A., & Su, J. (2006). Effects of carbonisation on pore evolution and gas permeation properties of carbon membranes from Kapton(R) polyimide. *Carbon*, 44, 2964-2972.
- [35] M. Robeson, L. (1991). Correlation of separation factor versus permeability for polymeric membranes. *Journal of Membrane Science*, 62(2), 165-185.
- [36] M. Robeson, L. (2008). The upper bound revisited. *Journal of Membrane Science*, 320, 390-400.
- [37] Mahdyarfar, M., Mohammadi, T., & Mohajeri, A. (2013). Defect formation and prevention during the preparation of supported carbon membranes. *New Carbon Materials*, 28(5), 369-377.
- [38] MAY-BRITT HÄGG, JON A. LIE, & LINDBRÅTHEN, A. (2006). Carbon Molecular Sieve Membranes. *Annals of the New York Academy of Sciences*, 984(1).
- [39] Menendez, I., & Fuertes, A. B. (2001). Aging of carbon membranes under different environments. *Carbon*, 39(5), 733-740.
- [40] Murphy, T. M., Langhe, D., Ponting, M., Baer, E., Freeman, B. D., & Paul, D. R. (2011). Physical aging of layered glassy polymer films via gas permeability tracking. *Polymer*, 52(26), 6117-6125.
- [41] Paola Bernardo, & Clarizia, G. (2013). 30 Years of Membrane Technology for Gas Separation. Paper presented at the 11th International Conference on Chemical and Process Engineering.
- [42] Rufford, T. E., Smart, S., Watson, G.C.Y., Graham, B.F., Boxall, J., Diniz da Costa, J.C. and May, E.F. (2012). The removal of CO₂ and N₂ from natural gas: A review of conventional and emerging process technologies. *Journal of Petroleum Science and Engineering*, 94-95, 123-125.
- [43] Sazali, N., Salleh, W. N. W., Ismail, A. F., Ismail, N. H., Yusof, N., Aziz, F., . . . Kadirgama, K. (2018). Influence of intermediate layers in tubular carbon membrane for gas separation performance. *International Journal of Hydrogen Energy*.
- [44] Sazali, N., Wnw, S., Ismail, A., Ismail, N., Yusof, N., Aziz, F., . . . Nahm, N. (2018). Controlled Dip-coating Times for Improving CO₂ Selective of PI/NCCbased Supported Carbon Membrane (Vol. 08).
- [45] Shao, L., Chung, T.-S., & Kumari, P. (2005). The evolution of physicochemical and transport properties of 6FDA-durene toward carbon membranes; from polymer, intermediate to carbon. *Microporous and Mesoporous Materials*, 84(1-3), 59-68.

- [46]Steel, K., & Koros, W. (2005). An investigation of the effects of pyrolysis parameters on gas separation properties of carbon materials. *Carbon*, 43(9), 1843-1856.
- [47]Stern, S. A., Mi, Y., Yamamoto, H., & Clair, A. K. S. (1989). Structure/permeability relationships of polyimide membranes. Applications to the separation of gas mixtures. *Journal of Polymer Science Part B: Polymer Physics*, 27(9), 1887-1909.
- [48]Tarik Naheiri, Schellhase, S., Javier Lopez, & Yang, J. (2011). Nitrogen and Oxygen Separation using Vacuum Swing Adsorption.
- [49]Teresa A. Centeno, José Luis Vilas, & Fuertes, A. B. (2004). Effects of phenolic resin pyrolysis conditions on carbon membrane performance for gas separation.
- [50]W.Baker, R. (2002). Future Directions of Membrane Gas Separation *Technology. Industrial & Engineering Chemistry Research*, 41(6), 1393-1411.
- [51]Wilcox, J. (2012). Cryogenic Distillation and Air Separation. *Carbon Capture: Springer New York*.
- [52]Wollbrink, A., Volgmann, K., Koch, J., Kanthasamy, K., Tegenkamp, C., Li, Y., . . . Caro, J. (2016). Amorphous, turbostratic and crystalline carbon membranes with hydrogen selectivity. *Carbon*, 106, 93-105.
- [53]Xiao, Y., & Chung, T. S. (2006). Polyimide-Carbonized Membranes for Gas Separation: Structural, Composition, and Morphological Control of Precursors AU - Tin, Pei Shi. *Separation & Purification Reviews*, 35(4), 285-318.
- [54]Yampolskii, Y. (2012). Polymeric Gas Separation Membranes. *Macromolecules*(45), 3298-3311.
- [55]Yoshimune, M., & Haraya, K. (2013). CO₂/CH₄ Mixed Gas Separation Using Carbon Hollow Fiber Membranes. *Energy Procedia*, 37(Supplement C), 1109-1116.
- [56]Zainal, W. N. H. W., Tan, S. H., & Ahmad, M. A. (2017). Carbon Membranes Prepared from a Polymer Blend of Polyethylene Glycol and Polyetherimide. *Chemical Engineering & Technology*, 40(1), 94-102.
- [57]Zhang, K., & Way, J. D. (2017). Palladium-copper membranes for hydrogen separation. *Separation and Purification Technology*, 186, 39-44.
- [58]Zito, P. F., Caravella, A., Brunetti, A., Drioli, E., & Barbieri, G. (2017). Knudsen and surface diffusion competing for gas permeation inside silicalite membranes. *Journal of Membrane Science*, 523(Supplement C), 456-469.
- [59]Meha, R., Liren, X., & William, J. K. (2015). Structure-performance characterization for carbon molecular sieve membranes using molecular scale gas probes. *Carbon*, 85, 429-442.
- [60]Janice, B. S. H., Alan, A., Julia, G. G., Nilson, R. M., Isabel, C. T., Liliane, D. P. (2017). Recent advances in the development of supported carbon membranes for gas separation. *International Journal of Hydrogen Energy*, 42, 24830-24845.
- [61]Sazali, N., Salleh, W. N. W., Nordin, N. A. H. M., Ismail, A. F. (2015). Matrimid-based carbon tubular membrane: Effect of carbonization environment. *Journal of Industrial and Engineering Chemistry*, 31, 167-171.
- [62]Hu, C. P., Polintan, C. K., Tayo, L. L., Chou, S. C., Tsai, H. A., Hung, W. S., Hu, C. C., Lee, K. R., Lai, J. Y. (2019). The gas separation performance adjustment of carbon molecular sieve membrane depending on the chain rigidity and free volume characteristic of the polymeric precursor. *Carbon*, 143, 343-351.
- [63]Pirouzfard, V.; Moghaddam, A. Z.; Omidkhah, M. R.; Hosseini, S. S. (2014). Investigating the Effect of Dianhydride Type and Pyrolysis Condition on the Gas Separation Performance of Membranes Derived From Blended Polyimides Through Statistical Analysis. *J. Ind. Eng. Chem*, 20 (3), 1061-1070.
- [64]Ma, X.; Lin, Y. S.; Wei, X.; Kniep, J. (2016). Ultrathin Carbon Molecular Sieve Membrane for Propylene/Propane Separation. *AIChE J*, 62 (2), 491-499.
- [65]Favvas, E. P.; Heliopoulos, N. S.; Papageorgiou, S. K.; Mitropoulos, A. C.; Kapantaidakis, G. C.; Kanellopoulos, N. K. (2015). Helium and Hydrogen Selective Carbon Hollow Fiber Membranes: The Effect of Pyrolysis Isothermal Time. *Sep. Purif. Technol*, 142, 176-181.
- [66]Kim, S. J.; Park, Y. I.; Nam, S. E.; Park, H.; Lee, P. S. (2016). Separations of F-Gases From Nitrogen Through Thin Carbon Membranes. *Sep. Purif. Technol*, 158,108-114.