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Influence of Pyrolysis Temperature and Heating Rate in the Fabrication of Carbon Membrane: A Review

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Abstract: Despite its brittleness and relatively high fabrication cost, the excellent performance of carbon membrane in gas separation outweighs such limitations. The carbon-based membranes have the capability to perform specific gas separations when compared to other types of membranes or any conventional separation technology that based on cryogenic, adsorption or absorption mechanisms. Basically, carbon membrane is a derivation of its polymeric precursor membrane. The derivation refers to the pyrolysis process of the polymeric membrane that turns it into a carbon membrane. During the process, the polymeric membrane undergoes a controlled thermal treatment and at the same time, inert atmosphere is continuously generated to remove any oxidizing agents. This process is proven to be highly critical and challenging because it determines the final pore structure and its corresponding performances of the carbon membrane. Heating rate and pyrolysis temperature are part of the pyrolysis process and the most tuned parameters to obtain a very fine carbon membrane according to an intended application-based performance. These parameters have been reported numerously for their significant impacts on the fabrication of carbon membranes and this paper provides the review.

Key words: Carbon membrane, pyrolysis, temperature, heating rate, effect

INTRODUCTION

In general, pyrolysis is a complicated process that involves many reactions occurring simultaneously such as condensation, dehydrogenation, hydrogen transfer and isomerization. This process occurs in the absence of oxygen at elevated temperatures. It causes the organic materials to have an increment in its element carbon content (Marsh and Rodriguez-Reinoso, 2006).

In membrane fabrication for gas separation, pyrolysis is applied to convert a polymeric membrane into carbon membrane to enhance its permeability and selectivity which are the basic components in the measurement of membrane performance. The enhancement is due to the fact that the polymeric membrane has structural limitation that affects its permeability and selectivity and this has been well-defined by the Robeson's upper bound. According to the upper bound, there is a trade-off relationship between the permeability and selectivity of gases for the polymeric membranes. It also shows that there is a limit for the polymeric membrane to reach higher level of gas separation performance that commercially attractive (Robeson, 2008). Therefore, it has been

discovered that polymeric membranes being subjected to pyrolysis have been able to surpass the limit and overcome the polymeric Robeson's trade-off curves (Itta *et al.*, 2011).

Most of the materials derived into carbon membranes are polymers with either thermoset or thermoplastic properties. They are usually pyrolyzed between 500 to 1000°C or less than a temperature point where graphitization starts to occur (Geiszler and Koros, 1996). Up to now, only certain polymers have shown executable properties to undergo pyrolysis treatment in the synthesis of carbon membranes. Some of them are polyetherimide (Salleh and Ismail, 2011), phenolic resin (Teixeira *et al.*, 2011), SPAEK (Xiao *et al.*, 2010), polyimide (Su and Lua 2006), polyphenylene oxide (Itta *et al.*, 2011), polyacrylonitrile (David and Ismail, 2003), cellulose acetate (He *et al.*, 2011), phenol formaldehyde (Zhang *et al.*, 2006) etc.

In pyrolysis, there are several tunable parameters that are commonly subjected to investigations such as pyrolysis temperature, heating rate, purge gas (atmosphere) and soak time. He and Hagg (2011) studied cellulose acetate-PVP based carbon membrane

has arranged the parameters based on their level of impact towards the membrane structure changes and performances. The order of each parameter is as followed; purge gas > pyrolysis temperature > heating rate > thermal soak time. The current paper reviews on the second and third parameters since they are heavily and frequently focused in most studies related to the synthesis of carbon membrane.

Pyrolysis: During pyrolysis, the structure of porous polymer will change into an almost dense carbon structure (Fuertes and Centeno, 1998). Further increase in temperature will even cause the structure to be denser. For example, work by Jones and Koros (1994) showed that the polyimide pyrolyzed at 550°C simply has denser structure than that of 500°C. Such little increment of 50°C has indeed shown significant impact on the structure changes. This pyrolysis process removes most of the heteroatoms in the polymer macromolecules carbon chain, leaving behind a stiff and crosslinked carbon matrix with an amorphous microporous structure created by the evolution of gaseous products. It also causes the rearrangement of the molecular structure of the polymeric precursor (Sedigh *et al.*, 2000). Volatile by-products such as H₂, H₂O, CO, CO₂, and smaller amounts of HCN, CH₄, and NH₃ (depending on the polymer) are released (Geiszler and Koros, 1996). The weight loss could reach as high as 70-95% (Lie and Hagg, 2006; Song *et al.*, 2008). The resultant carbon structure will also produce narrow constrictions in the pore structure that approach or lower than molecular dimensions of common gaseous species, such as N₂, H₂, CO₂, CO, O₂, and etc. (Fuertes and Centeno, 1998). In other words, the pyrolysis changes the average pore size (Steel and Koros, 2003), widens the pore size distribution (Smith *et al.*, 2004) and causes the structure to be disordered, amorphous and graphite-like which is known as turbostratic (Foley, 1995). It completely transforms the polymer into carbon rich materials with totally different molecular arrangement.

Pyrolysis temperature: Cellulose acetate, poly(vinylidene chloride), polyimides, Poly(Furfuryl Alcohol) (PFA) and phenolic resins are polymers that are initially cross-linked or becomes cross-linked during pyrolysis (Saufi and Ismail, 2004). Such crosslink prevents them

from forming large graphite-like crystals during pyrolysis, thus leading to the formation of disordered structures (non-graphitizing carbons) with a very narrow porosity (Fuertes, 2001). Some polymers require a stabilization (pre-pyrolysis) with air oxidation that allows the formation of oxygen bridges between their aromatic molecules. The bridges inhibits the rearrangement and growth of aromatic crystallites during pyrolysis and leads to a carbon structure with a more open porosity after pyrolysis (Fuertes, 2001). Several polymers have been selected and discussed under this section.

Pyrolysis temperature has been studied and reported widely to have dominant effects on the carbon membrane structure and performance. Steel and Koros (2003) work on Matrimid® polyimide reported a decrease in N₂ and O₂ permeability and an increase in the O₂/N₂ selectivity after raising the pyrolysis temperature from 500 to 800°C which finally changed the diffusive jump mechanism of the penetrant between the polymer precursor and the carbon molecular sieving material (CMS). Geiszler and Koros, (1996) reported that the increment of pyrolysis temperature on polyimide from 550 to 800°C has resulted in reductions of H₂ and N₂ gas permeability but more H₂/N₂ selective. These phenomena were accompanied by a greater percentage of weight loss. They found that there were several contributing factors that caused such effects by the pyrolysis temperatures which were the pyrolysis kinetics of the polyimide, the pyrolysis kinetics of the polyimide degradation byproducts, and the compactness of the turbostratic carbon structure when the pyrolysis temperature was increased (Geiszler and Koros, 1996). The pyrolysis kinetics was observed by the increment of the weight loss when the pyrolysis temperature was increased. The degradation byproducts was believed to cause plugging on the membrane pores. As the pyrolysis temperature increased, the densification of the carbon caused the shrinkage of pores and increased compactness. These structure's evolution will eventually affect the permeability and selectivity of the carbon membrane.

A statistical experimental design has been implemented to optimize the pyrolysis strategy on polyetherimide (PEI) hollow fiber membrane (Barbosa-Coutinho *et al.*, 2003). Figure 1 illustrates a common sequence in pyrolysis strategy to convert

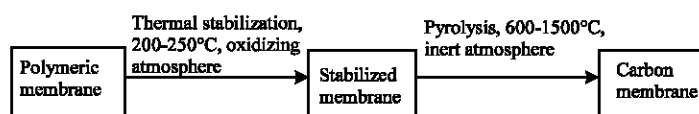


Fig. 1: Common sequence used in carbon membrane fabrication from thermoplastic polymeric membrane

thermoplastic into carbon membranes. Unlike thermoset polymers, thermoplastic polymer membranes must firstly be treated at mild temperature under continuous flow of oxidizing atmosphere. At this stage, the polymeric chain of the membrane will be incorporated by oxygenated groups such as hydroxyl and carbonyl (Fuentes, 2001). This formation promotes stability of the polymeric membrane during elevated temperature of thermal treatment.

Subsequently, the stabilized membrane was subjected to pyrolysis. Incomplete or insufficient stabilization would result in significant weight loss and structure deterioration during the pyrolysis. A completely stabilized membranes have less deformation and suffers only minor weight loss during the proceeding pyrolysis. A greater stability of the membrane could be achieved by injection of oxidizing atmosphere at the beginning of the stabilizing heating process rather than during the isothermal period (Barbosa-Coutinho *et al.*, 2003). Additionally, thermal-stabilization should be conducted at proper temperature which is not too high or low, or higher than its glass transition temperature (T_g) else, it would lead to melting, intense degradation and irregularities over the polymer structure. During the pyrolysis, chemical reactions, removal of heteroatoms and volatile emission occur concurrently. Water is generated due to cross-linking at the oxygenated groups, while hydrogen release caused by cross-linking of other sections of polymeric chain eventually causes the polymer to transform into a graphite-like structure (David and Ismail, 2003).

Extensive studies have been done by Centeno *et al.* (2004) on carbon membrane derived from phenolic resins. The studies included the effect of pyrolysis temperature, heating rate, soak time and atmosphere on the membrane permeability and selectivity. They reported that an increase of permeability could be done with lower pyrolysis temperature, lower heating rate, shorter soak time and inert atmosphere. However, this increment of permeability was reversibly proportional to its selectivity. There are several explanations worth highlighted from what they have found. Firstly, higher pyrolysis temperature caused sintering effect that eventually shrank the membrane pores. As a result, the carbon membrane performance turned from adsorption-selective to molecular sieve based separation. Secondly, higher heating rate triggered faster removal of volatiles from the membrane structure. Unfortunately, this situation might cause partial volatile deposition on the pores. Thirdly, longer soak time has caused the reduction of porosity which was due to structure rearrangement and alignment of carbonaceous aggregates. Inert purge, compared to

vacuum pyrolysis, generated higher porosity on the membrane pore structure. It quickly removed the volatile release and prevented the membrane pores from any depositions. This deposition phenomenon was also previously explained in the work of Geiszler and Koros (1996).

PFA precursor has also been well studied regarding their performance as a carbon membrane being affected by pyrolysis temperatures (Anderson *et al.*, 2008). Pyrolysis treatment at 300°C was found sufficed for the PFA precursor to degrade to a carbon solid. Its disfavor dehydrogenation started to occur from 600 to 1200°C which finally resulted in a graphite-like structure (Foley *et al.*, 1995) that leads to a fragile structure and the collapse of the micropores (Mariwala and Foley, 1994). Burket *et al.* (2006) added that between 300 and 400°C, PFA-made carbon membrane contained carbon and polymer chain that co-exist and possessed mesoporous structures. However, the mesopores collapsed and left a microporous structure when the pyrolysis temperature was increased to 600°C. The transformation from mesoporous to microporous structure has been shown to be accompanied by fragility of the carbon structure.

Anderson *et al.* (2008) has found that the increment of pyrolysis temperature resulted in the decrease of pore size but an increase to the membrane porosity as proven by the increment of gas permeance. The increment of pyrolysis temperature from 300 to 600°C has increased the O₂ and N₂ permeance attributed by the corresponding increase in porosity (Shiflett and Foley, 2000). This argument was also mentioned previously by Mariwala and Foley (1994) stating that the increasing pyrolysis temperature caused the narrowing of pore size distribution due to the growth of the aromatic microdomains that subsequently led to an increase in porosity and consumed the amorphous carbon. Singh-Ghosal and Koros (2000) observed that permeation activation energies increased with the increase in membrane selectivity which correlates to increase in pyrolysis temperature. The permeation activation energies of 4.1 (550°C) and 5.2 kcal mol⁻¹ (800°C) for O₂ and 6.1 kcal mol⁻¹ (550°C) and 6.6 kcal mol⁻¹ (800°C) for N₂ can be obtained. This increment of activation energy was due to the shrinkage of constrictions in the channel responsible for the selectivity of a carbon structure when higher pyrolysis temperatures are utilized (Steel and Koros, 2003).

According to the reported works mentioned previously, the pyrolysis of polymer membrane can be divided into two main stages in terms of pore development which are pore-opening and pore-enclosure. The pore opening would occur from the lower temperature

to medium temperature that can be indicated by the increment of permeability. It is due to the polymer-carbon structural modification and release of polymer subgroups decompositions that channels their way out to the membrane surface leaving micro-openings. This stage might be accompanied by pore enclosure but at minimum effects. Moving from medium temperature to higher or graphitization temperature, the pore enclosure dominantly takes place which causes the permeability to gradually decrease but increase in selectivity. This stage introduces pore shrinkage or densification of the whole carbon structure since the sintering effect takes place.

Pyrolysis heating rate: In carbon membrane fabrication, it has been evidenced that heating rate plays a major role in carbon structure construction. Heating rate affects the evolution rate of a volatile component when pyrolyzing a polymeric membrane. It is one of the determinant factors of final pore structure development of carbon membrane. It is also an indication to the period that the sample had been exposed to heat that subsequently influences the course of the reaction and diffusion processes. Heating rates can be as low as $0.5^{\circ}\text{C min}^{-1}$ and as high as $15^{\circ}\text{C min}^{-1}$ (Saufi and Ismail, 2004; Zhang *et al.*, 2006). Lower heating rate was commonly used to accommodate the release of volatile compounds and prevent defects (Chen *et al.*, 2011). Steel and Koros (2005) reported that a lower heating rate accompanied with longer soaking time caused the structure of the carbon membrane to be denser and separation of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ was found to be more difficult. On the other hand, higher heating rate causes the resultant carbon membrane to suffer from structure defects such as pinholes, microcracks, blisters and distortion which certainly impaired its performance (Saufi and Ismail, 2004).

A review by Ismail and Li (2008) stated that a lower heating rate was preferable to produce small pores and increase carbon crystallinity that will result in improved selectivity. Suda and Haraya (1997) reported that by decreasing heating rate the permeability decreased since it caused the pyrolysis to progress at a slower pace that eventually caused the pore to become smaller. Such slow pace exposes the carbon membrane under extended period of heat treatment which allows the sintering impact to take effect, thus reducing the pore size. Such pore reduction enhances the selectivity but typically at the expense of gas permeability. It is very important to understand that lower heating rate renders higher cost and time as well.

A thermogravimetric analysis reported by Su and Lua (2006) showed that the increase of heating rate delays the decomposition temperature to almost 150°C in difference compared to that of lower heating rate. However, both heating rates converged on the same weight loss before reaching an asymptote point. Lower heating rate would lead to the commencement of decomposition at lower

temperature and lower reaction rate. The rate of generation and diffusion of the gaseous products from the pyrolysis process have apparent influences on the pore structure evolution of the resulted carbon membrane. In a more detailed study, Su and Lua (2006) have shown that the impacts of heating rate on gas permeability were unique. Its increment may impair certain gases permeability but improve the others. Their study showed that the increase of heating rate from $0.5\text{-}4^{\circ}\text{C min}^{-1}$ increased the He and CO_2 permeability but decreased the N_2 permeability and did not influence the O_2 permeability. However, the influence of heating rates was found negligible when the pyrolysis temperature reached 800°C . Similar conclusion regarding the negligibility of heating rate at elevated pyrolysis temperature was also found by Shao *et al.* (2005) and Foley *et al.* (1995).

It has become almost a common finding that lower heating rate is necessary to minimize the pores to an extent where it still allows gases to diffuse easily and at the same time, reduces the risk of crack formation in the carbon membrane fabrication. Most of the works utilized $0.5\text{-}1^{\circ}\text{C min}^{-1}$ to ensure their carbon membrane is crack free (Saufi and Ismail, 2004; Salleh and Ismail, 2011; Itta *et al.*, 2011; He *et al.*, 2011). However, an exceptional work by Barbosa-Coutinho *et al.* (2003) showed that, $1^{\circ}\text{C min}^{-1}$ caused severe crack on their hollow fiber carbon membrane and used $3^{\circ}\text{C min}^{-1}$ instead. This phenomenon was believed to be due to the extended period of exposure to pyrolysis environment that introduced some graphite-like structure which was found fragile. Their work also showed that the heating rate has less dominating effect than pyrolysis temperature on the membrane structure during pyrolysis. However, at stabilization steps, lower heating rates could provide an extended period in membrane oxidation that leads to complete oxidation reactions and stabilized fibers were obtained before stepping into pyrolysis. Song *et al.* (2008) found that the rise of heating rate increased the weight loss, average pore size and porosity of their coal-based carbon membrane. Also, it reduced the gas flux and caused the pore size distribution to widen. Low heating rate favored the mild release of volatile compounds from the matrix thus making the carbon membranes have uniform pore structure with smaller pore size. On the other hand, higher heating rate led to explosive gas evolution and generated some irregular pores and was likely followed by the formation of pinholes and microscopic cracks.

CONCLUSION

It has been shown that the pyrolysis temperature and heating rate have direct impacts on the construction of carbon membrane structure from its polymer precursor. Higher pyrolysis temperature renders pore shrinkage in

the membrane structure. This narrow pore does not permit an easy diffusion of gases with large kinetic diameter and become highly selective towards the smaller gases. The heating rate is important in controlling the release of volatile compounds during the pyrolysis. Lower heating rate is preferable as it can prevent an explosive release of volatile compounds that can cause defects on the final carbon structure. However, lower heating rate extends the thermal exposure on the carbon that might trigger the emergence of a graphite-like structure. This graphite-like structure is very fragile and will not be favorable for physical handling. Appropriate pyrolysis temperature and heating rate are indeed major contributors in a fine fabrication of carbon membrane.

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