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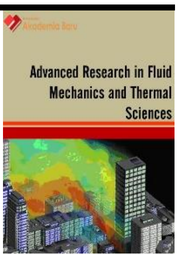

The Influence of Carbonization Temperature and Heating Rate Towards Carbon Membrane Performance: A Review

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ABSTRACT

Excellent performance of carbon-based membrane in gas separation applications outweighs their drawbacks of having costly fabrication process and membrane brittleness. Carbon membranes shows a promising potential in performing specific gas separation compared to current available separation technology that based on absorption of gas, adsorption or cryogenic mechanism. Carbonization are essential in converting polymeric-based membrane into carbon membrane, in which the membrane need to undergo thermal treatment prior fabrication of the carbon membrane. Concurrently, continuous generation of inert atmosphere helps to eliminate the oxidizing agents. Final pore structure and performance of carbon membrane are dependants on the condition of this process, and optimum condition of carbonization is one of the key factors to successful fabrication of high-performance carbon membrane. This work provides the insight of carbonization temperature and heating rate effects to the performance of carbon membrane.

Keywords:
Membrane fabrication; carbon membrane; carbonization; temperature and heating rate

1. Introduction

In membrane synthesis for application in separation of gas, carbonization process is used in converting polymeric membrane into carbon membrane. This approach helps to increase the permeability and selectivity which are important in determination of membrane performance. Compared to carbon membrane, polymeric based membrane possesses structural limitation which affect the performance in gas separation, explained by Robeson's upper bound. Upper bound describes the trade-off relationship between gas permeability and selectivity for polymeric membrane which also include the limitation in reaching higher gas separation performance level that can be considered as commercially viable [1]. Carbon membrane derived from carbonization of polymeric was found to be able to overcome the limit and exceed the polymeric Robeson's upper bound curves [2, 3]. Polymer materials that were converted into carbon membranes are usually

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having thermoset or thermoplastic characteristics. These polymer-based membranes undergo carbonization at temperature range usually between 500 to 1000°C or at graphitization temperature of the specific materials [4]. Currently, only some polymers possess the required properties to be subjected for carbonization in carbon membrane fabrication. The polymers include polyacrylonitrile [5], phenol formaldehyde [6], polyimide [7], SPAEK [8], polyetherimide [9], cellulose acetate [10], polyphenylene oxide [11], and phenolic resin [12].

In general, involvement of several simultaneous reactions during carbonization such as condensation, dehydrogenation, polymer isomerization and hydrogen transfer cause the system to be complex. Condition of the process which takes place at oxygen-free environment and at elevated temperature causes the carbon content to increase [13]. To obtain desired carbon membrane for utilization in specific application, heating rate and carbonization temperature during carbonization need to be finely tuned. Significant impact of both parameters on the fabrication of carbon membranes have been widely investigated and this paper provides the review.

2. Carbonization Process

In carbonization, there are four key factors that affect the performance of resultant carbon membrane fabricated. The factors are heating rate, carbonization temperature, purge gas and soak time which have been well-studied by various researchers. He and Hagg [14] in their work has outlined the order of parameter based on its influence towards the structural changes in membrane and membrane performance while investigating performance of cellulose acetate-PVP based carbon membrane. They revealed that purge gas has the highest impact followed by carbonization temperature, heating rate and thermal soak time respectively. This paper highlights on the effect of carbonization temperature and heating rate as most existing studies focuses on the aforementioned parameters.

From literature reported by Fuertes and Centeno [15], porous structure of polymer will change into almost dense carbon structure during carbonization. Temperature elevation during the process also causing the formation of denser carbon structure. Even a small temperature change can give significant impact to the carbon structure density. Jones and Koros [16] investigated density of carbon structure at different carbonization temperature, in which results revealed that polyimide subjected to carbonization at 550°C were having denser structure than at 500°C. The expansion of gaseous product during the process are causing molecular structure of polymer precursor to undergo rearrangement [17]. Heteroatoms in macromolecules of polymer were mostly removed, leaving the crosslinked carbon matrices with amorphous microporous structure. Depends on type of polymer chosen, by-products gases such as H_2,CO,CO_2 and small volume of HCN, CH_4 and NH_3 were released, causing weight loss around 70% to 95% [18]. The new structure of carbon membrane consists of narrow constrictions inside the pores, showing that carbonization allows modification to the polymeric membrane structure in developing a better membrane for gas separations [19]. To simplify, carbonization alters the membrane mean pore size, widen pore size distribution and formed a new disordered, amorphous and graphite-like membrane called turbostratic [20].

Some polymers that were initially crosslinked or crosslinked during subjection to carbonization are cellulose acetate, polyimide, phenolic resins, polyvinylidene chloride and polyfurfuryl alcohol (PFA) [21]. Significance of the crosslink in carbonization is formation of low porosity non-graphite carbon rather than formation of large crystals structure [22]. For certain polymers, they need to be stabilized via air oxidation prior to carbonization to allow development of oxygen bridges between the aromatic molecules. These bridges prevent further growth of aromatic crystals and also prevent rearrangement of structure, resulting in more open porous structure [23].

3. Carbonization Temperature

Significant effect of carbonization temperature to carbon membrane structure and performance has been heavily investigated by previous researchers. Steel and Koros [24] fabricated carbon membrane from Matrimid polyimide while investigating the membrane performance when carbonization temperature was raised from 500°C to 800°C. They revealed that gas permeance for N_2 and O_2 decreased but gas selectivity for O_2/N_2 increased. The rise in temperature caused the penetrants' diffusive jump mechanism between polymer precursor and carbon molecular sieving material (CMS) to change. Different study done by Geiszler and Koros [25], in which they increase the carbonization temperature from 550°C to 800°C produced similar result as Steel and Koros [24], whereby the permeability of H_2 and N_2 decreased, and selectivity for H_2/N_2 increased. Byproducts degradation were speculated to accumulate and block the membrane pores. As the carbon become denser at increasing temperature, the compactness increase and size of pores decrease. These events are another contributing factor that affect permeability and gas selectivity of carbon-based membranes. Barbosa-Coutinho [26] carried out a statistical design study for optimization of carbonization process on poly-etherimide (PEI) hollow-fibre type membrane.

In contrast with thermoset polymers, thermoplastic type polymeric membrane needs to undergo thermal pretreatment at mild temperature under continuously-flowed oxidized environment. The membrane polymeric chain binds with hydroxyl and carbonyl functional groups during the reaction [27]. Therefore, membrane stability increased after subjected to elevated temperature treatment prior to carbonization. Significantly, incomplete process of thermal pretreatment or unstabilized membrane would suffers notable weight loss and deteriorating structure during carbonization. Unlike the unstabilized membrane, stabilized membrane resulted in only small weight loss and less deformation during carbonization. One way to increase the stability of membrane is by injecting oxidizing atmosphere at the initial of stabilization process rather than during isothermal [28]. Temperature chosen for thermal-stabilization process should not be too high or too low, and should not exceed its glass transition temperature which lead to degradation and melting of polymeric structure. Water by-product was obtained resulted from the oxygenated group crosslinking and hydrogen were released from different polymer chain sections, causing the polymer to have a graphite-like structure [29]. Removal of heteroatoms, volatile gas emissions and chemical reaction was discovered to occur concurrently during the carbonization [30].

Centeno *et al.,* [31] conducted studies focusing on phenolic resins-derived carbon membrane, investigating influence of carbonization temperature, heating rate, soak time and experimental surroundings on permeability and selectivity of the membrane. They revealed that performing carbonization at high temperature, low heating rate together with short soak time at inert environment produced a membrane with high permeability. At high carbonization temperature, shrinkage of membrane pores occurred due to sintering effect. Thus, carbon membrane performance switched to molecular sieve-based separation from an adsorption-selective membrane type. Next, low heating rate slowed down the emission of volatile components from membrane structure and short soak time prevented the porosity reduction prompted by rearrangement and alignment of carbon aggregation. Lastly, inert atmosphere generated higher porosity of membrane structure compared to carbonization at vacuum environment. It helps to instantly removed volatile components and inhibit deposition on membrane pores, whereby the phenomenon was elaborated in previous literature by Geiszler and Koros [32]. However, it was noted that permeability is always inversely proportional to selectivity.

Another polymeric precursor that has been extensively studied for the effect of carbonization temperature was PFA [33]. At 300°C, PFA undergo degradation into solid carbon. At range 600°C to 1200°C, unfavourable dehydrogenation started to occur which resulted in a fragile and collapse of micropores having graphite-like structure [34, 35]. In between 300°C to 400°C, carbon membrane derived from PFA contained carbon and have a mesoporous structure from co-existing polymeric chain before it was converted into microporous structure at 600°C. This micropores was accompanied by a fragile carbon structure. Sazali *et al.,* [36] reported a decrease in membrane pore size with high membrane porosity and high gas permeance when carbonization temperature was increased. Increment in permeability of oxygen and nitrogen was due to the increase in porosity, which influenced from the increase in carbonization temperature of 300°C to 600°C [37]. This argument has been previously stated by Mariwala and Foley [34] in which they explained that pore size distribution reduction was due to aromatic microdomains growth when carbonization temperature was increased. Subsequently, porosity was also increase and consumed the amorphous carbon. Increase in selectivity and permeation activation energies are closely associated with carbonization temperature [38]. According to previous researcher, permeation activation energy for O_2 at 550°C and 800°C are 4.1 kcal mol^{-1} and 5.2 kcal mol^{-1} respectively while N_2 shows permeation activation energy of 6.1 kcal mol^{-1} and 6.6 kcal mol^{-1} at same temperature as aforementioned. Channels responsible for carbon structure selectivity was reduced when high carbonization temperature were employed [24]. Carbonization of polymeric based membrane in terms of pores development can be breakdown into two stages; pore opening and closure of pore. At low to medium temperature range, pore opening would occur indicated by the increased gas permeability. This is due to modification of polymer-carbon structure and discharge of decomposed polymer subgroups into membrane surfaces, leaving with micro-sized openings. This step could be accompanied by closure of pore but at a much minimized effect. Next, at higher or graphitization temperature, pore enclosure significantly took place, causing the decrease of gas permeability but an increase in selectivity of gas. This stage presented the whole carbon structure densification that started since the sintering effect took place.

4. Carbonization Heating Rate

In synthesis of carbon membrane, several literatures have proved that heating rate plays a vital role in constructing carbon structure. This parameter affects the evolution rate of volatile components during carbonization reaction. It also impacting the final pore structure of carbon membrane and indicator that shows the period of sample exposure to heat, which could affect the course of reaction and diffusion process. Minimum heating rate can be as low as 0.5°C min^{-1} and maximum up to 15°C min^{-1} [39]. Importance of low heating rate is to accommodate the discharge of volatile compound and to avoid defect [40]. From a study by Kim and co-workers [41], they stated that combination of low heating rate and long soaking time would produce a denser carbon membrane structure and hard to separate C_3H_6/C_3H_8. Contrarily, high heating rate would cause the fabricated carbon membrane to suffer various defects in their structure such as presence of pinhole, cracks, which lower the overall performance [42].

From a review done by Ismail and Li [43], they suggested that lower heating rate was favourable in order to produce smaller pores and to increase the crystallinity of carbon which can enhances its selectivity. Decrement in heating rate would lower the gas permeance as it delayed the progress of carbonization and the pore shrank. Slower progress helped to extend the time of heat treatment, offering enough time for sintering effect to takes place in reducing the size of pores. The reduction of pore increases gas selectivity and lower the gas permeability. Other things to be in consideration are that lower heating rate would have resulted in higher cost and time. Thermogravimetric analysis (TGA) was done by Su and Lua [44]. Increment in heating rate extend the decomposition temperature to have difference around 150°C compared to lower heating rate. Both heating rates eventually achieved the same value of weight loss before acquiring the asymptote point. In addition, lower heating rate lead to the decomposition to start at low temperature and reaction rate. Generation rate and product gas diffusion from carbonization have high impacts on the formation of carbon membrane's pore structure. In depth study by the same researchers proved that influence of heating rate on gas permeance performance were unique, whereby the phenomenon impaired several gas permeability but improve permeability of some other gases. Tuning the temperature from 0.5°C min^{-1} to 4°C min^{-1} improved the permeance for He and CO_2, decreased N_2 permeability but did not affect O_2 permeability. However, at 800°C, impact from heating rates was described to be negligible and agreed by [45, 46].

Commonly, it was well-known that lower heating rate was beneficial for pore size reduction while still permits the diffusion of gases and produced a crack-free membrane at the same time. Majority of existing literatures employed 0.5 to 1.0 °C min^{-1} to obtained undefective carbon membrane [47-49]. However, from experimental study by Barbosa-Coutinho *et al.,* [26], they found out that 1°C min^{-1} heating rate caused crack on hollow fiber carbon membrane and increase the heating rate to 3°C min^{-1}. They also reported that heating rate has lower effect compared to carbonization temperature. But if the membrane was stabilized, lower heating rate helped to lengthen the membrane oxidation, allowing complete oxidation reactions and stabilized fibres prior to carbonization. Further increase in heating rate consequently increase the weight loss, mean pore size and porosity of the membrane [50-52]. Gas flux was reduced, and this led to widening of pore size distribution. When low heating rate is utilized, structure of carbon membrane was found to be more uniformed with small pore size whilst the contrary would led to high release of explosive gases and forming irregular pores having pinholes and cracks.

5. Conclusions

From this paper, it can be concluded that carbonization temperature and heating rate have significant influence on the carbon membrane structure formation from its polymer precursor. High temperature during carbonization narrowed the pore in membrane structure, making it difficult for gas diffusion having large kinetic diameter while small gas molecules can pass through easily. Another factor which is heating rate is essential to control volatile compound released during carbonization. Low heating rate are more favorable as it can inhibit explosive emission of volatile compounds that could affect the final carbon structure. However, the drawback of low heating rate is that it extends the thermal exposure on carbon, causing development of a graphite-like structure. This structure is fragile and not suitable for physical handling [53, 54]. Lastly, it was known that carbonization temperature and heating rate are important parameters that need to be taken into account when fabricating carbon membrane.

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