Journal of Industrial and Engineering Chemistry 20 (2014) 1061–1070

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Investigating the effect of dianhydride type and pyrolysis condition on the gas separation performance of membranes derived from blended polyimides through statistical analysis

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ARTICLE INFO

Article history:
Received 16 March 2013
Accepted 21 June 2013
Available online 12 July 2013

Keywords:
Gas permeability and selectivity
CMS membranes
Modeling and optimization
Factorial design
Carbonization

ABSTRACT

In this study, properly designed experiments are utilized to improve and optimize the main parameters including the selection of precursors with different molecular structures, blend composition of precursors and conditions of carbonization. Optimum conditions are met for UIP-R/PBI, at blend composition of 94% and pyrolysis temperature of 620 °C at 10^{-7} Torr. Under such conditions, the model estimated permeability of CH_4 and CO_2 equal to 26.7 and 310 Barrer, while measured selectivity responses of CO_2/CH_4 is 77.5, respectively. As a result, greater values of separation efficiency are achieved in the range of 0.88–0.97 polyimide content in these blends.

1. Introduction

Carbon molecular sieve (CMS) membranes have been investigated in various applications, such as purification of gaseous blend, dehydration of fine chemical products and natural gas processing in order to replace other traditional processes for the purpose of cost and energy saving [1,2].

CMS membranes could particularly attain high permeability and selectivity in gas separations including O_2/N_2, CO_2/CH_4, N_2/CH_4 and CO_2/N_2 separations. They could thus surpass the "upper bound" limit for soluble polymeric materials after carbonization [3]. On the other hand, CMS membranes have attractive characteristics including exceptional selectivity for planar molecules, as well as excellent heat and corrosion resistance capabilities [4]. CMS membranes which are fabricated by pyrolysis of a polymeric membrane as the precursor, are characterized by a very thin microporosity [5].

Producing a high performance carbon membrane is a complicated task, due to involvement of many steps which must be designed and optimized properly. In other words, fabrication of the carbon membranes incorporates some important factors such as polymer type and chemical formula, morphology and microstructure of the precursor and pyrolysis conditions (i.e. final temperature, ramp rate, thermal soak, atmosphere and pressure) [3,6,7]. Therefore, it is necessary to have a good control on these factors in order to obtain a highly performed CMS membrane with desired characteristics [3,8].

Polyimides are good candidate precursors for making carbon membranes because they have high glass transition temperature, high melting point as well as great thermal and structural stability [9,10]. Many types of polyimides including various dianhydrides, pyromellitic dianhydride groups (PMDA, Kapton) [11–13], benzophenonetetracarboxylicdianhydride (BTDA, matrimid and P84) [8,14,15], 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA, UIP-R, S) [16,17] have been synthesized and then examined in terms of their performance as membrane materials.

Suda and Haraya [11] produced CMS membranes from PMDA-ODA by carbonizing dense films at temperatures of 600–1000 °C under vacuum environment. Permeability of the membranes was decreased by raising pyrolysis temperature of O_2, CO_2 and H_2 from 383, 1820 and 1600 Barrer to 0.96, 4.2 and 59 Barrer, respectively. Tin et al. [14] explored BTDA-ODA as a precursor in preparation of CMS membranes for gas separation. The carbonization process was carried out in the range of 550–800 °C under vacuum. The experimental data demonstrated that the highest selectivity was attained by pyrolysis of the carbon membranes at final temperature (800 °C). Meanwhile, these membranes show excellent values

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1226-086X/$ – see front matter
http://dx.doi.org/10.1016/j.jiec.2013.06.043

Nomenclature

$b_0, b_1, \ldots, b_n$	regression coefficients
DOF	degree of freedom
F-value	ratio of variances, computed value
i and j	subscripts (integer variables)
n	number of factors (variables)
P-value	statistical criterion
CV	coefficient of variation
R	correlation coefficient
R^2	coefficient of multiple determinations
R^2_{adj}	adjusted statistic coefficient
X_1, X_2, X_3	coded variables
$\overline{X}$	mean value of variables
Y	response

of permeation and selectivity, 500 Barrers and 88, respectively. Furthermore, Hayashi et al. [16] produced polyimide out of BPDA-ODA and carbonized the membrane at temperatures within the range of 600–900 °C. The carbonization performed above 600 °C increased the gas permeation by 2–4 orders of magnitude, while molecular sieving properties of the unmodified polyimide membrane were preserved.

Moreover, prior works have revealed appealing advantages suggested by the use of blending technology for advanced membranes fabrication [18,19]. For instance, Hosseini and Chung [18] studied blending high performance polymeric membranes of polyimides and PBI for development of special membranes. Their results demonstrated that blending of precursors could cause several amendments such as formation of integrated families of the polymers with various properties and physiochemical characteristics, or providing a simple or reproducible procedure. Blending technique and incorporation of PBI with polyimides in improvement of performance caused by the chain packing density enhancing and hindrance in segmental mobility of polyimide chains [18,19].

Among different fabrication steps of the CMS membrane, pyrolysis process is the key step which is conventionally used for the production of porous carbon. During the carbonization process, micro porosity is formed in the carbon membrane. This process governs both the molecular sieve properties and the ability of a CMS membrane for gas separation [20].

Several parameters may affect the carbonization process. In order to have a significant impact on the final structures and molecular sieving of a carbon membrane – minor changes have been made in the pyrolysis variables. The most significant factors of pyrolysis that affect the pore size distribution and consequently separation performance, are the pyrolysis temperature, heating rate, soaking time, pressure and concentration of pyrolysis atmosphere [1,3,21].

Pyrolysis temperature affects the carbon membranes considerably in terms of membrane structure, separation performance and mechanism of gas transport [16,17,22]. Shao et al. fabricated CMS membranes through pyrolysis of 6FDA-durene. Their produced polyimide was decomposed at 496 °C. The experimental data demonstrated that permeability of the membranes was enhanced by raising the pyrolysis temperature from 325 to 475 °C for pure gases, although gas permeability of the gases with smaller particles remains almost unchanged [22]. Increasing the final pyrolysis temperature will also produce a carbon membrane with greater crystallinity, compactness, density, and smaller average interplanar spacing between the carbon layers [23].

The pyrolysis atmosphere has a significant impact on properties of the carbon membranes inhibiting undesirable chemical burning of the precursor during the carbonization. The pyrolysis can be performed either in vacuum or inert atmosphere. The former is expected to yield more selective but less permeable carbon membranes in comparison with an inert gas (e.g. helium or argon) pyrolysis system [4,24]. Geiszler et al. have studied the effect of polyimide pyrolysis conditions (atmosphere) on properties and performance of the carbon molecular sieve membrane made from 6FDA-base polyimide. The CMS membranes were pyrolyzed under different atmospheres including helium, argon and vacuum (0.01–0.03 Torr). The results showed that the pyrolysis at vacuum has resulted in much higher selectivity but lower permeance as compared to that of inert purge for O_2/N_2 separation [24]. A similar phenomenon was noted by Vu for the CO_2/CH_4 separation. The CMS in Vu's study was produced from Matrimid precursors [25].

Modeling can be effectively applied to establish the relationship between one or more response variables and a set of quantitative experimental variables in the field of gas separation and membrane technology [26–30]. Khayet et al. applied a statistical method to examine the effect of various variables including concentrations of the polymer and its additives in casting solutions, solvent evaporation time and coagulation bath temperature on both structural characteristics of the membranes and performance of direct contact membrane distillation (DCMD). Analysis of variances showed that all parameters had significant effects on the responses, with the coagulation bath temperature playing the least important role while the concentration of PVDF-HFP had the greatest effects on both permeate flux and salt rejection coefficient [26]. Onsekizoglu et al. used a two-level factorial experimental design to study the effect of key operating variables both on the evaporation flux and the soluble solid during concentration through osmotic distillation (OD) and membrane distillation (MD) processes. The models were derived from experimental design to investigate all the interactions between the considered factors (osmotic agent concentration, flow rate and temperature difference between feed and osmotic agent). These models were later validated statistically by analysis of variance (ANOVA). Some models were developed to estimate evaporation flux and soluble solid content affected by operating analyzed variables. Results have revealed that all the linear terms of the variables have significant effects on the evaporation flux [27].

He and Hagg [28] also used orthogonal experimental design (OED) approach to explore the gas transport properties of hollow fiber carbon membranes by making modifications to the carbonization process. The obtained results uncovered the significance of carbonization parameters under study on performance of the carbon membrane with this order: purge gas > final carbonization temperature > heating rate > final soak time. Based on OED, carbonization in a CO_2-containing environment as a purge gas by applying final temperature and dwelling time of 823 K and 2 h, respectively, can be regarded as the optimal condition for fabrication of a high performance carbon membrane.

In another research [29], Su and Lua applied the statistical two-level factorial design to assess the effect of various pyrolysis variables on performance of the carbon membranes prepared from Kapton® 100HN polyimide. The effects of carbonization atmosphere, final temperature, heating rate and thermal soaking time were assessed at the final temperature on permeation rates of He, CO_2, O_2 and N_2. Statistically speaking, significant carbonization parameters including main factors and 2-factor interactions of the