

DEVELOPMENT OF ADSORPTION SELECTIVE CARBON MEMBRANE
USING CELLULOSE ACETATE FOR SEPARATION OF O₂/N₂ AND
C₁ – C₄ HYDROCARBONS/N₂

ABDUL RAHIM BIN JALIL

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia

FEBRUARY 2006

“To my beloved mother, father, my family who gave me encouragement towards this study and to my wife who gave me inspiration and encouragement towards the success of this study, may our dream come true”

ACKNOWLEDGMENT

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

I would like to express my gratefulness to Allah S.W.T for giving me strength and wisdom in my research work. In preparing this thesis, I was in contact with many people, researchers, academicians, technicians and practitioners. They all have contributed to my understanding and valuable thoughts during my research.

First and foremost, I would like to express my special thanks to my supervisor, Associate Professor Dr. Mohd Ghazali Bin Mohd Nawawi, for his encouragement, guidance, ideas which enlighten my curiosity, suggestion, advice and friendship. I am gratefully expressing my thanks to my whole family who understand me and gave me the spirit and continuing support to finish this study.

I am grateful to Universiti Teknologi Malaysia for granting me generous financial support under *Industrial and Technology Development* fellowship award that enabling this research to be done successfully.

My fellow colleagues who also should be recognized for their moral support. Their view and tips are useful indeed, but it is not possible to list them all in this limited space.

ABSTRACT

The objective of this study is to develop a new kind of carbon membrane which could separate gas based on the adsorption concept. This study was subjected to encounter challenges imposed by general trade off between permeability and selectivity of membrane. Membrane was prepared from a thermosetting polymer that acts as a carbon precursor in this type of membrane. The membrane is formed by pyrolysis of cellulose acetate supported over a microporous ceramic membrane used for microfiltration at 300⁰C, 325⁰C, 350⁰C, 400⁰C, 450⁰C, and 500⁰C under N₂ flowrate equal to 200 ml/min. The membrane then was further subjected to an oxidative treatment at temperature between 150⁰C to 400⁰C with an interval of 50⁰C. The pyrolysis temperature was found plays an important role in changing the morphology of the carbon membrane been developed. Increasing the pyrolysis temperature produces more pores with smaller diameter, thus reducing the permeability of the penetrates. The optimum pyrolysis temperature for O₂/N₂ separation is at 400⁰C which give the value of the selectivity about 3.92. This value has exceeded an excellent value that is selectivity above 3.0 as suggested by Kulprathinja (1988). A hierarchal way to developed the adsorption selective carbon membrane has been done. The prepared membrane shows high permeabilities and selectivity towards separation of gas mixtures formed by hydrocarbons and N₂. Membrane prepared at 400⁰C was further subjected to an air oxidation at 300⁰C and gave the value for single gas experiment, C₂H₆/N₂; 2.52, C₃H₈/N₂; 2.44, n-C₄H₁₀/N₂; 2.35. For binary gas experiment, the selectivity for C₂H₆/N₂; 3.3, C₃H₆/N₂; 14.4, n-C₄H₁₀/N₂; 26.05. A selective and high permeability carbon membrane based on cellulose acetate could be developed.

ABSTRAK

Objektif utama penyelidikan ini dijalankan adalah untuk menghasilkan sejenis membran karbon yang mampu memisahkan gas berdasarkan konsep penjerapan. Penyelidikan ini dijalankan untuk mengatasi dan mengetahui hubungan timbal balik antara kebolehtelapan dan kemimilihan membran karbon. Membran disediakan daripada bahan polimer (suhu terkawal) iaitu *cellulose acetate*. Membran karbon dihasilkan daripada proses pirolisis satu lapisan nipis polimer ini pada penyokong seramik pada suhu 300⁰C, 325⁰C, 350⁰C, 400⁰C, 450⁰C dan 500⁰C didalam aliran nitrogen pada kadar 200ml/min. Membran ini kemudian melalui proses pengoksidaan proses pengoksidaan antara 150⁰C hingga 400⁰C dengan beda suhu 50⁰C. Suhu pemanasan tanpa udara memainkan peranan yang paling penting dalam menghasilkan membran karbon ini. Suhu pirolisis yang terlalu tinggi akan menghasilkan liang-liang rongga dengan diameter yang lebih kecil dan dengan ini akan menyebabkan penurunan kepada nilai kebolehtelapan membran karbon yang dihasilkan. Suhu optimum bagi proses pemisahan O₂/N₂ adalah pada 400⁰C dimana nilai kemimilihannya ialah 3.92. Nilai ini telah melebihi nilai yang dicadangkan untuk pemisahan O₂/N₂ yang optimum iaitu 3.0 seperti dicadangkan oleh Kulprathinja (1988). Kaedah yang bersistematik telah dilakukan bagi mendapatkan suhu optimum pengoksidaan. Membran yang disediakan pada suhu pirolisis 400⁰C dan suhu pengoksidaan 300⁰C memberikan nisbah pemisahan gas bagi ujikaji gas tulen, C₂H₆/N₂; 2.52, C₃H₈/N₂; 2.44, n-C₄H₁₀/N₂; 2.35. Ujikaji bagi campuran gas hidrokarbon dan N₂, kemimilihan C₂H₆/N₂; 3.3, C₃H₆/N₂; 14.4, n-C₄H₁₀/N₂; 26.05. Membran karbon yang memiliki nilai ketelapan dan kemimilihan yang tinggi dapat dihasilkan.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
1	INTRODUCTION	
	1.1 Membrane-Based Gas Separation Process	1
	1.1.1 Historical and Current Status	1
	1.1.2 Problem Statement	2
	1.2 Objective of Work	5
	1.3 Scope of Work	5
2	LITERATURE REVIEW	
	2.1 Development of Adsorption Selective Carbon Membrane for Gas Separation	7
	2.1.1 Introduction	7
	2.1.2 Fundamentals of Membrane Technology	
	2.1.2.1 Advantages of Membrane Technology	11
	2.1.2.2 Fundamentals of Gas Permeation	13
	2.1.3 Basic Principle of Adsorption Selective Carbon Membrane	19
	2.1.4 Evolution and Development	21
	2.1.5 Carbon Membrane	24
	2.2 Ceramic Asymmetric Membrane	28
	2.3 Parameters Effecting Gas Separation Performance	32

2.3.1	Pyrolysis Parameter	32
2.3.2	Coating Procedure	33
2.3.3	Oxidation Time and Temperature	35
2.3.4	Pressure and Temperature Difference	35

3

RESEARCH METHODOLOGY

3.1	Materials	37
3.2	Experimental Methods	38
3.3	Preparation Of Carbon Membrane	38
3.3.1	Preparation of Carbon Membrane Support	38
3.3.2	Preparation of Carbon Precursor	38
3.3.3	Preparation of Adsorption Selective Carbon Membrane	39
3.4	Design and Fabrication of Gas separation Test Rig	45
3.5	Gas Permeation Measurement	48
3.6	Characterization of Prepared Carbon membrane	51
3.6.1	General Overview	51
3.6.2	Performance Study of the Membrane	51
3.6.2.1	Morphologies of Carbon Membrane	52
3.6.2.2	Effect of Separation Pressure and Temperature on Gas Separation Performance.	52
3.6.2.3	Effect of Oxidation Temperature on Gas Separation Performance.	52

4	RESULT AND DISCUSSION	
4.1	Introduction	53
4.2	Membrane Morphology	53
4.2.1	Effect of Pyrolysis Temperature on the Membrane Developed.	59
4.3	Permeability and Selectivity of Unmodified Ceramic Membrane	64
4.4	Permeability and Selectivity Properties of CA Carbon Membrane.	65
4.4.1	Permeability and selectivity of Oxygen and Nitrogen.	66
4.4.2	Effect of oxidative treatment on the permeability and selectivity of hydrocarbon, oxygen and nitrogen.	76
5	CONCLUSIONS AND RECOMMENDATIONS	
5.1	Conclusions	85
5.2	Recommendations	87
	REFERENCES	89

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Membrane Separation Process	13
2.2	General hierarchy of permeability of common gas	17
2.3	Advantages and Disadvantages of Ceramic Membranes	31
3.1	Carbonization condition used to prepare cellulose-based carbon membrane.	41
3.2	Oxidation condition	43
4.1	Permeability and selectivity of oxygen and nitrogen (1 bar) and different separation temperature.	67
4.2	Permeability and selectivity of oxygen and nitrogen (2 bar) and different separation temperature.	68
4.3	Permeability and selectivity of oxygen and nitrogen (3 bar) and different separation temperature.	69
4.4	Permeability and Selectivity of Modified Membrane (Oxidized at 150 ⁰ C)	77
4.5	Permeability and selectivity of methane and nitrogen (1 bar) at different separation temperature.	80

4.6	Separation of single gas (Temperature:27 ⁰ C; Pressure : 1 bar)	81
4.7	Separation of binary gas (Temperature:27 ⁰ C; Pressure : 1 bar)	81

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Schematic representation of a chemical process	10
2.2	Schematic representation of mass transport phenomena occurring in solution diffusion membrane	16
2.3	Structure of inorganic membrane	21
2.4	Schematic representation of different membrane morphologies	22
2.5	Schematic representation of an asymmetric membrane	29
2.6	Pore size range of ceramic membranes and related application fields	29
3.1	Preparation procedure for adsorption selective carbon membrane	44
3.2	Schematic representation of gas separation apparatus	46
3.3	Schematic representation of gas permeation cell	47
3.4	Schematic design of gas permeation cell	47
4.1	Surface View of unmodified ceramic membrane	54
4.2	Cross section view of unmodified ceramic membrane	54
4.3	Surface view of polymer membrane	55
4.4	Cross Section View of Membrane Prepared at Pyrolysis Temperatures 400 ⁰ C (Magnification 200X).	56
4.5	Cross Section View of Membrane Prepared at Pyrolysis Temperature 400 ⁰ C (Magnification 500X).	56
4.6	Surface View of Membrane Prepared at Pyrolysis Temperature 400 ⁰ C (Magnification 500X).	57

4.7	Cross Section View of Membrane Prepared at Pyrolysis Temperature 400 ⁰ C; Oxidation Temperature 300 ⁰ C. (Magnification 200X).	57
4.8	Cross Section View of Membrane Prepared at Pyrolysis Temperature 400 ⁰ C; Oxidation Temperature 300 ⁰ C. (Magnification 500X).	58
4.9	Surface View of Membrane Prepared at Pyrolysis Temperature 400 ⁰ C; Oxidation Temperature 300 ⁰ C. (Magnification 4000X).	58
4.10	Cross Section View of Membrane Prepared at Pyrolysis; 400 ⁰ C, Heating rate 5 ⁰ C/min (Magnification 200X).	60
4.11	Surface View of Membrane Prepared at Pyrolysis; 300 ⁰ C, Heating rate 2 ⁰ C/min (Magnification 200X).	60
4.12	Cross Section View of Membrane Prepared at Pyrolysis; 300 ⁰ C, Heating rate 2 ⁰ C/min (Magnification 200X).	61
4.13	Surface View of Membrane Prepared at Pyrolysis; 325 ⁰ C, Heating rate 2 ⁰ C/min (Magnification 500X).	61
4.14	Cross Section View of Membrane Prepared at Pyrolysis; 325 ⁰ C, Heating rate 2 ⁰ C/min (Magnification 500X).	62
4.15	Surface View of Membrane Prepared at Pyrolysis; 350 ⁰ C, Heating rate 2 ⁰ C/min (Magnification 500X).	62
4.16	Cross Section View of Membrane Prepared at Pyrolysis; 450 ⁰ C, Heating rate 2 ⁰ C/min (Magnification 500X).	63

4.17	Cross Section View of Membrane Prepared at Pyrolysis; 450 ⁰ C, Heating rate 2 ⁰ C/min (Magnification 500X).	63
4.18	Cross Section View of Membrane Prepared at Pyrolysis; 500 ⁰ C, Heating rate 2 ⁰ C/min (Magnification 4000X).	64
4.19	Separation properties of unmodified ceramic membrane at 1 bar	65
4.20	Separation Properties of CA based Carbon Membrane at 1 bar (a) 27 degree Celsius; (b) 55 degree Celsius; (c) 100 degree Celsius	72
4.21	Separation Properties of CA based Carbon Membrane at 2 bar (a) 27 degree Celsius; (b) 55 degree Celsius; (c) 100 degree Celsius	73
4.22	Separation Properties of CA based Carbon Membrane at 3 bar (a) 27 degree Celsius; (b) 55 degree Celsius; (c) 100 degree Celsius	74
4.23	Permselectivity as function of separation temperature for oxygen and nitrogen separation.	75
4.24	Separation properties of C8 at 1 bar.	78
4.25	Permselectivity of methane and nitrogen versus separation temperature.	79
4.26	Modification of gas permeability through cellulose acetate derived carbon membrane with temperature; single gas.	83
4.27	Modification of gas permeability through cellulose acetate derived carbon membrane with temperature; binary gas mixtures.	83

LIST OF SYMBOLS

A	-	Membrane area (cm^2)
c	-	Concentration (cm^3 (STP)/ cm^3)
d	-	Kinetic diameter
D	-	Diffusion coefficient (cm^2/s)
J	-	Diffusion flux (cm^3 (STP)/ $\text{cm}^2.\text{s}$)
MW	-	Molecular weight (g/mol)
Q	-	Volumetric flow rate (cm^3/s)
S	-	Solubility coefficient (cm^3 (STP) / $\text{cm}^3.\text{s}.\text{cmHg}$)
T	-	Temperature (Kelvin)
J_i	-	Flux of component i
l	-	Membrane thickness (cm)
dc/dx	-	Concentration gradient
D_i/D_j	-	Diffusivity
K_v	-	Geometric constant for viscous or Poiseuille flow through porous media (dimensionless)
$Perm_i$	-	Permeability of component i
p	-	Pressure (cm Hg)
p_{us}	-	Upstream pressure (cm Hg)
p_{ds}	-	Downstream pressure (cm Hg)
Δp	-	Pressure gradient (cm Hg)
Δp_c	-	Pressure drop by capillary action (cm Hg)
Δp_i	-	Difference of partial pressure of component i
\bar{p}	-	Average pressure (bar)
Q_i	-	Volumetric flow rate of component i (cm^3/s)
\AA	-	Angstrom (10^{-10})
α	-	Selectivity (dimensionless)

η	-	Viscosity (poise)
$\frac{P}{l}$	-	Pressure normalized flux ($\text{cm}^3(\text{STP}) / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$)
S_i/S_j	-	Selectivity solubility
\bar{v}	-	Mean molecular velocity (cm/s)

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A 1	Permeability and Selectivity of Unmodified Membrane	101
A 2	Permeability and Selectivity of Hydrocarbon and Nitrogen gas at 1 bar (single gas)	102
A 3	Permeability and Selectivity of Hydrocarbon and Nitrogen gas at 1 bar (binary gas)	103
A 4	Sample of Gas Permeability Calculation	104
B 1	Dimension of Permeation Cell	105
B 2	Assembly Component of Permeation Cell	106
B 3	Gas Separation Apparatus	107

CHAPTER 1

INTRODUCTION

1.1 Membrane-Based Gas Separation Process

1.1.1 Historical and Current Status

Membranes are increasingly playing on significant role in chemical technology and being used in variety of applications in our daily life. At the present time, there is a growing interest in the development of gas separation membranes based on material providing in terms of chemical and mechanical stability. For the past several decades, membrane process has gone from laboratory curiosity to commercial reality. The key functionality of the membranes actually is the ability to control the permeation of chemical species. In separation applications, the goal is to allow one component of a mixture to permeate the membrane while hindering other components (Shiflett, 2002). Mitchell (1831) reported the first scientific observation for gas separation process. He observed that balloons made of India rubber (natural rubber) put in gas atmosphere were blown up with different velocity is depending of the nature of gases. At about the same time in 1855, Fick performed his classical study, “Uber diffusion” which then was formulated as Fick’s first law for diffusion in membrane (Fick, 1995).

The most remarkable contribution to gas separation using membrane was attributed by Sir Thomas Graham in 1860 that proposed the formation of Graham's law and postulated solution diffusion mechanism (Graham, 1866). He discussed in modern terms and demonstrated experimentally that mixtures of gas can be separated via membrane. Successful commercialization of gas separation system is a major breakthrough in research and development of membrane technology. Recently, a considerable progress has been made in commercial use of membranes for gas separations, covering many existing and emerging applications.

1.1.2 Problem Statement

Conventional processes for the separation of certain gases from gaseous mixture are based on the physical properties of various constituent that we want to separate. An example is the removal of hydrogen sulfide from natural gas. This process leaves sulfides as a waste, thus adding the complexity of the whole process. A real application of the complexity of this process is in the refinery itself where a complex unit is design and operated in order to remove the sulfur produce in a safely manner.

An alternative ways is needed in order to improve the competitiveness of the process. Gas separation membranes seem the solution to overcome this problem. At present, the major interest in membrane technology is focused in findings inorganic material that resistant to thermal and chemical influences, withstand harsh environment and also could produce a higher permeability and selectivity compared to polymeric membrane.

As the new competitive edge, a major demand emerged in the field of gas separations using membrane. Polymeric membrane has been used extensively produced by various researchers and surprisingly result has been achieved. There is a lack in terms of stability of polymeric membrane that cannot be encountered by the conventional polymeric membranes but can be done by using carbon membrane. Carbon membrane could withstand a harsh operating environment such as high

operating pressure and temperature without loose of the performance. Carbon membrane technology has been focused in the gas separation process. It is an effort to developed carbon membrane who could give a higher permeability and selectivity of each process before it could apply to the industry broadly. The main problem that must be overcome before it could be applied to the industry is the fabrication of this material in a manner that it is reproducible and scalable for manufacturing (Fauzi, 2003).

It has reported that the major barrier in the developing carbon membrane compromise of many aspects. It involves many aspects such as producing the carbon membrane itself and also the module involved to attach them for carrying out the separation analysis. In terms of producing the carbon membrane itself, the material used as the carbon precursor itself has the significant impact on the overall cost for producing the carbon membrane. An investigation need to be carried out to find a more suitable carbon precursor other than polyimide, which is mainly used by other researcher. This is why this study try to find out the performance of carbon membrane developed from cellulose acetate. It is not a simple task, but by contributing a new material that can improve the separation performance without losing the economically processibility could be a breakthrough in the fields of gas separations using carbon membrane.

There are many ways in developing carbon membrane but mostly it come back to the objective of the development of the membrane itself, the pore of the membrane need to be controlled in a reproducible and tailored fashion. By tailoring the pore of the membrane, specific applications could be identified. It has been postulated that the presence of adsorbed molecules forms a barrier to the diffusion of non-adsorbed molecules and hence hinder their transport (Yang et al, 1999). Based on this postulated statement, research work has been carried out in order to find the compatibility of the carbon membrane based from cellulose acetate to separate absorbable and non-absorbable gases. Thus the motive of this research is subjected to the development of a new kind of carbon membrane that is adsorption selective carbon membrane instead of molecular sieve carbon membrane. It is capable of separating gas based on their adsorption characteristics of the gas molecule and the membrane itself.

One of the major problem encounters in the application of carbon membrane is the hydrophobic problem. One of the best solutions to overcome this problem is by coating the carbon membrane with suitable barrier without greatly inhabiting the flux of other permeating species. This can be accomplished by developing carbon composite membranes. Jones and Koros (1995) used Teflon Af1600 and Teflon Af2400 as hydrophobic element. They also suggest that the coating solution can be made by dissolving the polymeric material in an appropriate solvent so that the polymer concentration is between 0.5 and 2.0% by weight. They proposed some coating material such as poly (4-methyl-1-pentene), PMP. Compared to the work they have done, they found out that The Teflon AF material far less restrictive to the flux of O₂ and N₂ than using PMP as hydrophobic element.

Verma and Walker (1992) have proposed a simpler method where they treat the carbon surface with various agents such as H₂ and Cl₂ to make it more hydrophobic but the surface modification would likely change the molecular sieving properties of the membranes. The trends that the water permeance and O₂ permeance show are typical of capillary condensation. As the relative humidity the water film thickness increases and menisci will began to form inside the pore and the pore will began to fill with water blocking the flow of the oxygen (Cooper and Lin, 2002).

This problem was encountered in this study by adding a drying compartment using silica gel. The gas was pre-dried before pass through the selective carbon membrane. When we deal with the capability or usefulness of the membrane, we always refer to the efficiency of the membrane. The efficiency of membrane separation process does not only depend on the membrane alone. It is also depends on the way the membrane is installed in the form of membrane module. Many researchers have proposed membrane modules depends on their applications.

In the field of carbon membrane, the most challenging part to be considered is the poor mechanical stability of the carbon membrane. This study used a tubular ceramic membrane as a supporting module in terms to encounter this problem. A gas separation apparatus were also designed in order to attached the carbon membrane been developed

1.2 Objective of Work

Based on the background of this study, objectives of this study are categorized as following;

- (i) To develop a new type of adsorption selective carbon membranes for gas separation using cellulose acetate as a carbon precursor.
- (ii) To determine an optimum preparation condition of the new type of adsorption selective carbon membrane for membrane separation process.
- (iii) To analyze the membrane been developed in terms of selectivity and permeability using oxygen, nitrogen and C₁-C₄ hydrocarbon gas.

1.3 Scopes of Work

In order to achieve the objective mentioned in 1.3, below are the steps in order to accomplish this experiment. The scopes of work will be carried out

- (i) To prepare carbon membrane using cellulose acetate as a carbon precursor using dip coating technique. Asymmetric ceramic membrane was used as the supporting material.
- (ii) To design and fabricate gas separation unit in order to carry out gas separation analysis of single and binary mixtures (50/50 by volume) of gas. Types of gases used were oxygen, nitrogen methane, ethane, propane and *n*-butane.
- (iii) To determine the optimum pyrolysis condition for the carbon membrane been developed in the range of carbonization temperature at 300⁰C, 325⁰C, 350⁰C, 400⁰C, 450⁰C and 500⁰C.
- (iv) To determine an optimum oxidation temperature between 150⁰C to 400⁰C with an interval of 50⁰C.

- (v) To study the effect of permeation temperature (27°C , 55°C and 100°C) and feed pressure (1 bar, 2 bar and 3 bar).
- (vi) To analyze the component exist in the permeate stream using Hawlett Packard Agilent 6890N.
- (vii) To characterize and determine the structure and morphology of modified membrane using Nikon Microscopes and PHILIPS XL-40 Scanning Electron Microscopy (SEM).

REFERENCES

- Ahmad Fauzi Ismail. and David, L.I.B (2001).A review on the latest development of carbon membranes for gas separation. *Journal of Membrane Science*.**193**: 1-18.
- Ahmad Fauzi Ismail. and David, L.I.B (2003).Future direction of R&D in carbon membranes for gas separations. *Membrane Technology*. **April**. :4-8.
- Auriol, A and Tritten, D. (1973). *A process for the manufacture of porous filter supports*. French Patent, 2,463,636”.
- Ash.R, Barrer.M.R, Lowson.R.T (1973). Transport of single gases and binary mixtures in microporous carbon membrane. *Journal of Membrane Science*. **1**: 17
- Barrer, M.R. (1939). Permeation, Solution and Diffusion of Gases in Organic Polymers. *Trans. Faraday Society*. **35**: 628
- Barrer, M.R., Ash.R and Sharma, P. (1976). Sorption and flow of carbon dioxide and some hydrocarbons in microporous carbon membrane. *Journal of Chemical Society Faraday Transional*. **69**: 2166-2172
- Bhave, R. R.(1991) *Inorganic Membranes, Synthesis, Characteristics and Applications*. Van Nostrand Reinhold.
- Boddeker, K.W (1995).Commentary: Tracing membrane science. *Journal of Membrane Science*. **100**: 65-68.
- Bottino, A., Cannapelli, G. and Munari, S. (1986). Factors effecting the structure and properties of asymmetric polymer membranes. In: *Membrane and Membrane Process*. Plenum Press. 163-178

- Bruschke, H.E.A (1995). Industrial Application of Membrane Separation Process. *Pure and Applied Chemistry*. **67**: 993-1002.
- Breck, D.W. (1974). *Zeolite Molecular Sieves*. New York. John Wiley
- Centeno, T. A. and Fuertas, A. B. (1999). Supported carbon molecular sieve membranes based on phenolic resin. *Journal of Membrane Science*. **160**: 201-211.
- Centeno, T. A. and Fuertas, A. B. (2000). Carbon molecular sieve gas separation membranes based on poly(vinyl chloride-co-vinyl chloride) *Carbon* **38**: 1067-1073.
- Centeno, T. A., Vilas, J. L. and Fuertas, A. B. (2004). Effects of phenolic resin pyrolysis conditions on carbon membrane performance for gas separation. *Journal of Membrane Science* **228**: 45-54.
- Changhai Liang, , Guangyan Cha and Shucai Gua. (1999). Carbon membrane for gas separation derived from coal tar pitch. *Carbon*. **37**: 1391-1397
- Clausi, D.T., Mckelvey, S.A and Koros, W. J. (1999). Characterization of Substructure Resistance in Asymmetric Gas Separation Membranes. *Journal of Membrane Science*. **160**: 51-64
- Cooper, C.A. and Lin, Y. S. (2002). Microstructural and gas separation properties of CVD modified mesoporous γ - alumina membranes. *Journal of Membrane Science*. **195**: 31-50
- Cowper, C. J. and DeRose, A. J. "The Analysis Of Gases By Chromatography". Pergamon Series in Analytical Series Volume **7**.
- Deraquin, B.V and Levi, S. M. (1964). *The Physical Chemistry of Coating Thin Films on a Moving Support*. The Focal Press London
- Doshi, J.K (1987). *Enhanced Gas Separation Process* (U.S Patent 4,690,695)

- Fick, A.(1995). On Liquid Diffusion. *Journal of Membrane Science*.**100**:33-38.
- Foley, H. C., Lafyatis, D.S. and Jeannie Tung. (1991).Poly (furfuryl alcohol)-Derived Carbon Molecular Sieve: Dependence of Adsorptive Properties on Carbonization Temperature, Time and Poly (ethylene glycol) Additives. *Industrial Engineering and Chemical Research*. **30**: 865-873.
- Foley, H.C. and Acharya, M. (1999). Spray coating of nanoporous carbon membrane for air separation. *Journal of Membrane Science*.**161**:1-5.
- Foley, H. C. and Shiflett, M.B (2000). On the preparation of supported carbon membranes. *Journal of Membrane Science*.**179**: 275-282.
- Fuertas, A. B. (1998). Preparation of Supported Asymmetric Carbon Molecular Sieve Membranes. *Journal of Membrane Science*.**144**: 105-111.
- Fuertas, A. B. and Centeno, T. A. (1999). Preparation of supported carbon molecular sieve membranes. *Carbon*.**37**: 679-684
- Fuertas, A. B. (2000). Adsorption selective carbon membrane for gas separation. *Journal of Membrane Science*.**177**: 9-16.
- Fuertas, A. B. (2001). Effects of air oxidation on gas separation properties of adsorption selective carbon membranes. *Carbon*.**39**: 697-706.
- Fuertas, A. B. (2001). Preparation and characterization of adsorption selective carbon membrane for gas separation. *Adsorption*. **7**: 117-129.
- Gantzel, P. K. and Mertin, U (1970). Gas Separations with High Flux Cellulose Acetate Membranes. *Ind. Eng. Chem. Process Des. Develop.* **Vol 2**: 331-332
- Geankoplis, C. J. (1993). *Transport Process and Unit Operations*. 3rd Ed. Singapore: Prentice Hall International Editions.

- Geizler, V. C. and Koros, W. J (1996). Effect of Polyimide Pyrolysis Conditions on Carbon Molecular Sieve membrane Properties. *Industrial Engineering and Chemical Research*. **37**: 2999-3003.
- Ghazali, M.N.W. (1997). *Pervaporation Dehydration of Isopropanol-Water Systems Using Chitosan Membranes*:University of Waterloo. Ph.D. Thesis.
- Graham, T. (1866). On the Absorption and Dialytic Separation of Gases by Colloid Septa. Part I. Action of a Septum of Caoutchou. *Philos. Mag.* **32**: 401-420.
- Graham, T. (1995). On the law of diffusion of gases. *Journal of Membrane Science*.**100**: 17-21.
- Halil Kalircilar and Ali Culfaz. (2002) "Role of water content of clear synthesis solutions on the thickness of silicate layers grown on porous α -alumina tube" *Microporous and Mesoporous Material*. **52**. 39-54.
- Hatori, H., Yamada, H., Shiraishi, H., Nakama, H. and Yoshitomo, S. (1992). Carbon molecular sieve from polyimide. *Carbon*. **30**: 719-720
- Hatori, H., Yamada, H. and Shiraishi, H. (1992). Preparation of microporous carbon membrane from phase inversion membrane. *Journal of Applied Polymer Science*. **57**: 871-876
- Hayashi, J. Mizuta, Yamamoto, M, Kasubake, K and Morooka, S. (1996). Separation of ethane/ethylene and propane/propylene systems with carbonized BPDA-pp' ODA polyimide membranes. *Industrial Engineering Chemical Research*. **35**: 4176-4181
- Hensema, E.R. and C.A Smolders. (1990). *Latest developments in membrane technology for gas and vapour separation*. Process Technology Proceedings, Volume **8**. Elsevier Science Publishers.

- Hong, N.C.F. (2004). *Preparation of carbon molecular sieves membranes on porous substrate*. (U.S Patent 6,730,364)
- Jintong Li, Shichang Wang, Kazukiyo Nagai, Tsutomu Nakagawa and Albert W-H Mau (1998). Effect of polyethyleneglycol (PEG) on gas permeabilities in cellulose acetate (CA) blend membranes. *Journal of Membrane Science*. **138**: 143-152.
- Jones, C. W. and Koros, W. J. (1995). Characterization of Ultramicroporous Carbon Membranes with Humidified Feeds. *Industrial Engineering and Chemical Research*. **34**: 158-163.
- Jones, C. W. and Koros, W. J. (1995). Carbon composite membranes; A Solution to Adverse Humidity Effects. *Industrial Engineering and Chemical Research* **34**: 164-167.
- Jyh-Jeng Shieh, Tai-Sung Chung, Rong Wang, Srivinasan, M.P. and Paul, D.R. (2001). Gas separation performance of poly (4-vinylpyridine) /polyetherimide composite hollow fibers. *Journal of Membrane Science*. **182**: 111-123.
- Katsaros, F. K., Steriotis, T. A., Stubos, A. K., Mitropoulos, A., Kanellopoulos, N.K. and Tennison, S. (1997). High pressure gas permeability of microporous carbon membranes. *Microporous Material*. **8**: 171-176.
- Keizer, K. and Verweij, H. (1996). "Progress in inorganic membranes" *Chemical Technology* **37**
- Kesting, R.E. and Fritzche, A. K. (1993). *Polymeric Gas Separations Membranes*. New York. John Wiley & Sons Inc.
- Koresh, J.E and Soffer, A. (1980). Study of molecular sieve carbons: Part 1, Gradual pore opening and mechanism of molecular sieving. *Journal Chemical Society Faraday Trans*. **76**: 2457-2469.

- Koros, W.J and Chern, R.T.(1987). Separation of Gases Mixtures Using Polymer Membranes. In: *Handbook of Separation Process Technology*. New York Wiley-Interscience.
- Koros, W. J. (1994). *Composite Carbon Fluid Separation Membranes* (U.S Patent 5,288,304)
- Koros,W.J and Mahajan, R. (2000). Pushing the limits on possibilities on large scale gas separation: which strategies. *Journal of Membrane Science* **175**: 181-196.
- Koros, W.J. (2003). *Carbon Molecular Sieves and Methods for Making the Same* (U.S Patent 6,562,110)
- Kurdi, J. and Trembly, A. Y.(1999). Preparation of Defect Free Asymmetric Membranes for Gas Separations. *Journal of Applied Polymer Science*. **73**: 1471-1482.
- Kulprathipanja et al (1988). *Separation of Fluids by Means of Mixed Matrix Membranes*. (U.S Patent 4,740,219)
- Kyotani, T. (2000). Control of pore structure in carbon. *Carbon* .**38**: 269-286
- Lafyatis, D. S., Tung, J and Foley, H. C.(1991).Poly(furfuryl alcohol)-Derived Carbon Molecular Sieve: Dependence of Adsorptive properties on Carbonization Temperature, Time and poly(ethylene glycol) Additives. *Industrial Engineering and Chemical Research*. **37**: 2999-3003
- Kusabake, K., Yamamoto, M and Marooka, S (1998). Gas permeation and micropore structure of carbon molecular sieving membranes modified by oxidation. *Journal of Membrane Science*.**149**: 59-67.
- Mattson, J. S. and Mark H. B.(1971). *Activated Carbon* New York: Marcel Dekker,

- Menendez, I. and Fuertas, A. B.(2001). Aging of carbon membrane under different environment. *Carbon* .**39**: 733-740.
- Mitchell, J.K (1831). On the Penetrative of Fluids. *Royal Institution Journal*. **2**. 101-118.
- Misra, R., Barker, A. J. and East, J.(2002). Controlled drying to enhance properties of technical ceramics. *Chemical Engineering Journal* .**86**: 111-116
- Mulder, M (1991). *Basic Principle of Membrane Technology*. Netherlands. Kluwer Academic Publisher.
- Murphy, M.K., Beaver, E.R. and A.W. Rice. (1989). Post-treatment of asymmetric membranes for gas application. *Membrane Separations in Chemical Engineering*. **85**: 34-40.
- Odani, H. and Masuda, T. (1992). Design of Polymers Membranes for Gas Separation. In: Toshima, N. *Polymers for Gas Separation*. New York: VCH Publishers Inc. 107-116.
- Ogawa, M. and Nakano, Y. (2000). Separation of CO₂/CH₄ through carbonized membrane prepared by gel modification. *Journal of Membrane Science*. **173**: 123-132
- Patel, N., Keijiokabe and Oya, A.(2002). Designing carbon materials with unique shapes using polymer blending and coating technique. *Carbon* .**40**: 315-320
- Pinnau, I. and Koros, W.J. (1992). Gas Permeation Properties of Asymmetric Polycarbonate, Polyestercarbonate and Flourinated Polyimide Membranes Prepared by the Generalized Dry-Wet Phase Inversion Process. *Journal of Applied Polymer Science*. **71**: 81-96.
- Puri,P.S. (1996). Gas separation membranes current status. *La Chimica e Industria*. **78**: 815

- Raman, N. K. and Brinker, C. J. (1995) "Organic template approach to molecular sieving silica membranes". *Journal of Membrane Science*. **105**: 273-279.
- Rauntenbach, R., Struck, A., Melin, T., Rooks, M.F.M. Impact of operating pressure on the permeance of hollow fiber gas separation membranes. *Journal of Membrane Science*. **169**: 217-223.
- Rao, M.B (1992). *Gas Separation by Adsorbent Membranes*. (U.S Patent 5,104,425)
- Rao, M.B. and Sircar, S. (1993). Nanoporous carbon membrane for separation of gaseous mixture by selective surface flow. *Journal of Membrane Science*. **85**: 253-264
- Rao, M.B. and Sircar, S. (1996). Performance and pore characterization of nanoporous carbon membranes for separation of gas separation. *Journal of Membrane Science*. **110**: 109-118
- Reid, R.C.. and Breton, E. (1959). Water and ion flow across cellulosic membrane. *Journal of Applied Polymer Science*. **1**. 133-143.
- Reid, R.C, Praunitz, J.M. and Sherwood, T.K. (1997). *The Properties of Gases and Liquids*. New York. McGraw-Hill.
- Robeson, L.M (1991). Correlation Separation factor Versus Permeability for Polymeric Membranes. *Journal of Membrane Science*. **62**:165-185
- Robeson, L.M (1999). Polymer membranes for gas separation. *Current Opinion in Solid State and Materials Science for Gas Separation*. 549-552
- Shiflett, M. B. and Foley, H. C. (1999). Ultrasonic deposition of high selective nanoporous carbon membranes. *Science*. **285**: 1902-1905.

- Shiflett, M. B. and Foley, H. C. (2000). On the preparation of supported nanoporous carbon membranes. *Journal of Membrane Science*. **179**: 275-282.
- Shiflett, M. B (2002). *Synthesis, Characterization and Application of Nanoporous Carbon Membrane*. University of Delaware: Ph.D. Thesis.
- Singh, A. (1997). *Membrane Material with Enhanced Selectivity; an entropic interpretation*. University of Texas, Austin: Ph.D. Thesis.
- Soffer, A., Koresh, J.E. and Saggy, S. (1987). *Separation Device*. (U.S Patent 4,685,940)
- Soria, R. (1995). Overview on industrial membrane. *Catalyst Today* .**25**: 285.
- Stannet, V. (1955). The permeability of polymer films to gases – A simple relationship. *Journal of Polymer Science*. **16**: 89-91
- Stannet, V. (1968). Simple Gas. In: Crank, J. *Diffusion in Polymers*. New York. Academic Press.
- Steel, K. M. and Koros. W.J. (2003). Investigation of porosity of carbon materials and related effects on gas separation properties. *Carbon*. **41**: 253-266
- Stern. S. A (1972). Gas Permeation Process. In: Lacey, R.E. *Industrial Processing with Membranes*. Canada: John Wiley & Sons Inc. 279-303.
- Stern. S. A, Sen.S.K and Rao.A.K (1974). The permeations of gases through Symmetric and Asymmetric (Leob-type) Cellulose Acetate Membranes. *Journal Macromolecul Science-Physics* .**B10**: 507-528.
- Stern. S. A and Frisch. H.L (1983). Diffusion of small molecules in polymers. In: *CRC Critical Reviews in Solid State and Materials Science* Vol 11 No 2. 123-187

- Stern, S. A (1994). Polymers for Gas Separations: The Next Decade. *Journal of Membrane Science*.**94**: 1-65.
- Trick, K. A. and Sabila, T. E. (1995). Mechanisms of the pyrolysis of phenolic resin in a carbon/phenolic composite. *Carbon*. **33**: 719-720
- Ulhorn, R. J. R. and Huis, M.B.H.J in Veld, T., Keizer, K. and A.J. Burggraaf. (1990). Transport and separation of condensable gases with microporous ceramic membranes. *Process Technology Proceedings*. **8**: 491-497.
- Verma, S. K. and Walker, P. L. Jr (1992). Carbon molecular sieve with stable hydrophobic surface. *Carbon* **30**: 837-844.
- Verweij, H. and Renate, M. (1998). Improved Performance of Silica Membranes for Gas Separation. *Journal of Membrane Science*.**143**: 37-51.
- Vos, R. M., Maier, W. F. and Verweij, H.(1999). Hydrophobic silica membranes for gas separations. *Journal of Membrane Science*.**158**: 277-288
- Wang, D., Li, K., and Teo, W. K. (1995). Effects of temperature and pressure on gas permselection properties in asymmetric membranes. *Journal of Membrane Science*.**105**: 89-101
- Weber, W. F. and Waren, B (1986). Membranes Replacing Other Separation Technologies. *Chemical Engineering Progress*.**11**: 23-24
- Winston, W.S and Sirkar, K. K. (1992). Overview. In: Winston, W.S *Membrane Handbook*. New York. Van Nostrand Reinhold. 3 - 15.
- Weh, K., Noack, M., Sieber, I. and Caro, J. (2002). Permeation of single gases and gas mixtures through faujasite-type molecular sieve membranes. *Microporous and Mesoporous Material* .**54**: 27-36.

- Wessling, M (1993). *Relaxation Phenomena in Dense Gas Separation Membranes*. University of Waterloo. Ph.D Thesis.
- Xianshe Feng, Chuen Y. Pan, Ivory, J. and Ghosh, D. (1998). Integrated membrane/adsorption process for gas separation. *Chemical Engineering Science*. **53**: 181-196.
- Yang, R.T. (1987). *Gas Separation by Adsorption Process*. London. Imperial College Press.
- Yang, M., Crittenden, B. D., Perera, S. P., Moueddeb, H. and Dalmon, J. A. (1999). The hindering effect of adsorbed components on the permeation of non-adsorbing component through a microporous silicate membrane: the potential barrier theory. *Journal of Membrane Science*. **156**: 1-9.
- Yong, C., Fauda, A. E., and Matsura, T. (1989). Effect of drying condition on the performance and quality of synthetic membranes used for gas separations. *Membrane Separations in Chemical Engineering*. Volume **85**. 18-33.
- Zhau, W., Yoshino, M., Kita, H. and Okamoto, K. (2003). Preparation and gas permeation properties of carbon molecular sieve membranes based on sulfonated phenolic resin. *Journal of Membrane Science*. **217**: 55-67.
- Zoland, R. R. and Fleming, G.K. (1992). Definitions. In: Winston, W.S. and Sirkar, K.R. *Membrane Handbook*. New York: Van Nostrand Reinhold. 19-24.
- Zoland, R. R. and Fleming, G. K. (1992). Theory. In: Winston W.S and Sirkar, K.R. *Membrane Handbook*. New York: Van Nostrand Reinhold. 25-53
- Zoland, R. R. and Fleming, G. K. (1992). Design of Gas Permeation Systems. In: Winston, W.S and Sirkar, K. R. *Membrane Handbook*. New York: Van Nostrand Reinhold. 54-77.

Zoland, R. R. and Fleming, G. K. (1992). Applications. In: Winston, W.S and Sirkar, K. R. *Membrane Handbook*. New York: Van Nostrand Reinhold. 78-94.