Modelling and development of carbon molecular sieve membrane for gas separation

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**MODELLING AND DEVELOPMENT
OF CARBON MOLECULAR SIEVE
MEMBRANE FOR GAS SEPARATION**

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**SCHOOL OF
MECHANICAL AND AEROSPACE ENGINEERING**

2006

Modelling and Development of Carbon Molecular Sieve Membrane for Gas Separation

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ABSTRACT

The objective of the research project was to investigate the feasibility of preparing carbon molecular sieve membranes from Kapton® polyimide film. The effects of carbonisation parameters on the gas transport properties of the carbon membranes were studied using statistical analysis. Carbonisation temperature had the strongest influence on gas permeation through the carbon membranes. Both the carbonisation atmosphere and the thermal soak time had limited effects on the pore size of the carbon membranes. The heating rate did not have any influence on the development of the membrane structure during the carbonisation process. Nitrogen atmosphere coupled with lower final temperature resulted in the highest gas permeation rate. The final temperature had a greater effect on the membrane carbonised under nitrogen atmosphere rather than that under vacuum atmosphere. Lower carbonisation temperature coupled with longer thermal soak time would decrease the gas permeation rate. Vacuum atmosphere coupled with higher heating rate were advantageous to increase the gas permeation rate, while prolonged thermal soak time coupled with lower heating rate had the reverse effect.

The evolution of the structural and transport properties from polyimide to carbon membrane upon heat treatment was investigated. In the temperature range of 673-748 K, the heat-treated polyimide membranes showed similar X-ray diffraction patterns as that of the precursor and two minimum ideal separation factors for O₂/N₂ and CO₂/CH₄ were observed at 673 and 723 K. The structure variation was due to the change in the polyimide chain mobility and the variation of the concentration of charge transfer complexes. The membranes heat treated at 773 K showed appreciably high gas permeances due to the decomposition of the precursor and comparable ideal

selectivities to the samples processed at lower temperatures. Heat treatment at temperatures higher than 773 K resulted in amorphous carbon structure and increased molecular sieving properties.

Development of membrane structure and transport properties during carbonisation was studied. Most of the pores within the membrane were created during the early stages of carbonisation. Based on CO₂ adsorption (273 K), the membranes carbonised at 1073 K showed the highest characteristic energy for adsorption while the membranes carbonised at 1273 K had the highest micropore volume. The contribution of mesopores to the total pore volume significantly decreased with increasing carbonisation temperature. Increasing the carbonisation temperature from 823 to 1273 K under vacuum atmosphere, the gas permeation rate through the resulting carbon membranes firstly increased and reached a maximum value corresponding to 873 K and then apparently decreased. The membranes carbonised at 1073 K showed the highest O₂/N₂ selectivity of 11.46.

Carbonisation of the precursor was carried out under different atmospheres (vacuum, argon, helium and nitrogen) to investigate their influences on the membrane structure and transport properties. Having higher thermal conductivity than the other atmospheres, the helium atmosphere resulted in less significant thermal lag during the heat treatment. The real temperatures for the heat treatment under vacuum, argon, helium and nitrogen atmospheres were 818, 858, 875 and 863 K, respectively, for a programmed temperature of 873 K and 1027, 1049, 1072, and 1055 K, respectively, for a programmed temperature of 1073 K. The values of the apparent activation energy of the Kapton® film for pyrolysis carried out under argon, helium and nitrogen atmospheres were 395.01, 196.35 and 237.25 kJ/mol, respectively. Carbonisation

under vacuum resulted in the lowest in-plane size of the graphitic clusters and the lowest gas permeance. The membranes prepared under helium atmosphere had the highest BET area, total pore volume and micropore volume which decreased from 573.92 m²/g, 0.3363 cm³/g and 0.2167 cm³/g, respectively, to 359.61 m²/g, 0.1856 cm³/g and 0.1525 cm³/g, respectively, with increasing carbonisation temperature from 873 K to 1073K.

The carbon membranes obtained from the Kapton® films with different thicknesses showed different pore structure and gas permeation properties. The interplanar spacing within the amorphous carbon membrane increased with increasing precursor thickness from 7.6 to 25.4 µm but decreased with further increases in the precursor thickness of up to 127 µm after reaching a maximum value of 25.4 µm. The carbon membranes obtained from Kapton® films with thicknesses of 7.6, 12.7 and 25.4 µm had similar micropore volumes while the samples obtained from Kapton® films with thicknesses of 50.8 and 127 µm had lower micropore volumes. The carbon membrane with a precursor thickness of 12.7 µm showed the lowest time-lag of 17 min as determined by CO₂ permeation and the highest CO₂ and He permeances than the other membrane samples.

The pyrolysis kinetics of Kapton® polyimide 100HN was studied. Three different approaches including reaction mechanism fitting, analytical model fitting and iso-conversional method were used for the analyses of the thermogravimetric data. Reaction mechanism fitting was found to be not applicable for non-isothermal pyrolysis. Isoconversional method showed the dependence of the apparent activation energy on the degree of conversion but it could not give enough information for the study of pyrolysis kinetics. The mathematical treatment of the experimental data using

different analytical models produced different results. A new analytical model was proposed in which the kinetic parameters for the pyrolysis could be obtained. The predicted TG curve using the kinetic parameters from the proposed model matched the experimental thermogravimetric data very well for a wide range of conversion, indicating its applicability for the study of pyrolysis kinetics.

Theoretical studies of the diffusion of nonadsorbable gases including O₂, N₂ and CH₄ were carried out based on the slit-shaped carbon pore model. The upper limit of the gas permeance through the membranes occurred at a characteristic energy of $\Delta E_{gas} = 0$ kJ/mol as determined by Knudsen diffusion mechanism. The absolute value of the potential energy decreased sharply with increasing pore dimension. For pores smaller than 6 Å, the potential energy for all the gases studied was weak near the pore wall but increased near the centre of the pore due to the overlapping of the fluid-solid interaction. For diffusion through the membrane pore having the same pore diameter, the absolute values for the potential energy were in the following order: O₂<N₂<CH₄. The theoretical O₂ permeances were consistent with the experimental results for narrow pores and the theoretical N₂ and CH₄ permeances showed excellent consistence with experimental values.

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LIST OF SYMBOLS

a	Factor for the fractional factorial design of experiment The number of heating rate for isoconversional method (Chapter 4)	
a_0	Interplanar distance within graphite	[Å]
a_{C-C}	In-plane nearest neighbouring distance within graphite	[Å]
A	Factor for the fractional factorial design of experiment Sorption potential (Chapter 8)	[kJ/mol]
A_0	Pre-exponential factor	[min ⁻¹]
$A1$	Mapel unimolecular law	
$A2$	Avrami-Erofe'ev equation	
$A3$	Avrami-Erofe'ev equation	
$A4$	Avrami-Erofe'ev equation	
A_m	Surface area of the membrane	[m ²]
b	Factor for the fractional factorial design of experiment The number of heating rate for isoconversional method (Chapter 4)	
B	Factor for the fractional factorial design of experiment Molecule mobility (Chapter 8)	[mol·m ² /(J·s)]
c	Factor for the fractional factorial design of experiment Concentration (Chapter 8)	[mol/m ³]
C	Factor for the fractional factorial design of experiment	
C_a	Adsorbed phase concentration	[mol/m ³]
C_g	Gas phase concentration	[mol/m ³]
C_T	Total concentration within the membrane	[mol/m ³]
CV	Coefficient of variation	
$C(\lambda)$	Constant related to the wave length of the laser	[nm]
d	Factor for the fractional factorial design of experiment (Chapter 6) Interplanar spacing of the (002) plane	[Å]

d_n	Pore neck diameter	[m]
d_p	Pore size	[m]
D	Factor for the fractional factorial design of experiment (Chapter 4)	
	Diffusion coefficient	[m ² /s]
	Density conversion factor (Appendix B)	[cm ³ /cm ³]
$D1$	Parabolic law	
$D2$	Valensi equation	
$D3$	Jander equation	
$D4$	Brounshtein-Ginstling equation	
D_{ads}	Diffusion coefficient in the adsorbed phase	[m ² /s]
D_c	Corrected diffusion coefficient	[m ² /s]
$D_{c,ads}$	Corrected diffusivity in the adsorbed phase	[m ² /s]
$D_{c,gas}$	Corrected diffusivity in the gas phase	[m ² /s]
D_F	Fickian diffusivity	[m ² /s]
D_{gas}	Diffusivity in the gas phase	[m ² /s]
D_i^0	Diffusivity of the pure gas through the pore	[m ² /s]
E	Apparent activation energy	[kJ/mol]
E_0	Characteristic energy of CO ₂ adsorption	[kJ/mol]
E_a	Apparent activation energy corresponding to a conversion of α	[kJ/mol]
E_j	Apparent activation energy determined by a certain reaction model	[kJ/mol]
ΔE	Characteristic energy of diffusion	[kJ/mol]
ΔE_{ads}	Apparent activation energy of diffusion in the adsorbed phase	[kJ/mol]
ΔE_{gas}	Apparent activation energy of diffusion in the gas phase	[kJ/mol]
f	A function of time t and independent of variable y	
$f(H)$	Total surface area or volume of pores of size H in the sample	[cm ² (g·cm)] or [cm ³ /(g·cm)]

$f_{hs}[\rho(r)]$	Helmholtz free energy density of a uniform hard-sphere fluid	[J]
$f(\alpha)$	A function describing the dependence of the reaction rate on the extent of reaction	
$F[\rho(r)]$	Helmholtz free energy expressed as functional of molecular density distribution	[J]
$F_{hs}[\rho(r')]$	Helmholtz free energy representing hard sphere repulsive force	[J]
$g(\alpha)$	Integral form of rate equation	[min ⁻¹]
$g_j(\alpha)$	Integral form of rate equation corresponding to a certain reaction model	[min ⁻¹]
h	Step size in the 4 th order Runge-Kutta method	[s]
H	C centre-C centre separation across the pore	[Å]
	Pore size (Appendix A)	[Å]
i	Type of gas species (Chapters 1 and 3)	
	Number of temperature for the isothermal pyrolysis (Chapter 4)	
	Non-negative integers (Chapter 6)	
$I(E,T)$	Temperature integral	
I	Defining relation for the fractional factorial design of experiment	
I_D	Intensity of the D-peak	[arb. Units]
I_G	Intensity of the G-peak	[arb. Units]
j	Type of gas species (Chapters 1 and 3)	
	Type of reaction mechanism (Chapter 4)	
	Non-negative integers (Chapter 8)	
J	Transmembrane flux of the penetrant	[mol/s]
J_i	Steady-state flow rate of component i through the membrane	[mol/s]
J_i^0	The molar flow rate of the pure gas	[mol/s]
J_s	Tran membrane flux in straight pores	[mol/s]
k	Rate constant	[min ⁻¹]
$k(T)$	Temperature-dependent rate constant	[min ⁻¹]
k_0	Pre-exponential factor	[min ⁻¹]

k_1	Parameter used in the 4 th order Runge-Kutta method	
k_2	Parameter used in the 4 th order Runge-Kutta method	
k_3	Parameter used in the 4 th order Runge-Kutta method	
k_4	Parameter used in the 4 th order Runge-Kutta method	
$k_j(T)$	Temperature-dependent rate constant determined by a certain reaction model	[min ⁻¹]
$k_j(T_i)$	Temperature-dependent rate constant determined by a certain reaction model for isothermal pyrolysis	[min ⁻¹]
l	Thickness of the membrane	[m]
	Number of step to solve the differential equation using the 4 th order Runge-Kutta method (Chapter 4)	
l_A	Linear combinations of the observations to estimate the effect of parameter A	
l_{AB}	Linear combinations of the observations to estimate the two-factor interaction of A and B	
l_{AC}	Linear combinations of the observations to estimate the two-factor interaction of A and C	
l_{AD}	Linear combinations of the observations to estimate the two-factor interaction of A and D	
l_B	Linear combinations of the observations to estimate the effect of parameter B	
l_C	Linear combinations of the observations to estimate the effect of parameter C	
l_D	Linear combinations of the observations to estimate the effect of parameter D	
L_a	In-plane size of the graphitic clusters	[nm]
m	Refers to the property at maximum reaction rate	
m_0	The initial weight of the sample	[g]
m_f	The final weight of the sample	[g]
m_t	Actual weight of the sample at time t	[g]
M	Molecular weight of the adsorptive	[g]
n	Reaction order	
	Order of reflection (Chapter 3)	
	Number of layers of carbon atoms (Chapter 8)	

N	The amount of observations	
p	Pressure	[mmHg]
p_0	Saturation vapour pressure of saturated adsorbate	[mmHg]
p_{st}	Significance level for the statistical analysis	
$p(x)$	Integral of $\exp(-x)/(-x^2)$	
Δp	Pressure differential across a membrane	[Pa]
P	Gas permeance	[mol/(m ² ·s·Pa)]
P_i	Gas permeance of gas i	[mol/(m ² ·s·Pa)]
P_j	Gas permeance of gas j	[mol/(m ² ·s·Pa)]
P_H^0	Constant pressure maintained at the feed side of the membrane	[Pa]
$\bar{P}^0$	Pure gas permeability	[mol/(m·s·Pa)]
$\bar{P}_i^0$	Permeability of gas i	[mol/(m·s·Pa)]
$\bar{P}_j^0$	Permeability of gas j	[mol/(m·s·Pa)]
$\bar{P}_s^0$	Pure gas permeability through straight pores	[mol/(m·s·Pa)]
$P_L(t)$	Pressures on the permeate side of the membrane	[Pa]
P_L^*	Pressure before each test at the permeate side	[Pa]
$P_{SYS_1 I}$	System manifold pressure before I th equilibrium	[mmHg]
$P_{SYS_2 I}$	System manifold pressure after I th equilibrium	[mmHg]
P_{SAMI}	Sample pressure after I th equilibrium	[mmHg]
P_{STD}	Standard pressure	[mmHg]
$q(p, H)$	Quantity adsorbed per unit of area or volume at pressure p in an ideal pore of size H .	[cm ³ /cm ²] or [cm ³ /cm ³]
Q	Gas flux rate	[cm ³ /s]
Q_L^I	Steady-state flow rate at the low-pressure exit end	[mol/s]
$Q(p)$	Total quantity adsorbed per unit of weight at pressure p	[cm ³ /g]
r	A dependent variable	
	The molecule-molecule separation (Chapter 8 and Appendix A)	[Å]

r'	The molecule-molecule separation	[Å]
r_k	The Kelvin pore radius	[m]
R	Gas constant	[J/(mol·K)]
$R1$	Phase boundary controlled equation: one dimensional movement	
$R2$	Phase boundary controlled equation: contracting area	
$R3$	Phase boundary controlled equation: contracting volume	
S	Standard deviation	
t	Time	[min]
t_l	Time-lag for gas permeation	[min]
t_α	Time needed to reach a conversion α	[min]
t^*	Time required to obtain a constant-pressure flow at the high-pressure side of the membrane	[s]
T	Temperature	[K]
T_0	Temperature corresponding to a conversion of zero	[K]
T'	Average value of the experimental temperatures	[K]
T_{ABT}	Analysis bath temperature	[K]
T_i	Temperature of the isothermal pyrolysis	[K]
T_l	Calculated temperature using the 4 th order Runge-Kutta method	[K]
T_m	Temperature corresponding to the maximum weight-loss rate	[K]
T_{ref}	Reference temperature	[K]
T_{SYS}	System manifold temperature	[K]
$T_{\alpha,y}$	Temperature corresponding to a conversion of α at different heating rates	[K]
$\bar{u}$	Molecular mean velocity	[m/s]
$u_{ff}(r)/k$	LJ fluid-fluid interaction	[K]
u_{pore}/k	Interaction of a molecule with slit-shaped pore wall	[K]
u_r	Lennard-Jones 6-12 potential	[J/mol]

$u_{sf}(z)/k$	Interaction of a molecule with one pore wall	[K]
U_r	Uncertainty of variable r	
$U_{P_{SAMI}}$	Uncertainty of the measurement of sample pressure	[mmHg]
$U_{P_{SYS1}}$	Uncertainty of the measurement of system manifold pressure before I th equilibrium	[mmHg]
$U_{P_{SYS2}}$	Uncertainty of the measurement of system manifold pressure after I th equilibrium	[mmHg]
$U_{T_{SYS}}$	Uncertainty of the measurement of system manifold temperature	[K]
$U_{W_{SAM}}$	Uncertainty of weighing the sample	[g]
$U(r, r')$	Summation of the attractive part of the pairwise potential of a molecule at r with all other fluid molecules in the system at r'	[J/mol]
V	Pore volume determined by DR method	[cm ³ /g]
V_0	Limiting pore volume determined by DR method	[cm ³ /g]
V_{CUM}	Final pore volume of a sample	[cm ³ /g]
V_{CUMI}	Cumulative pore volume corresponding to the I th equilibrium point	[cm ³ /g]
V_{FC}	Volume of cold free space	[cm ³]
V_{FW}	Volume of warm free space	[cm ³]
V_I	Amount of gas adsorbed per gram of sample after I th equilibrium point	[cm ³ /g]
V_L	Volume in the permeate side of the apparatus	[m ³]
V_{LOW}	Lower manifold volume	[cm ³]
V_m	Molar volume of the adsorbate	[m ³ /mol]
$V(r)$	Potential acting on a molecule at r	[J/mol]
V_t	Total pore volume	[cm ³ /g]
$W[\rho(r)]$	Grand potential energy	[J]
W_{SAM}	Weight of sample	[g]
x	Ea/RT	
x_i	Volume fraction of component i at the feed side	

	Coded variables representing the parameters of the experiment (Chapter 6)	
	Value of the observation (Chapter 7)	
x_j	Volume fraction of component j at the feed side	
x_I	An independent variable	
$\bar{x}$	The mean of the observations	
y	Variable in the differential equation	
	Number of heating rates (Chapter 4)	
y_i	Volume fraction of component i at the permeate side	
y_j	Volume fraction of component j at the permeate side	
	Variable in the differential equation (Chapter 4)	
y_{iL}^I	Steady-state mole fraction of component i in that stream	
Y	Regression model used to analyse the effects	
z	Number of data items (in Chapter 4)	
	Distance between a fluid particle and a pore wall	[Å]

Greek Letters

α	Degree of conversion	
$\alpha_{i/j}$	Permselectivity (separation factor) for the component i over j	
α_A	Polarizability of gas molecule	[cm ³]
$\alpha_{\text{cal}}(T_j)$	Predicted degree of conversion at a temperature T_j	
$\alpha_{\text{exp}}(T_j)$	Experimental degree of conversion at a temperature T_j	
α_m	Conversion corresponding to the maximum weight-loss rate	
α_{st}	Type I error for statistical analysis	
β	Heating rate	[K/min]
	Affinity coefficient (Chapter 8)	
β_0	Regression constant (Chapter 6)	

β_1	Regression coefficients related to factor <i>A</i> (Chapter 6)	
β_2	Regression coefficients related to factor <i>B</i> (Chapter 6)	
β_3	Regression coefficients related to factor <i>C</i> (Chapter 6)	
β_4	Regression coefficients related to factor <i>D</i> (Chapter 6)	
β_{12}	Regression coefficients related to interaction <i>AB</i> (Chapter 6)	
β_{13}	Regression coefficients related to interaction <i>AC</i> (Chapter 6)	
β_{14}	Regression coefficients related to interaction <i>AD</i> (Chapter 6)	
β_y	Different heating rates	[K/min]
ε	Porosity	[cm ³ /cm ³]
ε/k_B	LJ interaction well depth	[K]
ε_{ff}/k_B	Fluid-fluid potential well depth	[K]
ε_M	Volume of pores in the membrane per unit volume of the membrane	[cm ³ /cm ³]
ε_{NN}/k_B	Interaction well depth between the adsorptive molecules	[K]
ε_{sf}/k_B	Solid-fluid interaction well depth	[K]
ε_{ss}/k_B	Solid-solid interaction well depth	[K]
γ	Surface tension of the adsorbate	[N/m]
λ	Wave length	[Å]
	Thermal conductivity (Chapter 7)	[W/(m·K)]
	Jump length of gas molecules within membrane pores (Chapter 8)	[m]
λ_{Ar}	Thermal conductivity of Ar	[W/(m·K)]
λ_{He}	Thermal conductivity of He	[W/(m·K)]
λ_{N_2}	Thermal conductivity of N ₂	[W/(m·K)]
μ	Chemical potential of the penetrant	[J/mol]
θ	Contact angle with which the adsorbate meets with the pore wall (Chapter 2)	[degree]
	Diffraction angle	[degree]
ρ	Density	[kg/m ³]

ρ_a	Surface number density of carbon atoms in a graphite layer	$[\text{nm}^{-2}]$
ρ_E	Energetical probability	
ρ_g	Geometrical probability	
ρ_p	Apparent density	$[\text{kg/m}^3]$
ρ_t	True density	$[\text{kg/m}^3]$
ρ_λ	Probability that the gas molecule makes a jump whose length is λ	
$\rho(r)$	Equilibrium density	$[\text{mol/cm}^3]$
σ	Gas solid nuclear separation at zero interaction energy	$[\text{\AA}]$
σ_{ff}	Fluid-fluid collision diameter	$[\text{\AA}]$
σ_{NN}	Diameter of the adsorptive molecule	$[\text{\AA}]$
σ_{sf}	Solid-fluid collision diameter	$[\text{\AA}]$
σ_{ss}	Solid-solid collision diameter	$[\text{\AA}]$
τ	Tortuosity	
Δ	Internuclear distance of parallel carbon layers	$[\text{nm}]$

CHAPTER 1

INTRODUCTION

1.1 MEMBRANE-BASED GAS SEPARATION

The ever-increasing amounts of energy consumed and the negative effects in separation processes in industry have motivated researchers to carry out intensive studies for energy efficient technologies (Sedigh *et al.*, 1999). Membrane-based separation is a promising technology to meet this challenge. Considered to be a permselective barrier existing between two homogenous phases, practical gas separation membrane needs to be highly permeable to some of the mixture components while significantly rejecting the other components. Although the criteria for evaluating membranes for a given application are complex, (1) durability and (2) mechanical integrity at operating conditions as well as (3) permselectivity and (4) permeability are the basic factors that should be balanced against cost in all cases (Koros and Mahajan, 2000). Permeability is an inherent property of membrane materials indicating the productivity achievable, while permselectivity governs the purity of the product obtained. Various types of gas molecules can be discriminated due to differences in size, shape or chemical structure. Transport of gas mixtures through a membrane and their separation takes place when a driving force is applied to the components in the feed stream, separating into two streams namely retentate and permeate. The driving force in a membrane process is the difference in the chemical potential. Polymeric materials have been commonly used as membrane materials and other materials such as ceramic, metal, zeolite and carbon also exist.

Membrane technologies have been studied and applied for several gas separations

(Damle *et al.*, 1994; Bhavé, 1991; Jones and Koros, 1994 (b); Koros and Mahajan, 2000) such as:

- (i) O₂ or N₂ enrichment of air,
- (ii) hydrogen recovery and purification from various hydrocarbons, purge streams in ammonia and raw coal gasification gas,
- (iii) removal of CO₂ from flue gas,
- (iv) acid gas (CO₂ and H₂S) removal from natural gas,
- (v) olefin-paraffin separations, and
- (vi) dehydration of air or natural gas.

1.2 MEMBRANE MODE OF OPERATION

Membrane material is commonly used in a modular configuration where a gas mixture under compression is fed to the upstream surface. The downstream side is always maintained at a lower pressure or vacuum. Typical examples for membrane separation modules are shown in Figure 1.1. Pressure difference between the upstream and downstream of the membrane sets up a concentration gradient across the thickness of the membrane, which acts as the driving force for gas diffusion. The components that diffuse faster easily pass through the membrane and can be collected from the downstream side as permeate, while other components continue to travel down and leave as retentate on the high pressure feed side. Permeability is defined as the transport flux per unit trans-membrane driving force per unit time per membrane area:

$$J = PA_m \Delta p \quad (1.1)$$

where J is the flux rate (mol/s), P is the gas permeation rate (mol/m²·s·Pa), A_m is the surface area of the membrane (m²) and Δp is the pressure differential across the

membrane (Pa). The permselectivity (also known as the selectivity or separation factor) is a measurement of the ability of the membrane to separate the components in a mixture. It is commonly expressed as:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (1.2)$$

where i and j are two components in a given mixture.

Figure 1.1 Operation schematic of membrane modules: (a) for flat membranes and (b) for tubular or hollow fibre membranes

1.3 MEMBRANE MATERIALS

Gas separation membranes used and studied are mainly based on polymeric materials, including polycarbonates, polysulfones, polyimides, polypyrrolones, and polyarylates (Geiszler, 1997). In recent years, porous and nonporous glass, ceramic, zeolite, metal and carbon membranes have also received increasing interest. Nonporous polymeric membranes have been conventionally and chiefly used as solution-diffusion gas separation membranes. These membranes show, however, low

permselectivity and high sensitivity to temperature, which make them impractical for use in a number of industrial gas separations (Sedigh *et al.*, 1999). This limitation has motivated the development of dense metal and silica-based membranes as well as porous inorganic membranes. Ceramic membranes are particularly intriguing in molecular separations because they can be used to separate small molecules at higher temperatures and under harsher conditions as compared to polymeric membranes and display good mechanical strength. At the same time, ceramic membranes show limited selectivity and it is difficult to seal them into stainless steel modules because of different thermal expansions at high temperatures (Stevens and Rezac, 1998). Zeolites with well-defined micropores constitute an excellent material to produce gas separation membranes, but the preparation of zeolite membranes in a crack-free and continuous form has been demonstrated to be quite difficult (Centeno and Fuertes, 2000; Shiflett and Foley, 2000). Silica membranes, containing both inorganic silicon dioxide and organic silicone phases, are investigated for molecular separations and show high permselectivity for hydrogen over other molecules and can be used at high temperatures (Stevens and Rezac, 1998). The problem with silica-based membranes is that they show low separation factors with respect to those gas mixtures consisting of components with similar molecular sizes (Shiflett and Foley, 2000). Dense metal membranes, which are used mainly for the separation of hydrogen from various gas mixtures, show relative poor mechanical stability (Maryam, 2000). Additionally, these materials are mechanically weak and only suitable for use in supported form (Hayashi *et al.*, 1997; Shiflett *et al.*, 2000).

Carbon molecular sieve membranes (CMSMs) are prepared by the pyrolysis/carbonisation of polymeric precursors. They have comparable or even higher permselectivity and permeation properties as well as thermal and chemical stability

than polymeric and other microporous inorganic membranes. Carbon molecular sieve membranes have been intensively studied for the past few years as a promising candidate for gas separations (Kusakabe *et al.*, 1998; Fuertes *et al.*, 1999). Carbon molecular sieve membranes are prepared by either (1) the carbonisation of preexisting polymeric substances (hollow fibres or thin polymeric films) or (2) the carbonisation of films deposited on macro- or mesoporous supports (carbon disks, ceramic plates or tubes, stainless steel tubes or alumina tubes) through brush-coating, spray-coating, dip-coating or ultrasonic deposition techniques (Suda and Haraya, 1995; Shiflett and Foley, 1999). Quite a large number of raw materials, including poly-furfuryl alcohol (PFA) (Chen and Yang, 1994; Wang *et al.*, 2000), biphenyl-tetracarboxylic dianhydride (BPDA), oxydianiline (ODA) (Hayashi *et al.*, 1995; Takeichi *et al.*, 2001), phenolic resin (PR) (Wang *et al.*, 1996; Centeno *et al.*, 2004;), polyetherimide (PEI) (Fuertes and Centeno, 1998b; Sedigh *et al.*, 2000), polyimide (Suda and Haraya, 1995; Okamoto *et al.*, 1999; Hatori *et al.*, 2004), coal tar pitch (Liang *et al.*, 1999), polyimide acid (Ogawa and Nakano, 1999), poly(vinylidene chloride-co-vinyl chloride) (PVDC-PVC) (Centeno and Fuertes, 2000), dimethylacetic amide (Petersen *et al.*, 1997), polyimide/polyvinylpyrrolidone (PVP) blend (Kim *et al.*, 2005), and copoly(4,4'-methylenebis (2,6-dimethyl)-2,2-bis(3,4-dicarboxylphenyl) hexafluoro propane/pyromellitic) diimide) (6FDA/PMDA-TMMDA) (Shao *et al.*, 2004) have been used as precursors. The pyrolysis/carbonisation, which is usually carried out at temperatures of 773-1273 K in vacuum or an inert atmosphere, removes most of the heteroatoms originally present in the polymeric macromolecules, leaving behind a stiff and cross-linked carbon matrix with amorphous porous structure created by the evolution of gaseous products generated during the reaction process.

1.4 RESEARCH OBJECTIVES AND SCOPE

The main objectives of this project are to develop effective carbon molecular sieve membranes from Kapton® polyimide films and study the evolution of pore structure and gas permeation properties of these membranes. The scope of work comprises the following areas:

1. To identify the effects of different carbonisation conditions on the carbon molecular sieve membranes.

Preparation of the carbon molecular sieve membranes would be carried out by pyrolysing Kapton® polyimide film 100HN. The influences of carbonisation parameters on the transport properties of the carbon membranes were studied using statistical analysis. The effects of the carbonisation atmosphere, the final temperature, the heating rate and the thermal soak time at the final temperature on the permeation rates of He, CO₂, O₂ and N₂ were examined.

2. To investigate the evolution of pore structure and gas permeation properties of the membranes during carbonisation.

Carbon molecular sieve membranes were prepared at different temperatures. The evolution of microporous structure as well as membrane transport properties with different carbonisation temperatures and different carbonisation atmospheres would be studied. CO₂ adsorption at 273 K and N₂ adsorption at 77 K were carried out to obtain the adsorption isotherms for the determination of pore volume and pore size distributions. Single gas permeation tests would be carried out to study the evolution of membrane transport properties. Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy and density measurement

were used to study the morphology of the carbon molecular sieve membranes. The separation properties of some membrane samples for O₂/N₂ were also studied.

3. To study the development of structure and gas permeation properties of the membrane material from polyimide to carbon.

Kapton® polyimide membrane was exposed to heat treatment at different temperatures ranging from 623 to 1073 K under nitrogen atmosphere. The structure change with heat-treatment temperature was studied using XRD, Raman spectroscopy, density measurement and N₂ adsorption at 77 K. The weight change during pyrolysis was evaluated through thermogravimetric (TG) analysis. The development of the transport properties from polyimide membrane to carbon membrane was characterised using single gas permeation measurements.

4. To study the pyrolysis kinetics of Kapton® polyimide films

A new analytical model was proposed for the study of pyrolysis kinetics. Isothermal and non-isothermal pyrolysis of Kapton® polyimide film 100HN were carried out in a thermogravimetric analyzer (TGA). The TG data were analysed using different methods and the applicability of each of them was evaluated. The kinetic study was to enhance the understanding of the reaction mechanism of the precursor pyrolysis and predict the pyrolytic conversion ratio at fixed temperature and/or time.

5. To study the permeation of nonadsorbable gases through the carbon membrane

The permeation of nonadsorbable gases (O₂, N₂ and CH₄) through carbon membrane was studied based on a regular slip-shaped pore model. The potential energy of the diffusion within the carbon pores with different sizes was

determined. The single gas permeation rates of these gases through the membrane pores were calculated.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The concept of carbon membrane can be dated back to 1970. Ash *et al.* (1970) produced microporous Graphon membranes through which the diffusion of helium was tested. Since then, many investigations have been carried out on carbon membranes for gas separation. Not only various polymeric materials, such as poly-furfuryl alcohol, biphenyl-tetracarboxylic dianhydride, oxydianiline, phenolic resin, polyimide, coal tar pitch and dimethylacetic amide have been used for preparing crack-free carbon membranes of high selectivity, but also a variety of techniques including ultrasonic deposition, dip coating, phase inversion and spin coating have been utilised. This chapter documents the background from which carbon membrane processing has progressed. In addition, applications and future directions of carbon membrane for gas separation are presented.

2.2 STRUCTURE OF CARBON

Carbon with trigonal sp^2 bonding can be classified into two different types of structures - graphite and turbostratic. Figures 2.1(a) and (b) show the structures of graphite and turbostratic carbon respectively. The crystal structure of graphite consists of layers in which the carbon atoms are arranged in an open honeycomb network, such that the A and B atoms on consecutive layers are on top of one another. The A' atoms in one plane are over the hexagon centres of the adjacent layers, and similarly are the B' atoms. This gives rise to an ABAB planar stacking arrangement, with an interplanar distance a_0 of 2.456 Å and an in-plane nearest neighbouring distance a_{C-C}

Figure 2.1 Structure of (a) graphite and (b) turbostratic carbon

of 1.421 Å. With respect to graphite, the tightly packed crystal structure can hardly allow for a significant permeation of gas molecules. By comparison, turbostratic carbon shows stacking disorder except for some defects in the planes. Weak disorder results in stacking faults that can lead to small increase in the interlayer distance. The

stacking of the individual graphited layers becomes uncorrelated when the interlayer spacing reaches a value of about $3.442\text{\AA}$, resulting in turbostratic carbon. Due to the occurrence of the imperfect stacking, gas molecules can permeate through the carbon. Carbon membranes obtained from the pyrolysis of polymeric material are believed to have such a turbostratic structure.

2.3 TRANSPORT MECHANISMS THROUGH CARBON MEMBRANES

Components in gas mixtures can be separated due to differences in their molecular mass, due to interaction with the carbon and due to their sizes based on the nature of pore structure in carbon membranes. There are mainly four different mechanisms: Knudsen diffusion, capillary condensation, molecular sieving and surface diffusion (selective adsorption), through which gas mixtures can be effectively separated. The four mechanisms are diagrammatically shown in Figure 2.2.

Knudsen diffusion

Capillary condensation

Molecular sieving

Surface diffusion

Figure 2.2 Mechanisms of mass transfer through carbon membranes

2.3.1 Knudsen Diffusion

When the pores have diameters approaching the mean free path dimensions of the molecules in the gas mixture, Knudsen diffusion (Knudsen flow) occurs (Bhave, 1991). These pores are small enough to preclude the gas phase flow by molecular diffusion. Through such a mechanism, the permeating species with different molecular weights collide more frequently with the wall than with other gas molecules, resulting in a selective separation in which the permeation rate of each component is inversely proportional to the square root of its molecular weight. The contribution of Knudsen diffusion is generally evident when the pore diameter measures approximately smaller than 1/10 that of the mean free path of the diffusing species. The selectivity of separation achieved by Knudsen diffusion is generally very low and not practical.

2.3.2 Capillary Condensation

When the diameter of the pores is larger than the largest molecular diameter of the components in the gas mixture and ranges up to 40-100 Å, capillary condensation occurs (Rao and Sircar, 1993b). At appropriate pressure and temperature, certain molecules in the gas mixture will condense within the pores by capillary condensation and flow through the pores as a condensed phase under a capillary pressure gradient across the membrane. The conditions for capillary condensation can be described by Kelvin equation:

$$\ln\left(\frac{p}{p_0}\right) = -\frac{2\gamma V_m \cos \theta}{RT r_k} \quad (2.1)$$

where γ is the surface tension of the adsorbate, V_m is the molar volume of the adsorbate, θ is the contact angle with which the adsorbate meets with the pore wall, and r_k is the Kelvin pore radius. Condensed components within the pores hinder the diffusion of non-condensing components and a selective separation is thus

accomplished. The extent of removal of a component from a gas mixture through this mechanism is often limited by the condensation partial pressure of the component and the pore size as well as the geometry of the membrane, even though a relative high separation factor can be achieved.

2.3.3 Molecular Sieving

Molecular sieving refers to the blocking of passage of gas molecules with certain size and shape and free passage of components with smaller size or different shape. Carbon membranes working through molecular sieving mechanism, named molecular sieving carbon membranes (MSCMs), often have finely distributed apertures that are slightly larger than certain component molecules and smaller than other molecules in the mixture, typically narrower than 4 Å. In the apertures, the interaction energy between the molecules and the carbon is theoretically comprised of both dispersive and repulsive forces. When the openings become small enough to around the size of diffusing molecules, the repulsive forces dominate and the molecules require certain activation energy to pass through the constriction. The larger is the size of a molecule, the higher is the activation energy as to specified pores, thus efficiently separating the gas components with only slight differences in size (Jones and Koros, 1994a). Molecular sieving carbon membranes have been proved to show high permeability and selectivity for gas mixtures such as O₂/N₂, CO₂/N₂, CO₂/CH₄, *etc* (Fuentes, 2000). Under some circumstances, molecular sieving carbon membranes may require operation at elevated temperatures for the purpose of achieving practically acceptable flux for the smaller components due to the resistance of the current membranes.

2.3.4 Surface Diffusion

Surface diffusion refers to the mechanism of gas molecules to be adsorbed on the pore surface and then transport through the pores along the surface. Carbon membranes dependent on this mechanism are named adsorption selective carbon membranes (ASCMs). Except for the requirement that gas molecules to be separated be adsorbed in a significant amount on the pore surface, the pore diameters of the membrane should be larger than the largest molecular diameter of the components in a gas mixture and smaller than about 2 to 5 times this diameter (typically in the range of 3-20 Å). As the adsorbed molecules accumulate more and more on the pore wall, the preferentially adsorbed component causes a difference in the surface concentration gradient and diffuses faster than the non-adsorbed ones under a pressure gradient. There is a hindrance effect resulting from the adsorbed components on the diffusion of non-adsorbed species through the void space in the pores for which the overall separation factor is increased. The separation factor is mainly controlled by the selectivity of adsorption between the components of the gas mixture on the pore surface and can be changed by regulating the pore size and surface chemistry. If all the components can be adsorbed, the relative strengths of adsorption will decide the selectivity. Based on the surface diffusion mechanism, larger or more polar molecules can be preferentially adsorbed rather than the smaller or less-polar molecules that are rejected at the high-pressure side of the membranes (Ash *et al.*, 1976; Bhawe, 1991). Generally, ASCMs have apertures wider than those of MSCMs. ASCMs are effective for the separation of non-adsorbable or weakly adsorbable gases (N₂, O₂, H₂, He, CH₄, *etc.*) from adsorbable gases (NH₃, SO₂, H₂S, hydrocarbons, *etc.*) (Fuertes *et al.*, 2001).

It is possible that more than one of these four mechanisms can act simultaneously due to the actual pore size distribution of the membrane and sizes of component molecules in the gas mixture as well as the operating pressure and temperature.

However, a single mechanism usually dominates and the resulted gas mixture separation is chiefly accomplished by means of this mechanism (Rao *et al.*, 1992).

2.4 CARBON MEMBRANES AND THEIR PROPERTIES

2.4.1 Morphology of Carbon Membranes

With respect to carbon membranes for gas separation, there are various types of classification depending upon different bases. Generally, carbon membranes can be divided into two categories: supported and unsupported membranes. Supported membranes have two different configurations: flat and tube; while unsupported carbon membranes consist of three configurations: flat (film), hollow fibre and capillary (Ismail and David, 2001). Carbon membranes for gas separation usually have pore diameters between 3 and 8 Å. According to the classification adopted by the International Union of Pure and Applied Chemistry, pores in this range are micropores (< 2 nm).

Figure 2.3 Morphology of carbon membranes

2.4.2 Pyrolysis

Carbon membranes are prepared from the pyrolysis of polymeric precursors. During the pyrolysis of a polymer, certain kinds of volatiles such as CO, CO₂, H₂, H₂O, HCN, CH₄, and NH₃ (depending on the polymer) as well as small amounts of typical less volatile byproducts benzene, toluene, phenol and other heavier molecules are produced due to the cleavage of ether bond, C-N bond, or imide ring *etc.* In the mean

while, isocyanate group, amino group, carbodiimide bond, or cyano group are developed and such reactions as hydrogen abstraction and intramolecular coupling occur, leading to a structure different from those of the polymer precursors (Inagaki *et al.*, 1991; Hatori *et al.*, 1996; Konno *et al.*, 2001; Ortelli *et al.*, 2001). Figure 2.4 shows the structural evolution of the pyrolysis process of polyimide (Suda and Haraya, 1997).

Figure 2.4 Pyrolysis process of Kapton polyimide membranes

A turbostratic structure is formed when carbon is obtained from the pyrolysis of polymeric materials, resulting in layer planes of graphite-like structure dispersed in the non-crystalline carbon. Gas molecules are commonly considered to diffuse through the imperfect voids in the turbostratic carbon. According to Suda and Haraya (1995, 1997), the two paths through which the gases can permeate are the cross-like voids of the amorphous region and the interlayer spacing of the graphite-like microcrystallines. The question of which path chiefly contributes to the molecular sieving effect has not been solved. With the increase of pyrolysis temperature, higher

crystallinity, density and a smaller interplanar spacing of the graphite layers of the carbon are formed, leading to higher gas permselectivities.

2.4.3 Preparation and Gas Separation Properties of Carbon Membranes

Carbon membranes are prepared by the pyrolysis of preexisting polymeric substrates (hollow fibres and self-supporting thin polymeric films) or polymeric films deposited on porous supports. Similar to polymer membranes, several configurations (shown in Figure 2.3) of carbon membranes have been developed. Correspondingly, typical techniques such as ultrasonic deposition, phase inversion, dip coating and spin coating have been used to prepare the polymeric precursors. Meso- or macroporous supports such as graphite disks, stainless steel tubes and alumina tubes have been utilised.

2.4.3.1 Tubular carbon membranes

Shiflett and his co-workers proposed a novel method called ultrasonic deposition to prepare mechanically robust and selective nanoporous carbon membranes with pore diameters of 4.5-5 Å (Shiflett and Foley, 1999, 2000, 2001; Shiflett *et al.*, 2000). An ultrasonic nozzle was used to achieve low momentum deposition, resulting in the precise control of coating 25-30 wt.% poly-furfuryl alcohol (PFA) in acetone on sintered stainless steel tubes. The nanoporous membranes carbonised between 423 and 873 K with hold times of 0-120 min showed permeances of $(0.0079-65) \times 10^{-10}$, $(0.106-136) \times 10^{-10}$, $(1.25-213) \times 10^{-10}$, $(1.38-409) \times 10^{-10}$ and $(2.48-5.23) \times 10^{-10}$ mol/(m²·s·Pa) for N₂, O₂, He, H₂ and N₂O respectively. The separation factors were 0.94-30.4 for O₂/N₂, 2.65-178 for He/N₂, 9.6-331 for H₂/N₂, and 13.5-17.3 for N₂O/N₂. The membranes carbonised in helium displayed permeances of two orders of magnitude higher than those carbonised in N₂. It was observed that adding zeolite or

titanium dioxide to the polymer solution could increase gas fluxes whilst maintaining high gas permselectivities.

Hayashi and his coworkers prepared pinhole-free and uniform carbon membranes from biphenyl-tetracarboxylic dianhydride (BPDA), oxydianiline (ODA) and diaminotoluene deposited on porous alumina tubes (Hayashi *et al.*, 1995, 1996, 1997; Yamamoto *et al.*, 1997). The mean pore size in these membranes decreased with increasing carbonisation temperature based on the increase of characteristic energy E for CO₂ sorption. Carbonisation at 1073 K increased the micropores of 0.33-0.40 nm and decreased those of 0.43-0.50 nm whilst carbonisation at 1173 K only decreased the micropores of 0.43-0.50 nm. Carbonisation temperatures lower than 773 K would hardly change the gas permeance but at 873-973 K, the permeance increased remarkably for all the penetrants and reached the maximum value when the carbonisation temperatures were between 923 K and 973 K. After modification with carbon deposits formed by pyrolysis of propylene at 923 K, the membranes showed permselectivities of 14 for O₂/N₂ and 73 for CO₂/N₂ at 308 K. Oxidation in air at 673 K led to the formation of oxygen-containing functional groups on the membrane surface and increased gas permeances without damaging the permselectivities. Post heat treatment at 873 K in an inert atmosphere could eliminate the functional groups, reduce the pore size and decrease the permeance of the oxidised membranes. (Yamamoto *et al.*, 1997; Kusakabe *et al.*, 1998).

Fuertes and his coworkers prepared adsorption selective carbon membranes by coating phenolic resin (PR) on tubular ceramic membranes (Fuertes, 2000; Centeno and Fuertes, 2001; Menendez and Fuertes, 2001; Fuertes, 2001; Centeno and Fuertes, 2002; Fuertes and Menendez, 2002; Centeno *et al.*, 2004). The effects of various

pyrolysis conditions on the performance of the PR based carbon membranes were studied (Centeno *et al.*, 2004). The membranes pyrolysed at 973 K in vacuum displayed high permselectivity values of 13.2 for O₂/N₂, 133 for He/N₂, 39 for CO₂/N₂, and 101 for CO₂/CH₄. Oxidation (before or after carbonisation) with air at 373-673 K for 30 min increased the permeance for all the gases used and a diminution of permselectivity for the permanent gas mixtures was observed as the oxidation temperature increased (Fuertes, 2000). The oxidised membranes exhibited increased permselectivities for the gas mixtures of hydrocarbon/permanent gas and hydrocarbon/hydrocarbon (e.g., propylene/propane), suggesting a change of transport mechanism from molecular sieving to surface diffusion (Fuertes, 2001; Fuertes and Menendez, 2002). The effective pore size in these membranes was estimated to be around 4.4 Å determined by methane diffusivity (Centeno and Fuertes, 2001). Exposure to air at 293 K caused a loss of permeance through these carbon membranes and storage under nitrogen decelerated the aging process, while storage in propylene could increase the gas permeance (Menendez *et al.*, 2001). Heat treatment could only partially recover these aged carbon membranes. These PR based carbon membranes showed high sensitivity to the test temperature, the separation between gases with different adsorption properties being affected considerably with small changes in temperature (Centeno and Fuertes, 2002).

Sedigh *et al.* (1999, 2000) prepared carbon membranes having pores mainly in the range of 3.6-3.8 Å by coating polyetherimides (PEIs) onto ceramic tubes. Scanning electron microscopy and energy dispersive spectroscopy analysis confirmed that the location of the carbon layer depended on the concentration of the initial polymeric precursor and on the rest of the dip-coating conditions. There was a considerable reduction in the number of micro- and meso-scope size cracks and pinholes in these

membranes after each coating/carbonisation step, while the separation properties of these membranes were enhanced but with diminished permeances. With respect to CO₂/H₂, these membranes exhibited relative selectivity toward CO₂ at 293 K but showed selectivity toward H₂ at higher temperatures. These carbon membranes always exhibited a minimum separation factor for gas mixtures consisting of equimolar composition.

Kusakabe *et al.* (1998) produced carbon membranes from BPDA and ODA coated on porous alumina tubes. They proved that the pore size was controlled by carbonisation and the pores larger than 0.5 nm were selectively eliminated by carbonisation at 1073-1173 K. Oxidation resulted in the formation of oxygen-containing functional groups on the surface of these carbon membranes and increased the micropore volume without damaging the pore size distribution. These functional groups can be eliminated by post heat treatment in an inert atmosphere.

Sircar *et al.* (1999a, 1999b) reported the separation properties of selective surface flow (SSF) carbon membranes prepared by carbonisation of PVC-acrylate terpolymer latex coated on macroporous alumina tube. The resulting carbon membranes allowed the larger and the more polar components of a feed gas mixture to selectively permeate through (Sircar *et al.*, 1999b). Using these SSF membranes, a high rejection of ~80% H₂S was achieved at a high recovery of ~80% CH₄ when the total feed gas pressure was ~0.45 MPa with the partial pressure of ~0.22 MPa for H₂S (Thaeron *et al.*, 1999). The SSF membrane was integrated with pressure swing adsorption (PSA) system for hydrogen recovery from the waste gases of PSA process (Sircar *et al.*, 1999a). The net hydrogen recovery was increased from a value of 77-78% by the base PSA process to 84-85% by using the integrated process.

Zhou *et al.* (2001, 2003) obtained carbon membranes from phenolic resin and sulfonated phenolic resin coated on porous alumina tubes. The membranes pyrolysed at 773 K with a thermal soak time of 1.5 h displayed gas permeances of 1950, 800 and 240 GPU [$10^{-6} \text{ cm}^3/(\text{s}\cdot\text{cm}^2\cdot\text{cmHg})$] for H_2 , CO_2 and O_2 , respectively. The introduction of the sulfonic acid group into the phenolic resin resulted in the evolution of gases with small and similar sizes (such as H_2O , SO_2 , CO_2 and CO) during pyrolysis as compared with phenolic resin except for improved matrix skeleton. The pore structure of the carbon membranes was made up of interconnected pores with different sizes and shapes.

Composite glass/ α - Al_2O_3 tubes and γ - Al_2O_3 / α - Al_2O_3 tubes were used as supports to prepare carbon membranes in the work reported by Wang *et al.* (2000). The tubes were pre-treated with 1M-ethanol solution of paratoluene sulfonic acid and then coated with furfuryl alcohol through vapour deposition. The resulting carbon membranes showed permselectivities of 27-29 for CO_2/CH_4 . Wei *et al.* (2002) used green tubes from phenol-formaldehyde novolac resin particles as supports on which a solution of phenol-formaldehyde novolac resin was coated through dip coating method. Their membranes showed separation factors of 3.72, 2.83, 4.69, 1.25 and 0.94 for H_2/N_2 , H_2/CH_4 , H_2/CO_2 , CO_2/N_2 , and O_2/N_2 respectively. Particle size, types of raw material and carbonisation conditions were demonstrated to have obvious effects on the pore structure of the carbon membranes. Katsaros *et al.* (1997) prepared carbon membranes by carbonisation and activation of an asymmetric phenolic resin structure comprising a dense resol layer supported on a macroporous novolac resin tube. These carbon membranes showed an average pore size of about 8 Å. The CO_2 permeance determined at temperatures around the critical varied greatly with the pressure and a maximum permeance occurred around 30-35 bar.

Damle *et al.* (1994) prepared microporous carbon membranes by modification of commercially available carbon membranes for liquid microfiltration application. The precursors were polyacrylonitrile (PAN), PFA, phenol-formaldehyde resin, cellulose, propylene and furfuryl alcohol-phenolic (FAP) resin. After polymer solution coating, plasma polymerization and pyrolysis, the permeabilities for H_2 through these membranes significantly decreased to 1×10^{-5} - 5×10^{-5} STDcm³/(s·cm²·mmHg) as compared to 6×10^{-3} STDcm³/(s·cm²·mmHg) for the unmodified carbon membrane. The selectivities of the modified carbon membranes were higher than those for the unmodified membrane and were still lower than the theoretical maximum values for Knudsen diffusion separation.

2.4.3.2 Flat carbon membranes

Fuertes *et al.* had done a lot of work on flat carbon membranes (Fuertes and Centeno, 1998a, 1998b, 1999; Fuertes *et al.*, 1999; Centeno and Fuertes, 1999, 2000). They used various polymers including Matrimid 5218® and Allotherm® 610-16, polyetherimide, PVDC-PVC, Novolak PR and BPDA-PDA to form thin carbon films using macroporous carbon disks as supports. An intermediate layer developed between the support and the carbon film using fine graphite particles could diminish the presence of defects of the final carbon molecular sieve membranes. The structure of the resulting carbon membranes was dominated by the structure of the polymeric precursors, casting solution and preparation conditions. The selectivities for different gas pairs changed with temperature and the highest values occurred at 298 K, being 5.5-14.0, 26.5-136, 0.8-45, and 37.4-160 for O_2/N_2 , He/N_2 , CO_2/CH_4 and CO_2/N_2 , respectively. The permeation rate of CO_2 did not change with testing temperature probably due to adsorption of CO_2 into micropores. It was proposed that CO_2

transport through these membranes resulted from a combination of transport in the gas phase and surface diffusion of the adsorbed CO₂ molecules across the micropores.

Rao and his coworkers (Rao *et al.*, 1992; Rao and Sircar, 1993a, 1993b, 1996) developed adsorption selective nanoporous carbon membranes. Macroporous graphite disks were used as supports on which a thin layer of PVC-acrylate terpolymer latex containing 0.1-0.14 μm polymer beads was coated. Carbonised at 1273 K for 3 h under nitrogen atmosphere, the carbon membranes exhibited larger permeabilities for hydrocarbons than those for H₂ and the permeabilities of the weakly adsorbed components were drastically reduced in the presence of the higher hydrocarbons (Rao and Sircar, 1996). Conditions such as feed gas pressure, sweep gas pressure, sweep gas type and flow rate had marked effects on the permeation properties of these carbon membranes. Four critical requirements were proposed for practical surface diffusion membranes. (a) The diameter of the pores in the membrane must be larger than the diameter of the adsorbing molecules but should not exceed three to four times the diameter of the largest molecules of the feed gas mixture to be separated. (b) The pores must be continuous across the thickness of the membrane and the surface density of these pores should be greater than 0.2. (c) The membrane thickness should not exceed 5 μm in order to obtain a practically acceptable permeance. (d) The thin membrane has to be supported on a meso- or macroporous support for structural integrity.

Singh-Ghosal and Koros (2000) obtained carbon membranes from polyimide having a rigid backbone with –CF₃ groups and the trimethyl-substituted meta-linked diamine without support. After investigating the changes in properties of these materials from a low-selectivity flexible polymer to a rigid high-selectivity carbon, they found that

the permselectivities increased with pyrolysis while the thermodynamic sorption selectivity did not change measurably. The apparent activation energies for diffusion increased with pyrolysis, indicating an increased resistance to diffusion. Steel and Koros (2003) investigated the porosity and the gas separation properties of the carbon membranes from Matrimid® polyimide. The pore in the carbon membranes was idealised as typical cell with three characteristic dimensions: the ‘floor to ceiling’ transverse dimension d_{TV} , the molecular sieving dimension d_c and the jump length dimension d_λ . Each characteristic dimension indicated a shift to a more compact structure as the final pyrolysis temperature and the length of thermal soak time increased. The changes in the membrane transport properties with pyrolysis temperature were strong functions of both the absolute penetrant size as well as the difference in size between the respective penetrants.

Molecular sieving effect of the carbon membranes from Kapton® polyimide film was studied by Suda and Haraya (1995, 1997). Both interplanar spacing and the amorphous portion in these carbon membranes decreased with increasing pyrolysis temperature, thus causing the molecular sieving effect. On the contrary, the gas permeabilities of the membranes became lower with increasing the pyrolysis temperatures from 873 to 1273 K (Suda and Haraya, 1995). In the meanwhile, the pore volume determined from CO₂ adsorption at 298 K decreased from 0.22 to 0.15 cm³/g with decreased pore size and sharper pore size distribution. The carbon membrane carbonised at 1223 K with a heating rate of 1.33 K/min under argon atmosphere showed the highest permselectivities of 4700 and 36 for H₂/N₂ and O₂/N₂, respectively, at 308 K. It was pointed out that the excellent gas separation property of these membranes was attributed to the molecular sieving effect coming mainly from

the dependence of diffusivity of the penetrants on the size of the micropore (Suda and Haraya, 1997).

Wang *et al.* (1995a, 1995b, 1996) prepared asymmetric flat carbon membranes from phenolic resin. Formed by thermo-pressure molding, the polymeric films were carbonised using conventional method but activated ununiformly on different sides in order to obtain asymmetric membranes. Wang *et al.* proposed that the separation mechanism of their carbon membranes was not only due to a molecular sieving effect but also due to different diffusivities of molecules with different diameters. Even though the pore size might be lower than the critical size of a gas molecule, the pore could not completely prevent its penetration. However, the apparent activation energy might be high enough to lead to a very low diffusivity. In order to enhance the selectivity of a mixture consisting of two components, the ideal pore size should be between the values of the critical size of the two molecules.

Shao *et al.* (2004) studied the casting solvent effects on the morphologies and the transport properties of a 6FDA/PMDA–TMMDA copolyimide [copoly(4,4'-methylenebis(2,6-dimethyl)-2,2-bis(3,4-dicarboxylphenyl)hexafluoropropane/pyromellitic diimide)] membrane and its derived carbon membranes. The carbon membranes were prepared by casting the solutions of the precursor onto a silicon wafer plate followed by carbonisation at 823, 923 and 1073 K with the same thermal soak time of 2 h. It was found that the carbon films pyrolysed at 823 K using different solvents of CH₂Cl₂ and DMF (N,N-dimethylformamide) showed different gas permeation rates. The crystalline structure in the polyimide films using DMF as solvent might delay the degradation and pyrolysis process, thus leading to less porous carbon structure and lower gas permeation rates compared to the samples using CH₂Cl₂ as the solvent. The

difference in the gas permeation rates was largely reduced when the pyrolysis temperature was increased from 823 to 1073 K, which indicated that the influence of the pyrolysis temperature might be more significant than the morphology of the polymeric precursors at elevated pyrolysis temperatures. Tin *et al.* (2004a) studied the effects of modification by immersing the polymeric films into a cross-linking reagent (10% p-xylenediamine in methanol) or pure methanol for specific durations on the gas permeation properties of the carbon membranes derived from Matrimid® 5218 polyimide. The permeabilities of the resulting carbon membranes decreased with increasing the cross-linking density and the methanol treatment, whilst the ideal selectivities for O₂/N₂, CO₂/CH₄ and CO₂/N₂ were remarkably improved after the methanol treatment. The swelling of the polyimide by the methanol induced chain mobility and increased the interstitial space among the chains, giving rise to the ease of structural organization, and thereby created narrower selective micropores. Tin *et al.* (2004b) also reported the CO₂/CH₄ separation properties of the carbon membranes from P84® polyimide. The membrane samples carbonised at 1073 K showed pure gas permeabilities of 499 and 5.6 Barrers for CO₂ and CH₄ respectively with an ideal selectivity of 89.

Kim *et al.* (2004, 2005) prepared CMSMs from polyimide/polyvinylpyrrolidone (PVP) blends with different contents of PVP. The average d-spacing in the resulting membranes increased with increased PVP content at the same pyrolysis temperature but decreased with increased pyrolysis temperatures. The gas permeabilities through the carbon membranes increased remarkably with incremental PVP contents due to the increased pore volume. The ideal selectivities for He/N₂, CO₂/N₂ and O₂/N₂ increased with increasing carbonisation temperature but decreased slightly with increasing PVP content (Kim *et al.*, 2004). The membranes derived from polyimide/

PVP blends with different molecular weights of PVP contained a certain amount of mesopores as compared to the microporous carbon membranes without PVP. The pore volumes of these membranes increased with higher molecular weight of PVP in the precursor due to the different sizes of PVP phase domains in the polyimide matrix (Kim *et al.*, 2005). Coal tar pitch precursors which were heat polymerised and preoxidised under different conditions were used to produce carbon membranes by Liang *et al.* (1999). Permeation studies showed that heat-polymerisation temperature, preoxidation temperature and carbonisation temperature had important influences on the properties of the final carbon membranes. Gas diffusion path through such membranes was a combination of Knudsen diffusion and viscous flow. Chen *et al.* (1994) coated PFA on macroporous electrode graphite to obtain carbon membranes. They proved that it would be possible to predict binary diffusivities from the concentration dependence of the single-component diffusivities. Good agreement was obtained between theoretical predictions and experimental data for binary diffusion. Takeichi *et al.* (2001) produced carbon membranes by carbonising porous polyimide films synthesized from pyromellitic dianhydride (PMDA) and ODA. They proposed that the pore size in the final carbon films was determined by the pore structure of the original polyimide films. In the study of Sato *et al.* (1995), Kapton® films were heated to 1073 K and 1173 K in a stream of CO₂. The resulting membranes showed type I adsorption isotherms and had surface area larger than 1000 m²/g. Hatori *et al.* (2004) studied the hydrogen separation properties of carbon membranes from Kapton® polyimide film with thickness of 125 µm. The samples carbonised at 1273 K under Argon atmosphere produced ideal permselectivities up to 5900 and 161 for H₂/CO and H₂/CO₂ respectively at a testing temperature of 323 K. The apparent

activation energy of H_2 surface diffusion was 2-6 times higher than that on the graphite surface due to the very narrow pore channels.

2.4.3.3 Hollow fibre carbon membranes

Koresh and Soffer (1987) reported the gas permeation of H_2 and CH_4 of H_2 - CH_4 mixture at low or high temperature through carbon hollow fibre membranes. The permeabilities of each component were found to be independent of the presence of a second gas over a considerable range of temperatures and mixture compositions. For a very low temperature of 193 K at which the adsorption of CH_4 should be significant, the permeation of H_2 was not affected by the existence of CH_4 . The researchers concluded that the small H_2 molecules and the large CH_4 molecules would reside at different minimum energy positions prior to the activated jump through a constriction.

Jones and Koros (1994a, 1994b) prepared ultramicroporous carbon membranes by pyrolysing an asymmetric hollow fibre polyimide precursor. The separation factors of such membranes were 11.0-14.0, 55-56, 160-190 and 400-500 for O_2/N_2 , CO_2/N_2 , CO_2/CH_4 , and H_2/CH_4 respectively. It was found that exposure to water vapour affected the carbon membranes and membrane performance losses in terms of selectivity and productivity increased with increasing humidity level (Jones and Koros, 1995a, 1995b). Factors such as feed pressure, membrane porosity, surface chemistry and feed flow configuration were shown to apparently influence the membrane performance. Carbon membranes might be highly vulnerable to adverse effects from exposure to organic contaminants due to their organophilic nature; exposure to paraffinic hydrocarbons of C6 and higher than C6 resulted in nearly total loss of membrane function (Jones and Koros, 1994b). Propylene was not only easily removed from the carbon membranes but was also surprisingly effective to remove

other sorbed compounds from the carbon surface as a cleaning agent. Pure propylene exposure followed by air purge was an effective regeneration process for carbon membranes. Vu *et al.* (2002) studied the high-pressure CO₂/CH₄ separation properties of carbon membranes from polyimide hollow fibre. For the pressure range of 200-1000 psia, the membranes showed CO₂/CH₄ selectivities of 59-69 at 297 K, 52-61 at 308 K and 44-52 at 323 K. The sorption effects and gas-phase nonidealities at high pressures could be the reasons for the decreases in the CO₂ permeance and the CO₂/CH₄ selectivities at increased feed pressures.

Geiszler and Koros (1996) studied the effects of pyrolysis conditions on membrane performances. The carbon membranes produced under vacuum showed higher O₂/N₂ and H₂/N₂ selectivities than those produced in inert atmospheres at the same temperatures. The mechanism of carbonisation reaction was supposed to change by varying the type of pyrolysis atmosphere from vacuum to a flowing inert gas. Reduction in purge gas flow rate, increase in pyrolysis temperature, and removal of residual oxygen were observed to contribute to the decrease in the permeate flux through these membranes.

In the studies of Ogawa and Nakano (1999), hollow fibre carbon membranes were formed by gelation of polyamic acid solution in a coagulant through phase inversion followed by imidisation and carbonisation. It concluded that the gelation process was an important factor to control the micropore volume, the gas permeance and the separation properties of these membranes. The rise of gelation temperature increased the cumulative micropore volume but decreased the permselectivity. The permeance for some gases increased with increasing gelation temperature higher than 298 K but decreased above 313 K. Kusuki *et al.* (1997) continuously prepared carbon membranes

by pyrolysing polyimide hollow fibre membranes from BPDA and aromatic diamines. They found that a thermo-stabilisation treatment before pyrolysis was important based on the fact that the precursor would soften during pyrolysis and the resulting membranes would show low performance without such a step. Rough linear relations between the logarithm of the permeation rates and the kinetic diameters were observed, suggesting that the molecular sieving effect was mainly attributed to diffusivity selectivity. These carbon membranes showed ideal selectivities of 100-630 for H_2/CH_4 with the H_2 permeability of 10^{-4} - 10^{-3} cm^3 (STP)/($cm^2 \cdot s \cdot cmHg$). Okamoto *et al.* (1999) prepared polyimide hollow fibre carbon membranes in a flow of air at 673 K followed by carbonisation in nitrogen at 873 or 903 K. Their membranes had an asymmetric structure and showed good stability as well as excellent separation performance for propylene/propane and 1,3- butadiene/n- butane.

Tanihara *et al.* (1999) compared the gas permeation properties of asymmetric polyimide hollow fibre membrane and the carbon membranes using the polyimide hollow fibre as the precursor. With increasing feed pressure, the permeances of H_2 , CO_2 and CH_4 through the precursor largely decreased whilst the permeances of these gases through the carbon membranes changed slightly. It considered that the membranes after carbonisation were not affected by the compaction effect which resulted in the variation of gas permeances with feed pressure. The existence of toluene of certain concentrations in the feed gas largely decreased the selectivity of polyimide membrane due to the plasticization of the active skin layer on the membrane. The regenerated polyimide membranes after exposure to toluene vapour showed a half of the selectivity for H_2/CH_4 of the virgin one. Inversely, little difference in the permeation properties was observed for the carbon membranes before and after exposure to toluene.

Barbosa-Coutinho *et al.* (2003) reported the optimization of the pyrolysis conditions for the preparation of carbon hollow fibre membranes from PEI/PVP. During the pyrolysis process, gases such as H_2O , CO_2 , and CO evolved in the temperature range of 693-953 K while H_2 evolved between 723 K and 1073 K. Oxidation before pyrolysis could result in less deformation and irregularities of the fibres. Too low a heating rate (i.e. 1.0 K/min) would bring about cracks and defects on the external surface of the fibres and too long a thermal soak time would favour the formation of a graphite-like structure, thus reducing the mechanical stability of the fibres.

Sznejer *et al.* (2004a) reported the transport and separation of hydrogen and light alkanes through hollow fibre carbon membrane at temperatures ranging from 298-673 K. The membrane tested in the study was an entire membrane module composed of 100 fibres with an approximate membrane area of 150 cm^2 . The selectivity of hydrogen from hydrocarbon was enhanced with increasing testing temperature, and the selectivity values for H_2/CH_4 , $\text{H}_2/\text{C}_2\text{H}_6$, $\text{H}_2/\text{C}_3\text{H}_6$, $\text{H}_2/\text{C}_4\text{H}_{10}$ and $\text{H}_2/\text{i-C}_4\text{H}_{10}$ at 673 K were 4.0, 62.2, 2000.0, 941.6 and 771.0, respectively.

2.4.3.4 Capillary carbon membranes

Petersen *et al.* (1997) used polyamic acid (PAA) as the raw material for capillary carbon membranes. A dual bath method was utilised such that the membranes were firstly coagulated in alcohol for a certain time and then treated with water. After imidisation, the capillary Kapton films were carbonised at 1223 K and were coated with a thin layer of poly-dimethylsiloxane in order to prevent gas flow through defect structures. It was found that the usage of solution of up to 19% of the PAA in dimethylacetic amide (DMAc) produced open structure with macro-voids close to the surface layer while higher concentrated solutions up to 25% resulted in less macro-

voids and a more sponge like structure with a less permeable top layer of about 2 μm in thickness. If a solution were to replace 30% of DMAc solvent with glycerol and water as a coagulant, the resulting thin layer was 0.5 μm in thickness and showed a regular sponge like structure. Single gas permeation tests exhibited an unexpected dependency between permeance and temperature that might be caused by two competing transport mechanisms: activated diffusion and surface diffusion or Knudsen diffusion through defect macropores. The maximum selectivities of these membranes were 327.3 for H_2/CO and 39.1 for H_2/CO_2 .

2.4.3.5 Composite membranes

Composite membranes containing carbon and other elements such as silica and zeolite have been prepared in recent years. Due to the different membrane structure, the latest development of this kind of membranes is separately introduced here. Park *et al.* (2002, 2003, 2004, 2005a) prepared unsupported and supported carbon-silica (C-SiO_2) membranes by the pyrolysis of poly(imide siloxane) (PIS) synthesized in different compositions from PMDA, BPDA, ODA and α,ω -Aminopropyl poly(dimethyl siloxane) (PDMS). The pyrolysis was carried out at different temperatures under Ar atmosphere. Within the C-SiO_2 membranes, the carbon was a continuous matrix while the SiO_2 was a dispersed phase in a bulk solid state. The top surface consisted of a SiO_2 rich phase in a continuous carbon matrix and the bottom surface was mainly a carbon-rich phase (Park *et al.*, 2002). During pyrolysis, the imide domains in PIS were transformed into a carbon-rich phase conferring a molecular sieving capability whilst siloxane domains were converted into a silica-rich phase providing further gas pathways (Park *et al.*, 2004). The gas separation properties were considerably influenced by the siloxane content; the gas permeabilities increased but the permselectivities decreased with increasing siloxane

content in the precursor. For the same siloxane content, different polymerization method also showed some influence on the transport properties of the pyrolysed C-SiO₂ membranes (Park and Lee, 2003). For the same volume fraction of PDMS moiety, a longer siloxane chain in the PIS resulted in a significant increase in the gas permeabilities and a reduction in the permselectivities of the C-SiO₂ membranes (Park *et al.*, 2004).

In another study (Park *et al.*, 2005b), the morphological changes arising from the difference in the molecular structure of the polymeric precursors were investigated. PISs were prepared using one-step (preferentially a random segmented copolymer) and two-step polymerization (a block segmented copolymer) methods. The carbonised C-SiO₂ membranes and their precursors that had random geometry showed higher permselectivity and lower gas permeability than the membranes and their precursors that had block geometry. C-SiO₂ membranes were also prepared from PI/Silica nanocomposite membranes using tetraethoxysilane (TEOS) as the silica precursor and PMDA and ODA as the polyimide precursors (Park and Lee, 2005a). The C-SiO₂ membranes showed promising selectivities of 7.4-12.5 for O₂/N₂ and 38-78 for CO₂/CH₄, and the permeabilities of O₂ and CO₂ increased with increasing silica loading in the carbon matrix. The C-SiO₂ membranes from ODA and TEOS showed higher CO₂ permeability than the membranes from PMDA and TEOS. The phenomenon might be caused by the change in the silica network resulting from using difunctional silicon alkoxides. The organic groups in the three-dimensional oxide network provided structural flexibility by reducing the degree of crosslinking.

2.5 THEORETICAL STUDY OF GAS PERMEATION

The mathematical modelling of transport within porous media is one of the classical problems in chemical engineering with important implications for the design of industrially applicable adsorption column, heterogeneous catalysis, membrane separation units and chromatographic separation (MacElroy and Boyle, 1999). Direct comparisons of gas permeation rates between experiments and mathematical models have been unsuccessful (Furukawa and Nitta, 2000). The main reason is that the theoretical studies are mainly based on well-defined pore structure whilst the preparation of crack-free carbon membranes is difficult and the determination of the effective thickness of such membranes may not be reliable. In addition, the permeation resistances at the entrance and exit of a membrane are not always taken into consideration in the theoretical study although they may be important to the calculated gas permeation rate.

MacElroy and Boyle (1999) simulated the transport of binary mixtures of H_2 and CH_4 through carbon membrane with varying thickness using nonequilibrium molecular dynamics technique. The carbon membrane was modelled as a set of isolated slit pores each separated by 20 basal graphite layers. If the pores controlling the separation process were short, the pore entrance/exit resistances to the mass transfer would be significant. The transport of strongly adsorbing CH_4 molecules was nearly not affected by the cross-coefficient of diffusion. The transmembrane flux of H_2 was observed to be significantly decreased during isobaric counter-diffusion. The viscous flow contribution to the fluxes of both species was negligible compared to the diffusive terms.

Xu *et al.* (2000, 2001) reported the nonequilibrium molecular dynamics simulations of transport and separation of CO_2/CH_4 through a porous membrane with

interconnected pores of distributed sizes. It was found that the adsorbed amounts of the gases increased with increasing porosity and reached a maximum at a porosity of 0.45-0.5 beyond which they both decreased with increasing porosity. This phenomenon was supposed to result from two competing effects: a higher porosity providing more accessible pore surface area for adsorption whilst simultaneously decreasing the interaction between the gas molecules and the pore surface due to the improved interconnectivity of the pore space. The calculated selectivity for CO₂/CH₄ separation was low at lower porosities due to the small pore surface area for CO₂ adsorption and tortuous transport paths for CH₄. The selectivity increased with increasing porosity due to the improved CO₂ flux and nearly constant CH₄ flux and reached a maximum of about 14 at a porosity of 0.6. Porosities greater than 0.6 were not applicable for the separation since the presence of large pores would lead to apparent increases in both CO₂ flux and CH₄ flux.

Vieira-Linhares and Seaton (2003) reported the separation of H₂/CH₄ through a selective surface flow carbon membrane by nonequilibrium molecular dynamics simulations. It was disclosed that H₂ could enter pores as small as 4.9 Å while CH₄ was restricted to pores larger than 5.9 Å. In the pores of 5.9-12 Å, the adsorption of H₂ and CH₄ would oscillate as a function of pore size. For the pores less than 6.0 Å, the separation of H₂/CH₄ would be based on molecular sieving since H₂ molecules would pass preferentially through the small membrane pores. Pores between 6.3 and 10.0 Å showed significant selective adsorption of CH₄, thus forming a packed single layer of CH₄ molecules and leaving little space for H₂ molecules. At a feeding pressure of 11.3 bar, a maximum selectivity around 170 of CH₄ over H₂ was obtained corresponding to a pore size of 7 Å. In pores larger than 10-12 Å, a preferential CH₄ adsorption was observed close to the pore surface while H₂ was restricted to the low-

density region in the middle of the pore. Poor separation of H_2/CH_4 was obtained due to the effective diffusion of H_2 through the low-density region. In another study, Seo *et al.* (2002) calculated the transport diffusion of hydrogen and hydrocarbons using dynamic Monte Carlo (MC) simulation method. The movements of the molecules were based on the selective adsorption followed by surface diffusion. The size of the pores within the carbon membranes was observed to be an important factor which would determine the selectivities of hydrocarbons over hydrogen.

Furukawa and Nitta (2000) studied the permeation of single CH_4 and C_2H_6 and their mixture across carbon membranes using nonequilibrium molecular dynamics simulation. The carbon membranes were modelled with three different pore shapes, i.e., a diamond path (DP), a zigzag path (ZP) and a straight path (SP). The amounts of C_2H_6 inside the membrane were always larger than those of CH_4 due to the larger adsorption power and were always in the order of $DP < ZP < SP$ membranes. The permeation resistances of C_2H_6 for the three membranes were always larger than those of CH_4 . The calculated permselectivities of C_2H_6 over CH_4 were smaller than the adsorption equilibrium separation factors but were higher than the ideal separation factors derived from pure gas simulation. The selectivity, which was related to both the competitive adsorption equilibrium and the permeation resistance of the two components, was in order of $DP < ZP < SP$ membranes.

Strano and Foley (2003) developed a parallel resistance transport model to describe the gas permeability, i.e., the permeability was considered as a sum of the contributions of highly selective membrane pores and a small population of less selective cylindrical defect pathways. By applying the model to the experimental data, the contribution of the defect with the area fraction α was estimated. For 200 nm

average defects, the model yielded the α values of 10^{-9} - 10^{-12} which corresponded to a range from 32 to 1 pore on a 10 cm^2 membrane sample. At low values of α , the influences of these defects were nearly undetectable for known fluxes as a function of pressure. The O_2/N_2 selectivity was highly sensitive to the area fraction of the defects within the films.

Gilron and Soffer (2002) studied the Knudsen diffusion of gases in carbon membranes with two types of simplified models, i.e., the parallel resistance model and the resistance-in-series model. For the parallel resistance model, the carbon membrane was considered to have an equivalent porous structure with pores of various diameters but uniform cross-section throughout the thickness of the membrane. For the resistance-in-series model, the membrane was considered to be composed of a collection of identical pores with diameter changing from a larger to a smaller one at some point along the membrane thickness. Based on the parallel resistance model, the gases H_2 , N_2 , CO_2 , and CH_4 showed an increase in the contribution of Knudsen diffusion to the total transport with increasing temperature. However, the parallel transport model resulted in an unrealistically high value for the tortuosity and an unacceptable conclusion that He would have significantly positive activation energy. Fitting the temperature-permeance data to the resistance-in-series model gave more realistic results for the membrane tortuosity.

2.6 APPLICATIONS OF CARBON MEMBRANES

It has been proved that carbon membranes have far superior permeability-selectivity combination than that of any known polymer membranes (Koresh and Soffer, 1987; Jones and Koros, 1994a). They show superior stability in the presence of organic vapours at high temperatures and nonoxidizing acidic or basic environments (Centeno

and Fuertes, 1999), and exhibit excellent heat resistance as well as high solvent resistance (Wang *et al.*, 2000; Wei *et al.*, 2002). Till now, carbon membranes have been tested for the separation of such gas mixtures as O₂/N₂, H₂/N₂, CO₂/CH₄, CO₂/N₂, CH₄/C₂H₆, C₂H₄/C₂H₆, C₃H₆/C₃H₈, H₂/CO₂, H₂/CO and He/N₂. Hollow fibre carbon membranes have been commercially fabricated by Israel's Carbon Membranes Ltd for SF₆ recovery. The other main potential applications are discussed below.

Oxygen and nitrogen are separately the third and fifth largest bulk chemicals produced worldwide (Koros and Mahajan, 2000). Carbon membranes show high selectivity for O₂/N₂, being in the range of 5-14 (Hayashi *et al.*, 1996; Centeno and Fuertes, 1999; Shiflett and Foley, 2000; Fuertes, 2000). This means that carbon membranes will definitely occupy a strong position in the separation of oxygen and nitrogen.

Natural gas is a mixture containing some hydrocarbons and other components such as H₂S, CO₂, and water. Removal of H₂S and CO₂ from desired lower hydrocarbons is necessary. Polymeric membranes have been successfully utilised in this field. Due to the continuing growth of the market and low separation factor of polymer membranes, novel membranes with higher selectivity and productivity are needed. Some researchers have fabricated carbon membranes that can successfully separate CO₂ and CH₄. For instance, the adsorption selective tubular carbon membranes from Centeno and Fuertes (2001) gave a selectivity of 150 for CO₂/CH₄, the separation factor of the supported flat carbon membranes from Fuertes and Centeno (1998a) was in the range of 6.7-37.3, the selectivity of the tubular carbon membranes from Wang *et al.* (2000) was 27-29, and the permselectivity of hollow fibre carbon membranes from Jones and

Koros (1994a) was 160-190. These results have provided a strong evidence for the commercial utilisation of carbon membranes in the purification of natural gas.

Separation of alkane and alkene is an important process in the petrochemical industry and is currently predominantly achieved by distillation, an extremely capital and energy consumable unit operation. Hayashi *et al.* (1996) reported carbon membranes showing selectivity of 4-7 for C_2H_4/C_2H_6 and 25-56 for C_3H_6/C_3H_8 . Carbon membranes from Okamoto *et al.* (1999) displayed a selectivity of 14 for C_3H_6/C_3H_8 . Because of the high permeability and selectivity, and the high stability, carbon membranes will play an important role in the separation of alkane and alkene.

Hydrogen recovery, including adjusting the ratio of H_2 and CO in synthetic gas, recovery of hydrogen from various hydrocarbon streams and recovery of hydrogen from purge streams in ammonia, is among the first wide scale commercial applications of membranes (Koros and Mahajan, 2000). Polymeric membranes, being dominant in these areas, show at least two shortcomings beside low selectivity and productivity. One is that hydrogen exits the unit at the lower pressure permeate side and thus adds recompression costs; the other is that resistance to hydrocarbons is poor. Carbon membranes can selectively allow the permeation of hydrocarbons while leaving hydrogen at the high pressure feed side.

Isomer separations are difficult but valuable for catalytic reactions. Lokhandwala *et al.* (1997) reported the preparation of carbon membranes by carbonisation of non-melting polymer. The critical pore sizes in the resulting carbon membranes were in the range of 3.9-5.5 Å. These membranes showed very high selectivities for the mixture of straight-chain and branched-chain isomers.

Itoh and Haraya (2000) reported the dehydrogenation of cyclohexane using a carbon membrane reactor composed of microporous carbon hollow fibres. The performance of the carbon membrane reactor was fairly good compared to that of a normal reactor. Szejner and Sheintuch (2004b) reported the efficiency of isobutane dehydrogenation using a carbon membrane reactor composed of 100 carbon hollow fibres. The maximum conversion achieved was 85% at 773 K.

2.7 SIGNIFICANCE OF THIS STUDY

Carbon membranes have been prepared from various precursors through different pyrolysis protocols. It is overwhelmingly accepted that the carbonisation process is one of the most important factors that determine the gas separation properties of the carbon membranes. Usually, the influences of the carbonisation process are evaluated by determining its effects on the permeation and separation properties. However, the key factor determining the membrane performance is the membrane pore structure. Unfortunately, the development of membrane pore structure and transport properties during the heat treatment process has not been thoroughly studied. Thus, the relationship knowledge between carbonisation, membrane pore structure and membrane performance is superficial. The aims of the present study are to understand the principles of pyrolysis on the precursor, to detect the membrane structural change from polyimide to amorphous carbon, to investigate the influences of the various carbonisation parameters including the atmosphere, the final temperature, the heating rate and the thermal soak time on the membrane structure and transport properties, and to find out the possible effects of carbonisation on membranes with different thickness. Additionally, the permeation of nonadsorbable gases within membrane pores with different diameters would also be included. The research reported in this thesis will make up the deficiency of the research work in this field.

2.8 FUTURE DIRECTION

From the aforementioned, carbon membranes have been prepared using various precursors by various techniques. These membranes have been proved to show excellent separation properties for a large number of gas mixtures. However, some disadvantages should be overcome before large-scale industrial utilisation of carbon membranes is feasible. The disadvantages shown by existing carbon membranes include (a) problems related to preparation such as ease of fabrication and reproducibility, high cost, shrinkage during carbonisation that causes cracking and deformation, and difficulty of controlling the microstructure and thickness of the surface dense layer (Haraya *et al.*, 1995; Fuertes *et al.*, 1999; Ogawa and Nakano, 1999); (b) vulnerability to some compounds such as water vapour, air and organic contaminants that are typically found in industrial process streams (Chen and Yang, 1994; Jones and Koros, 1995b; Wang *et al.*, 2000); and (c) brittleness that is a vital drawback requiring more careful handling (Koresh and Soffer, 1987; Shiflett and Foley, 2001).

In the near future, more attention will be focused on realising complex and well defined porous architectures and a gradual shift will take place from the exploration of new membrane concepts towards better control of membrane preparation and understanding of performance, long-term stability and process integration in the applications. Efforts will be made to study the optimum conditions to prepare carbon membranes with desired characteristics. More suitable and economical materials should be investigated in order to lessen the production cost and enhance the separation properties (Saufi and Ismail, 2004). Knowledge relevant to interaction between gas molecules and carbon, diffusion of gas molecules in micropores, relationship between membrane thickness and permeability or selectivity, should be

further investigated for the total understanding of membrane separations. Mixed-matrix membranes prepared from embedding molecular sieve carbon into polymeric matrix will become important to overcome the shortcomings shown by existing carbon membranes and polymeric membranes (Koros and Mahajan, 2000). Isomer separations are quite difficult due to the little difference in the critical dimensions between the straight-chain and branched-chain isomers. For such applications, the carbon membranes must have finely distributed pore sizes which are suitable for differentiating permeates with a dimension difference of 0.5 Å.

Carbon membrane reactors have been reported for dehydrogenation reactions (Itoh and Haraya, 2000; Szejner and Sheintuch, 2004b). These novel reactors showed comparatively good results although some problems still exist and need further study. Successful implementation of the membrane reactor is advantageous over the traditional fixed bed reactor. The reactor performance may be improved by increasing the membrane area, increasing the catalyst loading or improving the membrane reactor configuration.

CHAPTER 3

EXPERIMENTAL SET-UP AND PROCEDURES

3.1 INTRODUCTION

Carbon membranes are prepared by the pyrolysis of pre-existing polymeric substrates (e.g., hollow fibres or self-supported thin polymeric films) or the pyrolysis of films deposited on underlying porous supports. The molecular structure of the starting polymeric precursor is among the key factors that affect the performance of the final carbon membranes (Sedigh *et al.*, 1999). Consequently, the pyrolysis procedures must be optimised. Pyrolysis is generally carried out at temperatures of 773 -1273 K under vacuum, inert gas or oxidative gas, depending on the type of polymer and the required final membrane structure. During the pyrolysis process, most of the heteroatoms are removed, leaving behind a cross-linked and stiff carbon matrix. As reported by Suda and Haraya (1995, 1997), carbon membranes contain small amounts of oxygen, nitrogen and a trace of hydrogen as well as a large amount of carbon. Though carbon membranes are amorphous in nature, the structure of the polymeric precursors is still recognisable in the carbon membrane subdomains. This subdomain structure which is dependent on the polymer precursors and pyrolysis conditions, has a certain degree of influence on the performance of the carbon membranes. Generally, the important parameters and conditions for the pyrolysis process include the type of atmosphere (vacuum or inert gas such as Ar, N₂ and He or oxidative gas such as air and CO₂), final pyrolysis temperature, pyrolysis heating rate, hold time at final pyrolysis temperature and flow rate of inert/oxidative gas.

Polyimides have been increasingly used as precursors to prepare polymeric membr-

ane because of their superior permselectivity, permeance and stability compared with other polymers. Previous studies on carbon membranes prepared by pyrolysis of polyimide precursors showed excellent performances (Suda and Haraya, 1995; Hayashi, *et al.*, 1996; Fuertes *et al.*, 1999; Singh-Ghosal and Koros, 2000; Takeichi *et al.*, 2001). Pyrolysis of polyimide is a very complex process consisting of a series of degradation reactions along the polyimide chain. With increasing pyrolysis temperature, linkages along the polyimide chain are broken, starting from the weakest bonds and progressing to the strongest. The higher the pyrolysis temperature and the longer the hold time at the final temperature, the higher will be the crystallinity of the carbon membranes. Carbon membranes so prepared have an amorphous porous structure, layer planes of graphite-like structures dispersing into the non-crystalline carbon created by the evolution of gaseous products such as CO₂, CO, H₂O, N₂ and H₂ generated during the pyrolysis of the precursor (Geiszler *et al.*, 1996; Suda and Haraya, 1997). It is commonly accepted that certain components in a gas mixture can permeate through the cross-like voids of the amorphous region, leading to effective separation of these components.

3.2 EXPERIMENTAL METHODS

3.2.1 Material

The molecular structure of the polymer precursor is an important factor that will affect the performance of the carbonised membranes. Compared to other polymers that have been used to prepare polymeric membranes, polyimides have attracted much attention due to their superior penetrant diffusivity and molecular sieving characteristics (Sedigh *et al.*, 1999). Commercially available Kapton® polyimide film (DuPont) with a thickness of 25 μm , was used as the precursor to prepare the carbon molecular sieve membranes. Synthesised by polymerizing an aromatic dianhydride

and an aromatic diamine, Kapton® polyimide has excellent chemical resistance with no known organic solvents for the film. The structure of Kapton® polyimide shown in Figure 2.4 is considered to be suitable for the preparation of high performance carbon membranes through pyrolysis (Suda and Haraya, 1995; Suda and Haraya, 1997) due to the aforementioned properties. The general properties of Kapton® 100HN are given in Table 3.1.

Table 3.1 General properties of Kapton® 100 HN Film, 25 μm

Thermal property	Typical value	Test condition	Test method
Melting Point	None	None	ASTM E-794-85 (1989)
Thermal Conductivity (W/m·K)	0.12	296 K	ASTM F-433-77 (1987)
Specific Heat, J/g·K	1.09		Differential Calorimetry
Shrinkage, %	0.17	30 min at 423 K	IPC TM 650, Method 2.2.4A
	1.25	120 min at 673 K	ASTM D-5214-91
Density, g/cm ³ or g/mL	1.42		ASTM D-1505-90
Glass Transition Temperature (T _g)	Between 633 K and 683 K, different measurement techniques produce different results within the above temperature range.		

3.2.2 Pyrolysis System

Figure 3.1 Schematic diagram of the tube furnace pyrolysis system

Figure 3.2 Photograph of the tube furnace pyrolysis system

The pyrolysis system consists mainly of a horizontal electrical furnace into which the film sample is pyrolysed. It can be connected to two different modes of operation - vacuum pyrolysis and inert gas purge pyrolysis. In the former operation, a Welch 8905 vacuum pump was used to reduce the pressure to 10^{-2} Torr. In the latter operation, a nitrogen flow of 100 ml/min was supplied to the reactor from a cylinder through a valve and a rotameter. Pyrolysis of the film sample was carried out in a horizontal stainless-steel reactor (length of 950 mm and diameter of 70 mm) placed in the centre of the furnace (CTF 12/75/700 Carbolite). Before pyrolysis, the rotameter used for the determination of the gas flow rate was calibrated using the soap film burette method. Figure 3.2 shows a photograph of the tube furnace pyrolysis system.

3.2.3 Preparation of Carbon Membranes

The Kapton® film samples were cut into circular pieces with diameters around 30 mm and located between porous graphite discs placed inside the horizontal stainless-steel reactor. Before pyrolysis, the system was evacuated or purged with inert

atmosphere (nitrogen, helium or argon) for 60 min. Under each atmosphere, the preparation process involved raising the temperature to the specified temperature and holding it constant for a certain time. Subsequently, the membranes were cooled to the ambient temperature under each atmosphere.

3.2.3.1 Effect of carbonisation parameters

A statistical analysis using the 2^{4-1} factorial design of experiment was applied to study the possible influences of the carbonisation parameters on the transport properties of the Kapton® based carbon membranes. The two-level 8-run factorial design comprising the four main factors and the three interactive factors is shown in Table 3.1. Each parameter had two levels in which the high level (+1) and the low level (-1) of the carbonisation parameters were selected. Further details of this statistical approach are given in Chapter 6.

Table 3.2 Carbonisation parameters used in the factorial experiments

Factor	Parameter	High level (+)	Low level (-)
A	Atmosphere	Vacuum	Nitrogen
B	Temperature	1073 K	923 K
C	Heating rate	4.0 K/min	0.5 K/min
D	Thermal soak time	300 min	120 min
A=BCD		AB=CD	
B=ACD		AC=BD	
C=ABD		AD=BC	
D=ABC		I=ABCD	

3.2.3.2 Evolution of pore structure and transport properties

The change in pore structure and transport properties of the membranes with carbonisation temperature were studied. The carbon membranes were prepared at different temperatures under vacuum atmosphere (10^{-2} Torr). The carbonisation process involved raising the temperature at a heating rate of 5 K/min to 673 K and holding at 673 K for 60 min, and then continued at a heating rate of 0.5 K/min to a

final temperature ranging from 823 to 1273 K with no hold time. The samples prepared under vacuum are designated as CM-VT, where T is the carbonisation temperature.

3.2.3.3 Effects of different carbonisation atmospheres

The effects of carbonisation atmosphere on the membrane structure and the transport properties were examined. The carbon membranes were prepared under two different modes: inert gas (argon, helium and nitrogen) with a flow rate of 100 ml/min and vacuum atmosphere (10^{-2} Torr). The heat-treatment process involved raising the temperature at a heating rate of 5 K/min to 673 K and holding at 673 K for 60 min, and then continued at a heating rate of 0.5 K/min to a final temperature of 873 or 1073 K and holding at this temperature for 120 min. The samples prepared under vacuum and inert atmospheres of argon, helium or nitrogen are designated as CM-VTH2, CM-ArTH2, CM-HeTH2 and CM-NTH2, respectively, where T is the carbonisation temperature and H2 is the thermal soak time.

3.2.3.4 Carbon membranes with different thickness

The effect of membrane thickness on the pore structure and transport properties was studied. The starting materials to prepare carbon membranes were Kapton® polyimide films 30HN, 50HN, 100HN, 200HN and 500HN. The thicknesses of these precursors were 7.6, 12.7, 25.4, 50.8 and 127 μm , respectively. The heat-treatment process carried out under vacuum (10^{-2} Torr) involved raising the temperature at a heating rate of 5 K/min to 673 K and holding at 673 K for 60 min, and then continued at a heating rate of 0.5 K/min to a final temperature of 1073 K and holding at this temperature for 120 min. The membranes obtained are designated as CM-30, CM-50, CM-100, CM-200 and CM-500, respectively.

3.2.3.5 Intermediate state between polyimide and carbon membrane

To determine the possible evolution of the membrane structure and the transport properties from polymer to an intermediate state and then finally to carbon membrane during heat treatment, the polyimide precursor was heated at a rate of 5 K/min to a specified temperature (623, 673, 698, 723, 748 and 773 K) and holding at this temperature for 60 min. For the preparation of carbonised membranes, the polyimide membranes were firstly heated to 673 K at a heating rate of 5 K/min and a thermal soak time of 60 min, and then subsequently heated to 873 or 1073 K at a heating rate of 0.5 K/min with a thermal soak time of 120 min at the final temperature. The membranes obtained are designated as Kp-NT where T is the heat-treatment temperature.

3.2.4 Pyrolysis Kinetics of Kapton® Polyimide

The kinetics involved in the thermal decomposition of Kapton® polyimide 100HN under nitrogen atmosphere were studied by applying various fitting techniques to the isothermal and nonisothermal gravimetric data. The Kapton® film was cut into circular pieces and stored in a dry box. The pyrolysis was carried out using a differential thermogravimetric (DTG) analyzer (DTG60, Shimadzu). Small pieces of the samples were placed on an aluminium pan and purged with nitrogen for 60 min. Two different protocols were used in the pyrolysis processes: (i) nonisothermal pyrolysis (start at 323 K, heat to 673 K at a rate of 5 K/min, maintain the temperature at 673 K for 60 min, then heat to 1123 K at constant heating rates of 2, 4, 6, 8, and 10 K/min) and (ii) isothermal analysis (start at 323 K, heat to 673 K at a rate of 5 K/min, maintain the temperature at 673 K for 60 min, heat to temperatures 20 K less than the final temperatures at a heating rate of 5 K/min, heat to the final temperatures of 781, 786, 796, 800 and 805 K at a rate of 1 K/min, then maintain at the final temperature

for 600 min). The isothermal pyrolysis was thus conducted to avoid the possible effect of overshoot of the furnace temperature, to minimise any degradation before the commencement of the isothermal pyrolysis process and to allow the pyrolysis to start at the specified temperature. All the tests were performed in a nitrogen stream with a flow rate of 50 ml/min.

3.2.5 Characterisation Techniques

3.2.5.1 Thermogravimetric analysis

A series of preliminary carbonisation experiments were carried out using a thermogravimetric (TG) analyzer (Shimadzu DTA60). The Kapton® film (~2 mg) was cut into circular pieces and placed on an aluminium pan 5 mm in diameter and 2.5 mm in height. Since the lowest absolute pressure that the DTA system can stand is only 5-10 Torr, the TG experiments were performed under inert atmosphere (nitrogen, helium or argon) with a flow rate of 50 ml/min at atmospheric pressure instead of vacuum. Before each TG run, the samples were firstly heated from room temperature to 673 K at a heating rate of 5 K/min with a thermal soak time of 60 min at this temperature and then heated at specified rates between 0.5 and 10 K/min to a final temperature of 1123 K followed by cooling to the ambient temperature.

3.2.5.2 Density measurement

An ultra-pycnometer (upy-1000, Quantachrome) was used to measure the solid density of the carbon membranes. It depends on the Archimedes' principle of gas displacement to determine the sample solid phase volume. Helium was used as the purge gas that could penetrate the finest pores, thereby assuring maximum accuracy. Before each test, the samples were dried in an oven at 373 K in order to remove

moisture and volatile contents. The analysis was repeated 20 times until successive measurements converged to a consistent value.

3.2.5.3 Gas adsorption

CO₂ adsorption at 273 K and N₂ adsorption at 77 K were performed using an accelerated surface area and porosimetry system (ASAP2010, Micromeritics). For micropore analysis, CO₂ adsorption isotherm was obtained at a maximum relative pressure of 0.03. Incremental volume dosing was used to ensure the accuracy of these measurements. Normal N₂ adsorption was performed at relative pressures specified for meso- and macropore analyses. A thermal jacket around the sample tube was applied to maintain the constant temperature environment. Before the free-space measurement, the crushed samples were degassed overnight at 573 K. In order to eliminate problems associated with helium entrapment inside the micropores during the free-space measurements, the tests were always stopped after obtaining the free space and the samples were degassed again overnight at 573 K before analysis.

3.2.5.4 Gas permeation and separation

The single gas permeation rate was used to evaluate the effects of carbonisation parameters on the transport properties of the carbon membranes. The permeation rates of the gases with their molecular diameters in parentheses, viz., CO₂ (3.3 Å), O₂ (3.46 Å), He (2.6 Å), N₂ (3.64 Å) and CH₄ (3.8 Å), were measured using an experimental setup as shown in Figure 3.3. The test rig consisted of a stainless steel cell (Millipore) in which the membrane was mounted and sealed by means of O-rings, partitioning into a high-pressure supply side and a low-pressure permeate side. Both sides were fitted with an inlet port and a gas chamber (G₁ or G₂) with its corresponding regulating valves (H₁, H₂ or L₁, L₂) incorporated. The pressure (P_H^0) in G₁ was

measured using a differential pressure transducer (DP15, Validyne) and maintained at a constant value of 1 atm during the measurement. The variation of the pressure in G_2 was detected using a high-resolution absolute pressure transducer (627B, MKS). The volume (V_L) of the low-pressure side was measured by sealing off the high-pressure side using a metal disk which had the same thickness as that of the carbon membrane, and expanding helium into that side from another standard vessel of known volume and pressure. Before each test, a membrane was attached to the permeation cell and both sides were evacuated to 10^{-5} Torr absolute pressure using an oil-free molecular vacuum pump (1025, Alcatel). High-pressure high-purity gas supplied from the compressed gas cylinder was introduced to the membrane through the valve H_1 and the pressure in G_1 was maintained at a constant value P_H^0 . Vacuum was maintained in the low-pressure side of the membrane, and the permeate was pulled through the calibrated volume (V_L).

Figure 3.3 Experimental set-up for gas permeation and separation

Figure 3.4 (a) Photograph of the gas permeation set-up

Figure 3.4 (b) Photograph of the gas separation set-up

The variation of the pressure with time in the low-pressure side $P_L(t)$ was measured and the permeability of the single gas through the membrane was determined from equation (3.1) below. The pure gas permeability $\bar{P}^0$ through the membrane is defined as (Rao and Sircar, 1993b):

$$\ln \left[\frac{P_H^0 - P_L^*}{P_H^0 - P_L(t)} \right] = A_m \cdot \frac{\bar{P}^0}{l} \cdot \frac{RT}{V_L} \cdot (t - t^*) \quad (3.1)$$

where t is the time required to attain a pressure $P_L(t)$ at the low pressure side, t^* is a certain period of time needed to attain a constant pressure in the high pressure side, P_L^* is the pressure before each test at the low pressure side, A_m is the surface area of the membrane, R is the gas constant, T is the gas temperature and V_L is the calibrated volume of the low pressure side. A plot of $\ln \left[\frac{(P_H^0 - P_L^*)}{(P_H^0 - P_L(t))} \right]$ against $(t - t^*)$ should give a straight line from which the permeability can be obtained. Since the thickness of the membrane was needed when calculating the permeability, the gas permeance $(\bar{P}^0/l)$ was also used to represent the permeate rate of the single gases. The ideal separation factor for the components i and j is defined as the ratio of the permeation rate of each component by:

$$\alpha_{i/j} = \left(\bar{P}_i^0 \right) / \left(\bar{P}_j^0 \right) \quad (3.2)$$

For O₂/N₂ separation experiment, O₂ and N₂ were separately supplied at a controlled flow rate to the gas holder G₁ and He was used as the purge gas at the downstream end. The pressure difference between the upstream and the downstream sides was 1 atm. A gas chromatograph-mass spectrometer system (6890N-5973, Agilent) equipped with a thermal conductivity detector (TCD) was used to detect the

composition of the gas mixture at the downstream side. The flow rates of the gases were separately controlled by mass flow controllers (5850E, Brooks). The selectivity for the components i and j is defined as:

$$\alpha_{i/j} = \frac{(y_i/y_j)}{(x_i/x_j)} \quad (3.3)$$

where x_i and x_j are the volume fractions of the components at the upstream side while y_i and y_j are the volume fractions of the components at the downstream side.

3.2.5.5 Wide angle X-ray diffraction

X-ray diffraction (XRD) is used to determine the average d-spacing of the lattice layers and this d-spacing is useful to describe the structure of the carbon materials. The average d-spacing of the carbon materials can be obtained using Bragg's law

$$n\lambda = 2d \sin \theta \quad (3.4)$$

where n is the order of reflection, λ is the wavelength of X-ray (1.5405 Å, Cu), d is the interplanar spacing of the (002) plane, and θ is the diffraction angle (degree). The carbon membranes prepared at different conditions were analysed using X-ray diffractometry (PW1830, Philips) with Cu-K α radiation of 1.54 Å. The X-ray generator operated at 40 kV and 30 mA with a step size of 0.02 degree.

3.2.5.6 Raman spectroscopy

For amorphous carbon film, two peaks always appear in the Raman spectrum: the G-peak around 1580 cm⁻¹ and the D-peak around 1350 cm⁻¹. The G-peak is the Raman active E_{2g_2} mode of graphite involving the in-plane bond-stretching motion of sp²-hybridized C atoms whilst the D-peak is a breathing mode of A_{1g} symmetry involving phonons near the K zone boundary (Schwan *et al.*, 1996; Subramanyam *et*

al., 1997; Ferrari *et al.*, 2000). The ratio of the intensity of the D-peak (I_D) to the intensity of the G-peak (I_G), i.e., (I_D/I_G) is a typical parameter to quantify the degree of disorder in carbon materials, and the decrease of the I_D/I_G ratio indicates that the degree of graphitization increases (Ko, 1996). The I_D/I_G ratio can be correlated to the in-plane size of the graphitic clusters (L_a) using the Tuinstra-Koenig relation

$$L_a (nm) = C(\lambda)(I_D/I_G)^{-1} \quad (3.5)$$

where $C(\lambda)$ is a constant related to the wave length of the laser determined using the method developed by Matthews *et al.* (1999).

Raman spectroscopy was used to study the amorphous structure of the carbon membranes. The Raman spectra were obtained using a RANISHAW 1000 Raman spectroscopy. A HeNe laser was used to emit an intense laser beam with a fixed wavelength (632.8 nm). The emitted laser light passed through a lens and was focused on the membrane sample through a 50× magnification lens. The scattered Raman light was collected and a plot of photonintensity (count) versus the wave number shift from the laser line was the output. Raman spectra were routinely acquired in the range from 800 to 2000 cm^{-1} using a 1800 lines/mm grating.

CHAPTER 4

KINETIC STUDY OF PYROLYSIS OF KAPTON® 100HN

Pyrolysis is an elementary process in the carbonisation of polymers. The study of pyrolysis kinetics is important for understanding the mechanism and is necessary for the numerical simulations of the pyrolysis process. Both the isothermal and the nonisothermal thermogravimetric (TG) analyses are widely used to obtain kinetic information from the pyrolysis of polymers. The TG technique examines the mass change of a sample as a function of time during an isothermal pyrolysis or as a function of temperature in a non-isothermal test.

4.1 THEORETICAL BACKGROUND OF PYROLYSIS KINETICS

The rate of pyrolysis, which is dependent on the temperature and the mass change of the sample, can be expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A_0 \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (4.1)$$

where α is the degree of conversion defined as the ratio of the instantaneous weight loss to the total weight loss corresponding to the pyrolysis process $(m_0 - m_t)/(m_0 - m_f)$, t is the time, $f(\alpha)$ is a function known as reaction model, $k(T)$ is the temperature-dependent rate constant, E is the apparent activation energy, A_0 is the pre-exponential factor, T is the temperature, and R is the gas constant. Equation (4.1) is also used in its integral form, which for isothermal conditions, becomes

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T)t \quad (4.2)$$

For nonisothermal pyrolysis, equation (4.1) becomes

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_0}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT = \frac{A_0 E}{\beta R} p(x) = \frac{A_0}{\beta} I(E, T) \quad (4.3)$$

where β is the heating rate ($\beta = dT / dt$) and x is E / RT .

4.1.1 Reaction Mechanism Fitting Method

In the case of polymers, the integral function $g(\alpha)$ is either a sigmoidal function or a deceleration function (Fraga and Nunez, 2001). Different expressions of differential forms $f(\alpha)$ and integrated forms $g(\alpha)$ of mechanism for various solid-state reactions (Table 4.1) have been proposed and employed for the estimation of solid-state reaction mechanism from TG data (Ma *et al.*, 1991; Fraga and Nunez, 2001; Vyazovkin and Wight, 1997a).

Table 4.1 Reaction mechanisms to represent the solid-state process

Model	Symbol	$f(\alpha)$	$g(\alpha)$
Nucleation and nucler growth			
Mapel unimolecular law	A1	$1-\alpha$	$-\ln(1-\alpha)$
Avrami-Erofe'ev equation	A2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Avrami-Erofe'ev equation	A3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Avrami-Erofe'ev equation	A4	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
Diffusion			
Parabolic law	D1	$1/(2\alpha)$	α^2
Valensi equation	D2	$[- \ln(1-\alpha)]^{-1}$	$\alpha + (1-\alpha)\ln(1-\alpha)$
Jander equation	D3	$3(1-\alpha)^{1/3}/2[(1-\alpha)^{-1/3}-1]$	$[1-(1-\alpha)^{1/3}]^2$
Brounshtein-Ginstling equation	D4	$3/2[(1-\alpha)^{-1/3}-1]$	$1-2\alpha/3-(1-\alpha)^{2/3}$
Phase boundary controlled equation			
One dimensional movement	R1	Constant	α
Contracting area	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Contracting volume	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

For isothermal experiments carried out at different temperatures, another form of equation (4.2) is always used:

$$g_j(\alpha) = k_j(T)t \quad (4.4)$$

The subscript j is introduced to emphasise that substituting a particular reaction model into equation (4.4) results in evaluating the corresponding rate constant, which

is obtained from the slope of a plot of $g_j(\alpha)$ versus time t . At each isothermal pyrolysis temperature T_i , the rate constant can be evaluated for each reaction mechanism selected. The Arrhenius parameters are determined in the usual manner according to the Arrhenius equation in the logarithmic form

$$\ln k_j(T_i) = \ln A_{0j} - \frac{E_j}{RT_i} \quad (4.5)$$

For nonisothermal TG analysis, several analytical models have been proposed and employed to estimate the Arrhenius parameters. One of such models is the Coats-Redfern equation (Coats and Redfern, 1964)

$$\ln \left[\frac{g_j(\alpha)}{T^2} \right] = \ln \left[\frac{A_{0j}R}{\beta E_j} \left(1 - \frac{2RT'}{E_j} \right) \right] - \frac{E_j}{RT} \quad (4.6)$$

where T' is the average value of experimental temperatures. Inserting various forms of $g_j(\alpha)$ into equation (4.6) results in a set of Arrhenius parameters. A single pair of E and $\ln A_0$ is chosen as that corresponding to a reaction model, thereby giving the best linearity of the plot $\ln[g_j(\alpha)/T^2]$ versus $1/T$.

4.1.2 Isoconversional Method

Isoconversional method, based on the assumption that the reaction model is independent of heating rate or temperature, has been used to study the kinetics of polymer pyrolysis. It permits the estimation of apparent activation energy without the knowledge of reaction model (Budrugeac *et al.*, 1996). Under isothermal conditions, combining equations (4.4) and (4.5) gives

$$-\ln t_\alpha = \ln \left[\frac{A_0}{g(\alpha)} \right] - \frac{E_\alpha}{RT} \quad (4.7)$$

The plot of $-\ln t_\alpha$ versus $1/T$ is a straight line from which E_α can be determined. A nonlinear procedure reported by Vyazovkin (1997b) can be employed for the determination of E_α from the nonisothermal TG data: based on the fact that $g(\alpha)$ is independent of the heating rate, the ratio of the temperature integral $I(E_\alpha, T_\alpha)$ to the heating rate β is a constant for a set of experiments performed under different heating rates

$$\frac{I(E_\alpha, T_{\alpha,1})}{\beta_1} = \frac{I(E_\alpha, T_{\alpha,2})}{\beta_2} = \dots = \frac{I(E_\alpha, T_{\alpha,y})}{\beta_y} \quad (4.8)$$

where y is the number of heating rates. The apparent activation energy can be evaluated at any particular values of α by finding the value of E for which the function

$$\sum_a^y \sum_{b \neq a}^y \left[\frac{I(E_\alpha, T_{\alpha,a}) \beta_b}{I(E_\alpha, T_{\alpha,b}) \beta_a} \right] \quad (4.9)$$

is a minimum. The minimisation procedure is repeated to find the dependence of apparent activation energy on the extent of conversion.

4.1.3 Analytical Model Fitting Method

4.1.3.1 Coats-Redfern equation

The Coats-Redfern equation (Coats and Redfern, 1964) is:

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2 (1-n)} \right] = \ln \left[\left(\frac{A_0 R}{\beta E} \right) \left(1 - \frac{2RT'}{E} \right) \right] - \frac{E}{RT} \quad (4.10)$$

where T' is the mean experimental temperature. A plot of $\ln \left[(1 - (1 - \alpha)^{1-n}) / ((1 - n)T^2) \right]$ versus $1/T$ results in a straight line with a slope $-E/R$ if the value of n is properly selected and A_0 can be obtained from the intercept.

4.1.3.2 MacCallum-Tanner equation

The MacCallum-Tanner equation (MacCallum and Tanner, 1970) is

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{1 - n} \right] = \log \left(\frac{A_0 E}{\beta R} \right) - 0.483 E^{0.435} - \frac{(0.449 + 0.217 E) \times 10^3}{T} \quad (4.11)$$

By plotting $\log \left[\left(1 - (1 - \alpha)^{1-n} \right) / (1 - n) \right]$ against $1/T$, a straight line can be obtained with correctly chosen value of n . E and A_0 can then be evaluated from the slope and the intercept of the line, respectively.

4.1.3.3 van Krevelen equation

The van Krevelen equation (van Krevelen *et al.*, 1951) is:

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{1 - n} \right] = \ln \left[\frac{A_0}{\beta} \left(\frac{0.368}{T_{ref}} \right)^{E/RT_{ref}} \left(\frac{E}{RT_{ref}} \right)^{-1} \right] + \left(\frac{E}{RT_{ref}} + 1 \right) \ln T \quad (4.12)$$

The plot of $\ln \left[\left(1 - (1 - \alpha)^{1-n} \right) / (1 - n) \right]$ against $\ln T$ gives a straight line for a correctly chosen reaction order, and the values for E and A_0 can be determined from the slope and intercept of the line, respectively.

4.2 PROPOSED MODEL

Most commonly, the conversion functional relationship $f(\alpha)$ is defined to be proportional to the mass quotient of the unreacted material:

$$f(\alpha) = (1 - \alpha)^n \quad (4.13)$$

where n is the index of expansion. Based on the assumptions that the temperature dependence of the rate constant $k(T)$ can be separated from the reaction model $f(\alpha)$ for equation (4.1) and the pyrolysis of Kapton® polyimide is a one-stage reaction, substituting equation (4.13) into equation (4.1) gives:

$$\frac{d\alpha}{dt} = A_0 \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \quad (4.14)$$

The integrated form of equation (4.1) with respect to temperature can be expressed as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} \quad (4.15)$$

For $n = 1$:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = -\ln(1-\alpha) \quad (4.16)$$

For $n \neq 1$:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A_0}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (4.17)$$

Published analytical models such as Coats-Redfern equation (Coats and Redfern, 1964), MacCallum-Tanner equation (MacCallum and Tanner, 1970) and van Krevelen equation (van Krevelen *et al.*, 1951) are applicable to nonisothermal pyrolysis and are derived from equations (4.15) and (4.17).

Under nonisothermal conditions, the temperature is expressed as a function of time

($T = T_0 + \beta \times t$) and equation (4.14) becomes:

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \quad (4.18)$$

When the reaction rate reaches the maximum value and $n \neq 1$, $\frac{d}{dt}\left(\frac{d\alpha}{dt}\right)$ is zero and

differentiation of equation (4.14) with respect to time yields:

$$\begin{aligned} \left(\frac{d^2\alpha}{dt^2}\right)_m &= A_0 \exp\left(-\frac{E}{RT_m}\right) \left(\frac{E}{RT_m^2}\right) \left(\frac{dT_m}{dt}\right) (1-\alpha)_m^n + A_0 \exp\left(-\frac{E}{RT_m}\right) n(1-\alpha)_m^{n-1} \left(-\frac{d\alpha}{dt}\right)_m \\ &= \left(\frac{d\alpha}{dt}\right)_m \times \left[\frac{\beta E}{RT_m^2} - A_0 \exp\left(-\frac{E}{RT_m}\right) n(1-\alpha)_m^{n-1} \right] \end{aligned} \quad (4.19)$$

Equating $\frac{\partial^2 \alpha}{\partial t^2} = 0$ gives

$$\ln \left[\frac{\beta}{n(1-\alpha)_m^{n-1} T_m^2} \right] = -\frac{E}{RT_m} + \ln \left(\frac{A_0 R}{E} \right) \quad (4.20)$$

or

$$\ln \left[\frac{\beta}{n(1-\alpha)_m^{n-1} T_m^2} \right] = -\frac{E}{RT_m} + \ln A_0 - \ln \left(\frac{E}{R} \right) \quad (4.21)$$

where the subscript 'm' refers to the property at maximum reaction rate. Plotting

$\ln \left[\beta / (n(1-\alpha)_m^{n-1} T_m^2) \right]$ against $1/T_m$ gives a straight line if n were properly chosen.

The values for E and A_0 can be separately obtained from the slope and intercept of this line, respectively.

4.3 ANALYSIS OF TG AND DTG DATA

TG curves showing changes in sample weight with time during pyrolysis for various temperatures under isothermal conditions are shown in Figure 4.1. TG and DTG curves for nonisothermal pyrolysis are shown in Figures 4.2 and 4.3, respectively.

Figure 4.1 TG curves of Kapton® 100HN during isothermal pyrolysis

Figure 4.2 TG curves of Kapton®100HN during nonisothermal pyrolysis

Figure 4.3 DTG curves of Kapton®100HN during nonisothermal pyrolysis

The maximum isothermal pyrolysis temperature was chosen so that the weight loss was less than 1% during the first 2 min because too fast and significant decomposition might occur during settling of the experimental temperature at the beginning of the experiments. Under both isothermal and nonisothermal conditions, a single stage of weight loss occurs during the pyrolysis of Kapton® film. The isothermal and nonisothermal TG curves show different mass change characteristics, indicating differences in the reaction mechanism during pyrolysis. For the isothermal experiments carried out at higher temperatures (Figure 4.1), the rate of decomposition is high during the first 200 min and thereafter it tends to slow down. The higher the temperature, the higher is the reaction rate during this initial period of time. The mass changes during isothermal pyrolysis at lower temperatures are moderate and more stable. The weight loss during the first 200 min accounts for 43-73% of the overall weight loss during the whole pyrolysis process for the temperatures shown.

The nonisothermal pyrolysis covered a much wider range of temperatures and the various runs carried out under different heating rates produced nearly the same amount of residues (about 55%) at the final temperature of 1123 K (Figure 4.2). The decomposition of Kapton® 100HN begins at about 773 K and the sample weight decreases significantly within a narrow temperature range of 823-923 K with the evolution of mainly CO and CO₂ as the gaseous products. Beyond this temperature range, the weight change eases, resulting in gradual decreases with increasing temperature due to the evolution of CH₄, H₂ as well as N₂ (Konno *et al.*, 1997, 2001). The nonisothermal TG curves shift to the right-hand side with increasing heating rate because of the shorter time needed to reach a certain temperature. The dependency of the quantity $d\alpha/dT$ on the heating rate is shown in Figure 4.3; $d\alpha/dT$ increases with

increasing temperature initially and thereafter it decreases with increasing temperature.

4.4 KINETIC CALCULATIONS

Based on the various reaction mechanisms given in Table 4.1 and using the Arrhenius equation, the Arrhenius parameters determined from the isothermal TG data of Kapton® 100HN in Figure 4.1 are presented in Table 4.2.

Table 4.2 Arrhenius parameters for isothermal pyrolysis of Kapton® 100HN

Mechanism	E (kJ/mol)	$\ln A_0$ (min ⁻¹)	Correlation
A1	348.10	48.28	0.9952
A2	354.95	48.47	0.9949
A3	359.31	48.71	0.9930
A4	370.01	50.05	0.9956
D1	360.35	48.83	0.9958
D2	346.70	46.70	0.9945
D3	348.43	46.37	0.9954
D4	332.82	43.39	0.9958
R1	365.05	49.37	0.9937
R2	345.58	46.37	0.9949
R3	354.29	47.53	0.9949

Using the Coats-Redfern equation, the kinetic parameters obtained from the nonisothermal TG data in Figure 4.2 based on the various mechanisms (ref. Table 4.1) are given in Table 4.3.

Table 4.3 Arrhenius parameters for nonisothermal pyrolysis of Kapton® 100HN at 2 K/min

Mechanism	E (kJ/mol)	$\ln A_0$ (min ⁻¹)	Correlation
A1	131.69	15.41	0.9796
A2	59.07	4.59	0.9750
A3	34.86	0.90	0.9686
A4	22.76	-0.83	0.9593
D1	228.22	27.34	0.9704
D2	247.73	28.85	0.9536
D3	257.67	30.53	0.9785
D4	246.05	28.36	0.9755
R1	107.33	10.76	0.9664
R2	117.81	12.02	0.9736
R3	122.05	12.41	0.9760

Figure 4.4 Reduced time plots for the reaction mechanisms and Isothermal TG data for Kapton® pyrolysis at 781 K

The Arrhenius parameters estimated by fitting various reaction mechanisms to the isothermal TG data are almost independent of the reaction mechanisms as observed from Table 4.2. Examination of the reduced time plots (Gotor *et al.*, 2000) (Figure 4.4 and t_{α} is the time required to reach a specified conversion, e.g., 90%) suggests that models *R2* and *R3* provide the best fits to the experimental data even though models *D1* and *D4* give the best linear correlation coefficient in Table 4.2. The Arrhenius parameters determined from the non-isothermal TG data (Table 4.3) are highly variable, indicating a strong dependence on the reaction mechanism selected. Based on the correlation coefficient, *A1*, *D3* and *R3* are the best mechanisms for nonisothermal pyrolysis. Examination of Tables 4.2 and 4.3 shows that the reaction mechanism fitting method results in a distinct inconsistency between the kinetic parameters for isothermal and nonisothermal pyrolysis. The reason for this opposing trend may be that the nonisothermal experiments allow fits that vary with the

temperature sensitivity ($E, \ln A_0$) and reaction model $f(\alpha)$ simultaneously while the isothermal runs isolate the temperature as an experimental variable (Vyazovkin and Wight, 1997b). In the reaction model, the choice of the assigned index n is critical and will affect the kinetic parameters that are determined, especially for the nonisothermal pyrolysis tests. Generally, the errors in the functional form of reaction mechanism may be concealed when fitting various models to the nonisothermal TG data, but showing large differences in the resulting kinetic parameters.

Kinetic predictions using the Arrhenius parameters from the reaction mechanism fitting were carried out and some of the results are shown in Figures 4.5 and 4.6. The predicted isothermal curves (Figure 4.5) show that not all the results for the different reaction models are consistent and in agreement with the experimental data although their kinetic parameters are based on high correlation coefficients. The reaction mechanism *D4* has the highest correlation coefficient of 0.9958 as shown in Table 4.2, but the predicted curve based on this model is significantly different from the experimental data. Variations in conversion with time predicted using *R2* and *R3* fit very well to the experimental data although these two models give correlation coefficients lower than those from some other models. As very high correlation coefficients of linear regression are usually obtained for different forms of $f(\alpha)$, one cannot be sure whether the lower values of the correlation coefficient are due to the improper choice of $f(\alpha)$ or the experimental errors inherent to the measurements of TG curves (Budrugeac *et al.*, 1996). So the linear correlation coefficient has the limitation for verifying the correctness of a reaction mechanism in the study of pyrolysis kinetics.

Figure 4.5 Comparison of experimental isothermal TG data (781K) with the predicted data from the mechanisms A1, A2, D2, D4, R2 and R3 (ref. Table 4.1)

Figure 4.6 Comparison of experimental nonisothermal TG data ($\beta=2$ K/min) with the predicted data from the mechanisms A1, D3 and R3 (ref. Table 4.1)

The predicted nonisothermal kinetic curves (Figure 4.6) largely deviate from the experimental data, proving the inapplicability of the reaction mechanism fitting method to the nonisothermal pyrolysis kinetics of Kapton® 100HN.

The application of isoconversional method to the isothermal TG data (pyrolysis temperatures of 781, 786, 796, 800 and 805 K) allows the determination of the apparent activation energy at fixed conversions as shown in Figure 4.7. The apparent activation energy increases from about 228.45 kJ/mol at 3% conversion to about 249.30 kJ/mol at 25% conversion and thence it subsequently decreases with increasing conversion. For the nonisothermal TG data (heating rates of 2, 4, 6, 8 and 10 K/min and temperature range of 673-1123 K), the values for the temperature integral $I(E, T)$ were estimated using the 4th order Runge-Kutta method through a computer program written in C++. The differential equation

$$y' = f(t, y) \quad (4.22)$$

is expressed as:

$$y(t+h) = y(t) + \int_t^{t+h} f(t, y) dt \quad (4.23)$$

The above equation can be solved using the 4th order Runge-Kutta method:

$$y_{l+1} = y_l + h \cdot (k_1 + 2k_2 + 2k_3 + k_4) / 6 \quad (4.24)$$

where

$$k_1 = f(t_l, y_l),$$

$$k_2 = f(t_l + h/2, y_l + k_1 \cdot h/2),$$

$$k_3 = f(t_l + h/2, y_l + k_2 \cdot h/2), \text{ and}$$

$$k_4 = f(t_l + h, y_l + k_3 \cdot h).$$

Applying the above method to Equation (4.17) gives

$$I' = I^0 \cdot \exp(E / RT) = f(T, I) \quad (4.25)$$

$$I_{l+1} = I_l + h \cdot (k_1 + 2k_2 + 2k_3 + k_4) / 6 \quad (4.26)$$

where

$$k_1 = I^0 \cdot \exp(E / RT_l)$$

$$k_2 = (I + k_1 \cdot h / 2)^0 \cdot \exp[E / R / (T_l + h / 2)]$$

$$k_3 = (I + k_2 \cdot h / 2)^0 \cdot \exp[E / R / (T_l + h / 2)]$$

$$k_4 = (I + k_3 \cdot h)^0 \cdot \exp[E / R / (T_l + h)]$$

The values for E shown in Figure 4.7 increase from 223 kJ/mol at 3% conversion to about 356 kJ/mol at 85% conversion. Hence, the apparent activation energy decreases to about 218 kJ/mol near the completion of the pyrolysis cycle.

Figure 4.7 Dependence of the apparent activation energy on the degree of conversion determined using isoconversional method for the isothermal TG data (open squares: $T = 781, 786, 796, 800$ and 805 K) and nonisothermal TG data (open circles: $\beta = 2, 4, 6, 8$, and 10 K/min)

As indicated in Figure 4.7, the values for E from the isothermal and the nonisothermal TG data are not in agreement. The complexity of the reaction mechanism may be revealed in the form of a functional dependence of the apparent activation energy on the degree of conversion (Vyazovkin and Wight, 1997b). Therefore, the different trends shown by the two curves may be indicative of the variation of the reaction mechanism under each heating programme. However, the isoconversional method is not frequently used because it cannot give any other information relating to the pre-exponential factor or reaction model. The variation of the Arrhenius parameters with the extent of pyrolysis poses difficulties in the interpretation of the kinetic data (Vyazovkin and Wight, 1997b). Furthermore, the values for E derived from short-term isothermal experiments may not be suitable to represent the behaviour of pyrolysis because they are usually obtained under temperatures near or above the melting points (Abate *et al.*, 2002).

The nonisothermal TG data for the pyrolysis of Kapton® 100HN were applied to the proposed model and the three analytical models listed in Section 4.1.3. For the proposed model, equation (4.21) was plotted in Figure 4.8 using the data for the temperatures that corresponded to the highest weight-loss rates (as obtained from the DTG plots of $d\alpha/dt$ versus t) in the Kapton® samples for the five different heating rates. The linearity of the relationship is good, demonstrating a close fit for the proposed model. The nonisothermal TG data for a heating rate of 6 K/min and a temperature range of 673-1023 K were applied in conjunction with Coats-Redfern, MacCallum-Tanner and van Krevelen equations to yield the curves as shown in Figures 4.9, 4.10 and 4.11, respectively.

Figure 4.8 Plot of proposed model for the pyrolysis of Kapton® 100HN

Figure 4.9 Plot of Coats-Redfern equation for the pyrolysis of Kapton® 100HN

Figure 4.10 Plot of MacCallum-Tanner equation for the pyrolysis of Kapton® 100HN

Figure 4.11 Plot of van Krevelen equation for the pyrolysis of Kapton® 100HN

Their linearities are not as good as that for the model proposed here. For the purpose of comparison, the kinetic parameters and correlation coefficients for all these models are listed in Table 4.4 whilst the average kinetic parameters are given in Table 4.5.

Table 4.4 Kinetic parameters for the pyrolysis of Kapton® 100HN

Model	β (K/min)	E (kJ/mol)	n	$\ln A_0$ (min ⁻¹)	Correlation
Coats-Redfern	2	142.29	1.32	16.27	0.9814
	4	155.32	1.30	18.59	0.9842
	6	171.34	1.61	21.17	0.9895
	8	162.84	1.59	20.03	0.9857
	10	177.40	1.63	22.24	0.9835
MacCallum-Tanner	2	149.09	1.34	25.79	0.9846
	4	159.53	1.25	27.00	0.9863
	6	178.69	1.62	29.72	0.9898
	8	166.82	1.53	27.73	0.9876
	10	170.62	1.45	28.12	0.9826
van Krevelen	2	168.65	1.64	20.22	0.9876
	4	183.55	1.59	22.74	0.9895
	6	199.89	1.90	25.30	0.9924
	8	196.55	1.94	24.90	0.9905
	10	196.52	1.79	24.90	0.9870
Proposed model	2,4,6,8,10	274.37	2.18	36.40	0.9964

Table 4.5 Average kinetic parameters from the different analytical models

Analytical model	E (kJ/mol)	n	$\ln A_0$ (min ⁻¹)
Coats-Redfern	161.84	1.49	19.66
MacCallum-Tanner	164.95	1.44	27.67
van Krevelen	189.03	1.77	23.61
Proposed Model	274.37	2.18	36.40

The values of E and n derived from Coats-Redfern and MacCallum-Tanner models are in agreement with each other while those from van Krevelen model are slightly higher than the two former models. Using the model proposed in this study, the values for E , n and $\ln A_0$ are 274.37 kJ/mol, 2.18 and 36.40 min⁻¹ respectively, which are different from those determined by the other three equations. Incidentally, the value of E using the isoconversional method in Figure 4.7 is approximately 300 kJ/mol for $\alpha = 0.4$ to 0.5 (correspond to the highest $d\alpha/dT$ value of each curve in

Figure 4.3) and therefore is closer to the value of 274.37 kJ/mol as determined by the proposed model here. In addition, the values for apparent activation energy for Kapton® 100HN decomposition are somewhat higher than those of other polymers due to the commencement of the pyrolysis process at a higher temperature (Chan and Balke, 1997; Regnier and Guibe, 1997; Albano *et al.*, 2000; Lee *et al.*, 2001).

Factors such as temperature, conversion grade and heating rate may influence the pyrolysis kinetics (Chan and Balke, 1997; Regnier and Guibe, 1997; Wang *et al.*, 2000). Heating rate can influence the pyrolysis kinetics in many different ways. On one hand, the kinetic parameters change with the heating rate due to the relationship between the apparatus response and the reactions occurring in the sample. This phenomenon may be resulted from the thermal lag in the instrument as well as in the thermal conductivity of samples (Jimenez *et al.*, 1993; Marin *et al.*, 1996). On the other hand, the diffusion of the gaseous products is so fast that it will not apparently affect the pyrolysis kinetics at low heating rates such as these in the pyrolysis tests reported here. Essentially, polymer pyrolysis is a complicated reaction that is composed of a series of elemental steps, each having its own kinetic parameters (Regnier and Guibe, 1997). The variation of the kinetic parameters, which are dependent on the heating rate, may be an indication of changes in reaction mechanism during the pyrolysis process. In addition, there are some deviations of the true heating rates as compared to the programmed one, which can also lead to different results (Urbanovici and Segal, 1993). With respect to the temperature, kinetic parameters change more or less with it although they are assumed to take the same values with changing temperature (Wang *et al.*, 2000).

The mathematical treatment of the experimental data is another factor that may have influence on the results. Comparisons between the experimental and the predicted conversion versus temperature relationship for the various models are shown in Figure 4.12. The predicted results were obtained using the 4th order Runge-Kutta method for a heating rate of 10 K/min. The deviations of the predicted results from the experimental data are shown in Table 4.6. From Figure 4.12, Coats-Redfern and van Krevelen equations yield better agreement with the experimental data than MacCallum-Tanner equation over the entire temperature range, which is consistent with the deviations shown in Table 4.6. The predicted results based on MacCallum-Tanner equation apparently deviate from the experimental data significantly.

Figure 4.12 Comparison of experimental data with the predicted results from different models for a heating rate of 10 K/min

The deviation ($S = \sqrt{\sum (\alpha_{\text{cal}}(T_j) - \alpha_{\text{exp}}(T_j))^2 / (z - 1)}$, where $\alpha_{\text{cal}}(T_j)$ is the predicted data, $\alpha_{\text{exp}}(T_j)$ is the experimental data and z is the number of data items) for the

predicted data using the kinetic parameters from the proposed model is 0.0398 which is the lowest of all the models. Hence, the predicted curve based on the proposed model is very close to the experimental TG curve.

Table 4.6 Deviation for the predicted nonisothermal TG data for a heating rate of 10 K/min

Model	van Krevelen	MacCallum-Tanner	Coats-Redfern	Proposed model
Deviation	0.0681	0.5921	0.0801	0.0398

Different results are obtained from Coats-Redfern, MacCallum-Tanner and van Krevelen models due to the various approximation techniques used in the integration of equation (4.3) (Hatakeyama and Quinn, 1994). From this point of view, neither the correctness of an analytical model to determine one single parameter nor the validity of approximation technique in solving the integral in equation (4.3) is enough to guarantee the validity of this model. The overall contribution of the apparent activation energy, the pre-exponential factor and the reaction order or the reaction model should be considered and the degree of consistency of the predicted conversion at given temperatures with the experimental data is a more reliable criterion for the evaluation of an analytical model.

CHAPTER 5

INTERMEDIATE STATE BETWEEN POLYIMIDE AND CARBON

This chapter investigated the evolution of the membrane structure and the transport properties from polymer to an intermediate state and to carbon membrane during heat treatment. The change in the transport properties was monitored through single gas permeation tests, and the pore structure of the carbonised membranes was analysed through N₂ (77 K) adsorption, X-ray diffractometry and Raman spectroscopy.

5.1 STRUCTURAL CHARACTERISATION

5.1.1 X-ray Diffraction

Figure 5.1 gives the XRD spectra of the polyimide membrane and the membranes heat treated at different temperatures under nitrogen atmosphere. The X-ray spectrum of the polyimide membrane displays three main characteristic reflections with the peaks at $2\theta \approx 15.10^\circ$, 22.44° and 26.12° and the most intense peak appears at $2\theta \approx 22.44^\circ$. This diffraction pattern elucidates the semi-crystalline nature of the Kapton® polyimide. The membranes heat treated at low temperatures (623-748 K) show very similar X-ray diffraction patterns to that of the original polyimide membrane. In comparison with the precursor, the pyrolysed membranes show a narrower diffraction pattern, indicating an increase in crystallinity. The broad asymmetric peaks around $2\theta \approx 23.78^\circ$ and 23.98° shown by the spectra of Kp-N873 and Kp-N1073 are typical of amorphous carbon and the peaks may be assigned to disordered graphitic 002 planes. With increasing heat treatment temperature from 873 to 1073 K, the 002 peak shifting to higher degree verified the narrowed interplanar

Figure 5.1 XRD spectra for the original Kapton film (1), and the films heat treated at 623, 673, 698, 723, 748, 773, 873 and 1073 K (2-9)

spacing and the development of crystallinity. The average d-spacing values for these two samples determined from Bragg equation were 3.74 and 3.71 Å for 873 and 1073 K, respectively. The membrane heat treated at 773 K gave a broad peak at $2\theta \approx 22.54^\circ$ with an average d-spacing of 3.94 Å, which was similar to the patterns to Kp-N873 and Kp-N1073. However, the sample Kp-N773 was obtained at a temperature whereby the decomposition of the Kapont® polyimide had just begun, according to the TG analysis of the Kapton® film. Thus, sample Kp-N773 possessed certain properties of polymer membrane as well as amorphous carbon membrane. It is an intermediate state between polymer and carbon as proposed by some researchers (Barsema *et al.*, 2004; Shao *et al.*, 2005).

5.1.2 Raman Spectra

The Raman spectra of Kp-N873 and Kp-N1073 in Figure 5.2 shows that the G-peaks are 1593 cm^{-1} and 1592 cm^{-1} and the D-peaks are 1340 cm^{-1} and 1338 cm^{-1} (ref.

Section 3.2.5.6). The G-peak and the D-peak for the two samples were broad and somewhat overlapping, resulting in a smaller separation between the two spectral components. With increasing heat-treatment temperature from 873 K to 1073 K, the carbon membranes showed pronounced decreases in the absorption peak intensity of the G-peak as well as the D-peak. These carbon membranes are amorphous based on the Raman spectra patterns because the D mode is invisible in perfect graphite and only becomes active in the presence of disorder (Ferrari and Robertson, 2000).

Figure 5.2 Raman spectra of the membranes heat-treated at 873 and 1073 K

The intensity of the G-peak (I_G) and the intensity of the D-peak (I_D) were estimated from the two-peak Gaussian curve fitting. A decrease in the I_D/I_G ratio from 2.51 and 2.46 based on the peak width was obtained when the membranes were heat treated from 873 to 1073 K. The in-plane sizes of the graphitic clusters L_a for Kp-N873 and Kp-N1073 were found to be 3.30 nm and 3.36 nm, respectively (ref. Section 3.2.5.6). Based on the L_a values and the peak positions, these two samples

could have nanocrystalline graphitic structures with graphitic cluster diameters of 3.30 nm and 3.36 nm for Kp-N873 and Kp-N1073, respectively. Since the increase of the I_D/I_G ratio is inversely proportional to the crystalline size for the disordered graphite (Yan *et al.*, 2005), a more “ordered” structure was obtained with increasing the heat-treatment temperature from 873 K to 1073 K.

5.1.3 Pore Structure Analysis

Figure 5.3 shows N_2 (77 K) adsorption isotherms of the two carbon membranes Kp-N873 and Kp-N1073. The pore structure properties determined from the adsorption isotherms are shown in Table 5.1. The isotherms show an abrupt increase in the low-pressure region and then become flat with increasing relative pressure. The N_2 (77 K) adsorption isotherm of Kp-N1073 shows a tail as saturation pressure is approached. Both isotherms are typical Type I isotherms as indicated by a solid containing micropores no more than a few molecular diameters in width (Gregg and Sing, 1997).

Figure 5.3 N_2 adsorption isotherms of the membranes heat treated at 873 and 1073 K

Table 5.1 Pore structure properties of the samples obtained at 873 and 1073 K

Sample	BET surface area (m ² /g)	Total pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)
Kp-N873	497.61	0.2354	0.1974
Kp-N1073	334.29	0.1823	0.1464

The carbon membranes obtained at 873 K show higher nitrogen uptake than the membranes obtained at 1073 K, indicating the existence of more pores available for nitrogen adsorption. With increasing heat treatment temperature from 873 K to 1073 K, the BET surface area, the micropore volume and the total pore volume decreased from 497.61 m²/g, 0.1974 cm³/g and 0.2354 cm³/g to 334.29 m²/g, 0.1464 cm³/g and 0.1823 cm³/g, respectively (as shown in Table 5.1). From the TG analysis (Figure 7.1), the decomposition of the precursor commenced around 773 K, showing a maximum weight loss rate around 825 K for a heating rate of 0.5 K/min. The rate of the pyrolysis reaction was very high in the temperature range of 773-873 K, but slowed down after 873 K. The maximum decomposition rate at around 825 K might imply the maximum rate of pore formation. Hence, a large amount of pores including micropores and mesopores might be created whilst holding the temperature at 873 K for 120 min. Further increase in the heat-treatment temperature to 1073 K with a thermal soak time of 120 min resulted in significant shrinkage of the existing pores although certain amount of new pores were generated during the pyrolysis reaction. Consequently, the pores accessible to nitrogen adsorption significantly decreased.

Figure 5.4 Pore size distributions determined from N₂ adsorption using DFT method for the membranes heat-treated at 873 and 1073 K

Figure 5.4 shows the pore size distributions of Kp-N873 and Kp-N1073 as determined by a DFT software (V2.02, Micromeritics). Since the first point in the adsorption isotherm was obtained at a relative pressure of 0.06, the smallest pore size determined was around 20 Å and the pore size distribution in the micropore range could not be obtained. For both samples, small amounts of meso- and macropores existed, contributing very little to the total pore volume.

5.2 GAS PERMEATION PROPERTIES

The effects of heat treatment on the membrane transport properties are shown in Figure 5.5 for temperatures from 623–1073 K. The evolution of the ideal selectivities (ratio of the pure gas permeances) for O₂/N₂ and CO₂/CH₄ with the heat treatment temperature is shown in Figure 5.6. The variation of the gas permeance with the kinetic diameter of the penetrating gas molecules showed the molecular sieving effect of the membranes tested. The membranes heat treated at 623, 673, 698 and 723 K

showed very low and almost identical gas permeances for all the gases tested as seen in Figure 5.5. A heat treatment temperature of 748 K resulted in a certain increase in the gas permeances although this sample exhibited similar XRD patterns as the samples treated at lower temperatures as shown in Figure 5.1. Further increases in the heat-treatment temperatures to 773 and 873 K resulted in significant improvements in the gas permeation rate. However, the membrane heat treated at 1073 K showed very low gas permeances, indicating a drastic change in the pore structure as compared with the membrane treated at 873 K. The change in the gas permeance with the heat treatment temperature was consistent with the results of TG analysis: the decomposition of Kapton® polyimide commenced around 773 K and the weight loss for the temperature range of 773-873 K was dominant.

Figure 5.5 Pure gas permeances for the Kapton® membrane and the membranes heat treated at temperatures of 623-1073 K

Figure 5.6 Ideal selectivities for the Kapton® membrane and the membranes heat treated at temperatures of 623-1073 K

The ideal selectivities for both O₂/N₂ and CO₂/CH₄ decrease with increasing temperature from 623 to 673 K as shown in Figure 5.6. At 673 and 723 K, two minimum values for both selectivities were obtained. As a semi-crystalline polyimide, Kapton® contains both amorphous and ordered regions, and heat treatment around the glass transition temperature (673 K) may improve the concentration of charge transfer complexes (CTCs) and promote further ordering/packing of the polyimide chains (Feger and Franke, 1996). Consequently, the chains in the ordered regions are capable of strong intermolecular interactions and may result in reduced permeation rate of the gas molecules (Dunson, 2000). The minimum selectivities as shown by Kp-N673 and Kp-N723 may be resulted from the enhanced chain mobility and the decreased d-spacing (Shao *et al.*, 2005).

Figure 5.7 Densities of the Kapton® membrane and the membranes heat treated at temperatures of 623-773 K

The values for the true density (ρ_t) as well as the specific volume ($1/\rho_t$) determined for the polyimide membrane and the derived membranes heat-treated between 623 and 773 K are given in Figure 5.7. It could be seen that the two lowest values of density also occurred at the same temperatures of 673 and 723 K which brought about the two minimum ideal selectivities. The heat treatment may affect the concentration of the CTCs which in turn may lead to changes in the polyimide chain packing patterns and the fractional free volume, and therefore bringing about changes in the true density and selectivity. Treatment temperatures higher than 723 K resulted in continuously increased ideal selectivities for O_2/N_2 and CO_2/CH_4 .

The selectivities of O_2/N_2 and CO_2/CH_4 are 6 and 70 for Kp-N873 and 17 and 320 for Kp-N1073, respectively. Since the pores are considered to evolve due to the diffusion of the gaseous products during pyrolysis and the maximum weight change rate occurs around 825 K for a heating rate of 0.5 K/min, it may surmise that the

penetrable pores in the membranes are mainly created during the early stages of decomposition. The increased crystallinity as observed from the Raman spectra analysis and the XRD spectra analysis of Kp-N1073 may account for the sharp decrease in the gas permeances for a temperature of 1073 K: the carbon developing into a more compact structure that is nearly impermeable for the gas molecules although the pyrolysis is in progress and far from completion. The decreased pore volume determined by N₂ (77 K) adsorption is another proof of this suggested occurrence. It can also be deduced, based on N₂ (77 K) adsorption, that the heat treatment at 1073 K leads to more pronounced shrinkage of wide pores as compared to the narrow pores, thereby improving the permselectivities. It should be noted that some wide pores still exist in Kp-N873 and Kp-N1073 as revealed by N₂ adsorption (Figure 5.4). Based on the separation factors shown above, most of the mesopores may not exist as straight pores. Otherwise, the carbon membranes cannot give these separation factors. Consequently, most of the wide pores may not exist as straight pores. They may be connected through micropores, narrow channels between meso- and/or micropores, and the micropores predominantly control the transport properties of the carbon membranes (Zhou *et al.*, 2003).

The membranes that were heat treated at 773 K showed higher gas permeances than the membranes heat treated at lower temperatures but comparable selectivities. These properties may be attributed to the decomposition of the polyimide with heat treatment temperature. Thus, Kp-N773 has an intermediate structure exhibiting properties of both polymeric material and amorphous carbon. The change in the selectivity shown by the membranes obtained at 673-748 K in Figure 5.6 is also an indication of the structural change upon heat treatment. This current study cannot directly prove the possible variations such as the concentration of CTCs, the chain

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mobility, the amorphousness and the crystallinity of the polyimide membrane undergoing heat treatment at the temperatures ranging from 673 to 773 K. Further study is needed to investigate the influences of heat treatment at 673-773 K on the physicochemical properties as well as the structure of the Kapton® polyimide and the separation characteristics of the resulting carbon membranes.

CHAPTER 6

STATISTICAL ANALYSIS OF CARBONISATION PARAMETERS

Carbonisation parameters such as the carbonisation atmosphere (vacuum, inert or oxidative), the final temperature, the heating rate at which the final temperature is attained and the thermal soak time at the final temperature are very important factors that will affect the membrane performances for permeability or permselectivity of a mixture of gases to be separated. Therefore, these four carbonisation parameters were considered in this study to determine the significance of each parameter on the gas permeation properties of the resulting carbon membranes using statistical analysis.

6.1 DESIGN OF EXPERIMENT

In order to reduce the number of experiments without losing much information, a statistical analysis using the 2^{4-1} factorial design of experiment was applied to study the possible influences of the carbonisation parameters on the transport properties of the Kapton® based carbon membranes (Montgomery and Runger, 2003; Steel, 2000). The carbonisation parameters examined were atmosphere (A), final temperature (B), heating rate (C) and thermal soak time (D) at final temperature (Table 6.1). Each parameter had two levels in which the high level (+1) and the low level (-1) of the carbonisation parameters were selected. The 2^{4-1} fractional factorial design was formed by selecting only those treatment combinations that yielded a plus on the *ABCD* effect. Details of the 2^{4-1} design including the main factors as well as the two-factor interactions are given in Table 6.2.

Table 6.1 2^{4-1} Fractional factorial design of experiment

Run	Treatment combination	Basic design			
		A	B	C	D
1	(1)	–	–	–	–
2	ad	+	–	–	+
3	bd	–	+	–	+
4	ab	+	+	–	–
5	cd	–	–	+	+
6	ac	+	–	+	–
7	bc	–	+	+	–
8	abcd	+	+	+	+

Table 6.2 Plus and minus signs for the 2^{4-1} fractional factorial design

Run	A	B	C	D	AB	AC	AD
1	–	–	–	–	+	+	+
2	+	–	–	+	–	–	+
3	–	+	–	+	–	+	–
4	+	+	–	–	+	–	–
5	–	–	+	+	+	–	–
6	+	–	+	–	–	+	–
7	–	+	+	–	–	–	+
8	+	+	+	+	+	+	+

The lowercase letters in Table 6.1 represent the treatment combination. If a letter is present, the corresponding factor is run at the high level in that treatment combination; if it is absent, the factor is run at its low level. The treatment combination with all factors at the low level is represented by (1). For example, treatment combination *ab* indicates that factors *A* and *B* are at the high level while factors *C* and *D* are at the low level. The interactions *CD*, *BD*, *BC*, *BCD*, *ACD*, *ABD* and *ABC* are not included in Table 6.2 because they have the same effects as *AB*, *AC*, *AD*, *A*, *B*, *C* and *D*, respectively. In design of experiment, the main factors and some interactions are called aliases if they have the same effect. For a 2^{4-1} fractional factorial design, the defining relation used to produce the aliases is

$I = ABCD$. The main factors are aliased with the three-factor interactions; for example, the alias of A is

$$A \cdot I = A \cdot ABCD \text{ or } A = A^2BCD = BCD$$

and similarly $B = ACD$, $C = ABD$ and $D = ABC$. The two-factor interactions are aliased with each other; for example, the alias of AB is

$$AB \cdot I = AB \cdot ABCD \text{ or } AB = A^2B^2CD = CD$$

The other aliases are $AC = BD$ and $AD = BC$.

A total of 8 batches of carbon membranes were fabricated, namely, CM1-CM8.

6.2 PORE STRUCTURE ANALYSIS

Figure 6.1 shows the adsorption isotherms of N_2 adsorption at 77 K for samples CM1, CM5 and CM6. Results for these samples were selected because they provided high permeation rates for the test gases studied.

Figure 6.1 Nitrogen adsorption isotherms for the samples CM1 (N_2 , 923 K, 0.5 K/min and 120 min); CM5 (N_2 , 923 K, 4.0 K/min and 300 min) and CM6 (vacuum, 923 K, 4.0 K/min and 120 min)

Figure 6.2 Pore size distributions for the samples CM1 (N₂, 923 K, 0.5 K/min and 120 min); CM5 (N₂, 923 K, 4.0 K/min and 300 min) and CM6 (vacuum, 923 K, 4.0 K/min and 120 min)

Sample CM5 exhibits a type I adsorption isotherm according to IUPAC which is associated with microporous structures, and the adsorption equilibrium is established at a very low relative pressure. Samples CM1 and CM6 give similar adsorption characteristics as the two isotherms are identical in every aspect. The isotherms for CM1 and CM6 are also of type I with the amount adsorbed undergoing a very steep increase at a pressure approaching the saturation. Figure 6.2 shows the pore size distributions for the three samples CM1, CM5 and CM6 that were determined using the DFT software (Micromeritics) over the whole pressure range. A brief introduction of DFT method is given in Appendix A. The sample CM5 is microporous, exhibiting micropores with sizes between 3.93 and 10.01 Å and the micropore volume is 0.1683 cm³/g. CM1 and CM6 exhibit bimodal pore size distributions, having both micropores and macropores. The micropore volumes for CM1 and CM6 are 0.0705 and 0.1772 cm³/g, respectively whilst the corresponding volumes for the wider pores are 0.1796 and 0.1724 cm³/g. Based on the design of experiment (Table 6.2), CM1 and CM6

were prepared at the same carbonisation temperature (B-: 923 K) and thermal soak time (D-: 120 min). Thus, it can be deduced that a low carbonisation temperature (B-) and a short hold time (D-) are favourable for the creation of wider pores. Long thermal soak time (D+) results in the shrinkage of the wider pores and this might be the reason that no wider pores were detected in the sample CM5 although it was also prepared at the low carbonisation temperature (B-). The presence of macropores, even in small quantities, will lead to poor molecular sieving capability as all the gases can easily penetrate through the membrane without any hindrance.

6.3 STATISTICAL ANALYSIS

6.3.1 Determining Carbonisation Parameter Effects

Based on the results of the pure gas permeation, the significance of the carbonisation parameters and their interactions are evaluated by hypothesis testing. Statistically, it is named a type I error if a null hypothesis is rejected when it is true and the probability of a type I error is α_{st} . A value of this probability is usually specified and called the significance level. The probability value represented by the p_{st} value is the smallest level of significance that will lead to rejection of the null hypothesis. A significance value of 0.1 was selected to evaluate which parameters would have significant influences on the gas permeation rate, which is a tool to reveal the pore structural properties of the membrane. The software Minitab® 14 (Minitab Inc.) was used to perform the statistical analysis and a factorial fit was performed when determining the effects of each factor. The regression model is

$$\hat{y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 \quad (6.1)$$

where β_0 , β_1 , β_2 , β_3 , β_4 , β_{12} , β_{13} and β_{14} represent the regression coefficients (given in Table 4) while x_1 , x_2 , x_3 and x_4 are the coded variables ($-1 \leq x_i \leq +1$)

representing A , B , C and D , respectively. If no degrees of freedom were available to generate the p_{st} values, all the main effects and the 2-factor interactions with relative large estimates were used in a new regression analysis. The linear combinations of the observations used to estimate of the main effects of A , B , C and D are

$$l_A = A + BCD = \frac{1}{4}[-(1) + ad - bd + ab - cd + ac - bc + abcd]$$

$$l_B = B + ACD = \frac{1}{4}[-(1) - ad + bd + ab - cd - ac + bc + abcd]$$

$$l_C = C + ABD = \frac{1}{4}[-(1) - ad - bd - ab + cd + ac + bc + abcd]$$

$$l_D = D + ABC = \frac{1}{4}[-(1) + ad + bd - ab + cd - ac - bc + abcd]$$

The linear combinations of the observations used to estimate the two-factor interactions are

$$l_{AB} = AB + CD = \frac{1}{4}[(1) - ad - bd + ab + cd - ac - bc + abcd]$$

$$l_{AC} = AC + BD = \frac{1}{4}[(1) - ad + bd - ab - cd + ac - bc + abcd]$$

$$l_{AD} = AD + BC = \frac{1}{4}[(1) + ad - bd - ab - cd - ac + bc + abcd]$$

With reference to Table 6.3, an illustration of the regression model used to analyse the effects of CO₂ permeability is:

$$Y = 352.8 - 139.4A - 272.5B + 31.3C - 126.1D + 105.9AB + 134.6AC - 43AD \quad (6.2)$$

The estimates of the effects, the coefficients and the probability values determined using Minitab are given in Table 6.3.

Table 6.3 Results of factorial fit from Minitab

Predictor	He			CO ₂		
	Effect	Coefficient	p_{st}	Effect	Coefficient	p_{st}
Constant		274.5	0.085		352.8	0.077
A	-98.8	-49.4	0.409	-278.7	-139.3	0.191
B	-413.5	-206.8	0.113	-545.0	-272.5	0.100
C	152.6	76.3	0.287	62.7	31.3	0.599
D	-152.4	-76.2	0.288	-252.2	-126.1	0.209
AB+CD	74.0	37.0	---	211.8	105.9	0.246
AC+BD	158.0	79.0	0.279	269.1	134.6	0.197
AD+BC	-165.3	-82.6	0.268	-86.0	-43.0	---

Predictor	O ₂			N ₂		
	Effect	Coefficient	p_{st}	Effect	Coefficient	p_{st}
Constant		102.11	0.011		39.76	0.066
A	-56.65	-28.33	0.038	-9.59	-4.79	0.455
B	-139.74	-69.87	0.015	-36.14	-18.07	0.144
C	-1.61	-0.80	0.717	-17.73	-8.86	0.280
D	-79.98	-39.99	0.027	-32.68	-16.34	0.159
AB+CD	61.30	30.65	0.035	8.32	4.16	---
AC+BD	68.32	34.16	0.031	30.93	15.46	0.167
AD+BC	-3.38	-1.69	---	8.46	4.23	0.495

6.3.2 Analysis of Main Effects

The main effect plots shown in Figures 6.3(1-4) illustrate the influences of each carbonisation parameter. The final temperature (B) gives the lowest p_{st} values which are either less than 0.1 or slightly higher than 0.1. Therefore, the final temperature may be the controlling parameter for the formation and development of membrane structure during the carbonisation process. The steepest slope shown by the final temperature effect plots (Figures 6.3(1-4)) is further proof of its significance. Similar conclusions were reached for the Matrimid® precursor (Steel, 2000; Steel and Koros, 2003). Due to the large p_{st} values for He and N₂ permeations and the low p_{st} values for CO₂ and O₂ permeations, the carbonisation atmosphere (A) may be important for the pores in certain size ranges. Comparing with the final temperature, the carbonisation atmosphere shows lesser influence judging from the slope of the main effect plots.

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Figure 6.3(1) Main effect plots (Minitab) for the permeabilities of He

Figure 6.3(2) Main effect plots (Minitab) for the permeabilities of CO₂

Figure 6.3(3) Main effect plots (Minitab) for the permeabilities of O₂ **Figure 6.3(4) Main effect plots (Minitab) for the permeabilities of N₂**

The heating rate (C) is insignificant because its p_{st} values in Table 6.3 are much larger than 0.1 for all the gases selected. It can be seen from Figures 6.3(1-4) that increasing the heating rate (C) from 0.5 to 4 K/min increases the permeabilities for He and CO₂, but decreases the permeability for N₂ and does not affect the permeability for O₂. Therefore, increasing the heating rate selectively promotes the development of narrower pores and reduces the quantities of larger pores although its influence may not be too significant. The thermal soak time (D) yields low p_{st} values for O₂ and N₂ permeations but high p_{st} values for He and CO₂ permeations, indicating that this parameter may be significant for the larger pores. The main effect plots in Figures 6.3(1-4) show that changing the pyrolysis atmosphere from nitrogen to vacuum, increasing the final temperature from 923 to 1073 K, or prolonging the thermal soak time from 120 to 300 min result in decreased permeabilities for each of the gases.

6.3.3 Analysis of Interaction Effects

The influences of the interactions are given in Figures 6.4(1-4). Since the analyses of the main effect plots show that the carbonisation temperature (B) has significant influences on the transport properties of the carbon membranes, the interaction of this factor with the other three factors will be discussed first. Figures 6.4(1-4) show that low carbonisation temperature (B-) coupled with nitrogen atmosphere give higher gas permeabilities, but reduced permeabilities are observed for both carbonisation atmospheres when the final temperature increases from 923 to 1073 K. It is also noted that the slope of the line for the nitrogen atmosphere is the steeper of the two atmospheres for the four gases studied. Therefore, it is surmised that the final temperature has a greater effect on carbonisation under nitrogen atmosphere than that for vacuum condition.

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Figure 6.4(1) Interaction effect plots (Minitab) for the permeabilities of He

Figure 6.4(2) Interaction effect plots (Minitab) for the permeabilities of CO₂

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Figure 6.4(3) Interaction effect plots (Minitab) for the permeabilities of O₂

Figure 6.4(4) Interaction effect plots (Minitab) for the permeabilities of N₂

Usually, carbon prepared from the pyrolysis of organic materials has a turbostratic structure, in which layer-planes of graphite-like structures are dispersed in the non-crystalline carbon. Various types of pores with diameters of several angstroms may exist at the surface and inside the structure through which the gas molecules can penetrate. The CMSMs for gas separation carbonised at temperatures lower than 1273 K have more of these voids and the crystallisation proceeds at elevated carbonisation temperatures, resulting in narrower and smaller cross-linked voids and interplanar spacing (Sedigh *et al.*, 1999). The change in the permeation rate with the carbonisation temperature shown in this study is consistent with those reported by other researchers (Petersen *et al.*, 1997; Steel and Koros, 2003). Nitrogen flow is believed to accelerate the decomposition reaction through increased heat and mass transfer to form a more open porous membrane, thus leading to higher gas permeation rate (Geiszler and Koros, 1996; Vu *et al.*, 2002).

For a carbonisation temperature of 923 K, a variation of the heating rate from 0.5 to 4 K/min does not apparently affect the permeability for O₂ but brings about increased permeabilities for He and CO₂ and decreased permeability for N₂. The influence of varying heating rate on gas permeability at 1073 K is negligible for all the four gases. Lower heating rate will lead to the commencement of decomposition at lower temperature and lower reaction rate as shown in Figures 6.4(1-4). The rate of generation and diffusion of the gaseous products from the pyrolysis process have apparent influence on the pore structure evolution of the resulted carbon membranes (Wei *et al.*, 2000). At a final temperature of 923 K, the decomposition of the polyimide continued and some new pores were created for which the influence from the heating rate was still prevalent as shown in Figures 6.4(1-4). However, the rate of decomposition was small and became almost identical for different heating rates when

the temperature was up to 1073 K. Normally, carbonisation up to 1073 K results in significant shrinkage of the pores for all sizes and thus very low permeation rates for all the gases will be obtained as shown in Figures 6.4(1-4). Low carbonisation temperature at 923 K coupled with prolonged thermal soak time result in decreased gas permeabilities whilst no changes in the gas permeabilities are found with thermal soak time at a carbonisation temperature of 1073 K (Figures 6.4(1-4)). Increasing the thermal soak time at a carbonisation temperature of 923 K, the pore structures within the membrane slowly shrink, thereby decreasing the permeation rate for all the gases even though some new pores may be created during the additional soak time. At a final temperature of 1073 K, the pores in all sizes shrink due to increased crystallisation; the effect of thermal soak time does not seem to affect the pore structure because of the dominant effect of the carbonisation temperature.

The interaction between the carbonisation atmosphere and the heating rate also shows some effects on the transport properties of the carbon membranes, and among the interactions, nitrogen atmosphere (A-) coupled with low heating rate (C-) lead to high gas permeation rates for most cases. Under nitrogen atmosphere, increasing heating rate does not show any apparent effect on He permeation but decreases the permeabilities for CO₂, O₂ and N₂. However, under vacuum atmosphere, increasing heating rate increases the permeabilities for all the gases. In both cases, there is an apparent relationship between the extent of influence of the carbonisation atmosphere and the size of gas molecules. Prolonging the thermal soak time from 120 to 300 min results in decreased permeation rates for CO₂, O₂ and N₂ under both carbonisation atmospheres. Further shrinkage of the pores with prolonged thermal soak time may be responsible for this trend. Increasing thermal soak time (D+) under vacuum decreases the permeability for He, but has no effect when subjected to nitrogen atmosphere. A

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possible reason is that prolonged carbonisation under nitrogen atmosphere tends to open up the pores which is over counteracted by the shrinkage of pores resulting from increased thermal soak time, thereby resulting in slightly smaller pore sizes. However, this has no apparent effect on the He molecules due to its smaller molecular size but not to the larger molecules of CO₂, O₂ and N₂.

The interaction plots of the heating rate and the thermal soak time show that varying the thermal soak time at a heating rate of 4 K/min does not appear to affect the permeation of He, CO₂ and O₂ but decreases the permeability for N₂. Lower heating rate (C-) coupled with prolonged thermal soak time (D+) reduce the permeation rate for all the gases. As shown in Figure 4.2, the TG curves shift to the right with increasing heating rate, which means that the decomposition of the precursor commences at a lower temperature for a lower heating rate. Therefore, the pore structure in the membrane is more fully developed at a lower heating rate before a certain final temperature is reached, and prolonged thermal soak time would lead to shrinkage of the pores to some extent, thereby resulting in decreasing permeabilities for all gases.

CHAPTER 7

EVOLUTION OF MEMBRANE STRUCTURE DURING CARBONISATION

During the carbonisation of the polymeric film, an amorphous porous membrane structure is formed by the evolution of the gaseous products resulting from the rearrangement of the molecular structure of the starting precursor. The development of the membrane structure during carbonisation has a significant impact on the transport properties of resulting carbon membrane. The effects of vacuum, argon, helium and nitrogen atmospheres on the development of the membrane structure and the transport properties during carbonisation were investigated. The effect of membrane thickness on the membrane properties was also examined. The resulting carbon membranes were characterised using CO₂ adsorption at 273 K, N₂ adsorption at 77 K, X-ray diffraction, Raman spectroscopy and single gas permeation measurements.

7.1 CARBON MEMBRANES FROM DIFFERENT TEMPERATURES

7.1.1 Thermogravimetry of Kapton® Film

The thermogravimetric curve of Kapton® 100HN film at a heating rate of 0.5 K/min is shown in Figure 7.1. Differential thermogravimetric (DTG) curve showing the weight change per unit time is also shown in Figure 7.1. At a heating rate of 0.5 K/min, the pyrolysis of Kapton® 100HN covered a wide range of temperature with a residue around 55% at the final temperature. The Kapton® 100HN begins to decompose around 773 K and the sample weight decreases significantly within a narrow temperature range of 773-923 K. The decomposition of Kapton® film 100HN

Figure 7.1 TG and DTG curves for the pyrolysis of Kapton® 100HN

gives rise to a simple DTG peak and the maximum weight loss rate occurs around 825 K. According to Jones and Koros (1994a), heat treatment at higher temperatures will lead to higher crystallinity, higher density and narrower interplanar spacing of the pyrolysed carbon. Pyrolysis at high temperature with low heating rate and long soak time is thus helpful to minimize the effective pores except for diminishing the possibility of the formation of cracks in the resulting carbon membranes.

7.1.2 X-ray Diffraction Pattern

The X-ray diffraction profiles for the original Kapton® 100HN and the carbon membranes prepared at different temperatures under vacuum atmosphere are given in Figure 7.2. The relationship between the carbonisation temperature and the diffraction angle as well as the resulting crystallographic parameter d-spacing obtained from the X-ray diffraction profiles are shown in Figure 7.3. Compared to the precursor, the carbonised membranes showed an increasing crystallinity with increasing temperature

Figure 7.2 XRD profiles for Kapton® 100HN and the membranes carbonised at different temperatures under vacuum

Figure 7.3 Relationship between carbonisation temperature and XRD parameters of the carbon membranes prepared under vacuum

as observed from the diffraction patterns. In addition, each membrane sample had a different full width at half maximum value of (002) peak, which is a strong evidence of the different micropore structures as shown in Figure 7.3. The spectra of the carbon membranes show broad asymmetric peaks around $2\theta \approx 25^\circ$, which is typical of amorphous carbon and the peak may be assigned to disordered graphitic (002) planes. Another very weak peak appears around $2\theta \approx 43^\circ$ with d-spacing of 2.10 Å which is the same d-spacing as the (100) plane in graphite. As shown in Figure 7.3, the (002) peak shifts to higher degree with increasing carbonisation temperature, verifying the narrowing interplanar spacing and development in crystallinity. With increasing temperature of 823, 873, 973, 1073, 1173, and 1273 K, carbonisation under vacuum resulted in membranes with average d-spacing values of 3.85, 3.78, 3.76, 3.72, 3.70 and 3.65 Å, respectively.

7.1.3 Pore Structure Analysis

N₂ and CO₂ adsorption tests were performed on the carbon membranes obtained at different temperatures under vacuum. Figure 7.4 shows the CO₂ adsorption isotherms for the membranes carbonised at different temperatures. For this 0-0.03 range of relative pressures, the isotherms obtained are for microporous materials. During the early stages of carbonisation, with increasing temperature from 823 to 973 K, the CO₂ uptakes for CM-V823, CM-V873 and CM-V973 increase significantly over the entire relative pressure range covered. This trend is an indication of the development of microporosity with increasing temperature during the heat treatment process. However, further increase in the carbonisation temperature up to 1173 K show the CO₂ uptakes remaining nearly the same for CM-V973, CM-V1073 and CM-V1173. This indicated a slow down of the microporosity development with increasing temper-

Figure 7.4 CO₂ adsorption isotherms of the carbon membranes prepared at different temperatures under vacuum atmosphere

Figure 7.5 DR plots of CO₂ adsorption for the samples prepared at different temperatures under vacuum

-ature for these samples. The increased CO₂ uptake of the carbon membrane carbonised at 1273 K shows an increased microporosity development for CM-V1273 after the last stagnated phase.

The CO₂ adsorption isotherms were analysed using Dubinin-Radushkevich (DR) equation. The DR plots are shown in Figure 7.5 and the textural parameters calculated by the DR method from the CO₂ adsorption data are given in Table 7.1.

Table 7.1 Textural parameters determined from CO₂ adsorption isotherms

Sample	DR method	
	V ₀ (cm ³ /g)	E ₀ (kJ/mol)
CM-V823	0.16	22.75
CM-V873	0.22	22.84
CM-V973	0.25	23.72
CM-V1073	0.23	24.85
CM-V1173	0.23	24.32
CM-V1273	0.34	21.95

The DR plots in Figure 7.5 are typical patterns for microporous materials. Strictly, each DR plot was composed of two linear branches. This branched pattern, which is an indication of a change in the microporous structure, is more obvious for the samples CM-1173 and CM-1273. In Table 7.1, the characteristic energy increased with increasing carbonisation temperature until a maximum value was reached, and thereafter it decreased with increasing temperature. The increase in the characteristic energy reflects the narrowing of existing pores, and the simultaneous enhancement in the micropore volume indicates further development in microporosity. Consequently, some new pores were created with increasing heat treatment temperature while some existing pores shrank. For carbonisation temperatures greater than 1073 K, the characteristic energy decreased whilst the micropore volume increased, indicating the development of new pores overwhelming the shrinkage of existing pores (some pores had shrunk such that they were not detectable by CO₂ adsorption). Based on the

results from X-ray diffraction tests (Figure 7.3), the average d-spacing gradually decreased with increasing carbonisation temperature. This trend implies the continuous shrinkage of existing pores and the development of new pores with increasing carbonisation temperature.

Figure 7.6 gives the pore size distributions determined by the Horvath-Kawazoe (HK) method for the six samples subjected to various carbonisation temperatures. Generally, it shows that the total pore volume increases with increasing carbonisation temperature as increasing new pores are generated. The shrinkage of existing pores with increasing temperature might be too evident as these pores had shrunk to sizes which might not be detected by CO₂ adsorption.

Figure 7.6 Pore size distributions obtained from CO₂ adsorption (samples 1-6 represent CM-V823, CM-V873, CM-V973, CM-1073, CM-V1173 and CM-V1273)

The N₂ adsorption (77 K) isotherms for the carbon membranes prepared under vacuum are given in Figure 7.7. The carbonisation temperature shows marked influence on N₂ uptake: the N₂ uptake increases with increasing temperature from 823

K to 873 K, followed by significant decreases with further temperature increases up to 1073 K, and finally it increases again up to 1273 K after a minimum value at 1073 K. As shown in Figure 7.1, the decomposition rate of Kapton® at a heating rate of 0.5 K/min is high in the temperature range of 773-873 K but it tends to slow down after 873 K. During this period of decomposition, a large amount of pores including micropores and mesopores were created. The increase in carbonisation temperature from 873 up to 1073 K resulted in significant shrinkage of large pores although a certain amount of new pores were generated. Thus, the pores accessible to N₂ molecules decreased accordingly. When the temperature was higher than 1073 K, some new pores might be created due to further cleavage or rearrangement of some bonds. Therefore, the nitrogen uptake increased again with increasing carbonisation temperature up to 1273 K although some large existing pores shrank to dimensions that were not permeable for nitrogen molecules.

Figure 7.7 N₂ adsorption isotherms of the carbon membranes prepared at different temperatures under vacuum atmosphere

Figure 7.8 shows the pore size distributions determined from N_2 adsorption isotherms. Generally, the pore volume of the mesopores for each sample was very low. For the samples carbonised at the lowest temperature of 823 K, the pores showed a multi-mode distribution. With increasing carbonisation temperature, the pore volume of the mesopores decreased significantly and the pore size distribution became a single-mode one. The mesopores within CM-V873 had the highest pore volume among the samples tested, and the samples carbonised at 1173 and 1273 K contained pores in a very narrow range.

Figure 7.8 Pore size distributions of the mesopore range determined from N_2 adsorption

It should be noted that the pores determined by N_2 adsorption are between 17.6 and 81.8 angstrom whilst the pores determined by CO_2 adsorption are in the range of 4-8.5 angstrom. However, the CO_2 and N_2 adsorption isotherms showed that carbonisation opened up or sintered the micropores within the membranes and provided useful information on the variation of micropore volume after pyrolysing the thermal labile

phases within the polymeric precursor although the contribution of the pores in the range of 8.6-17.5 angstrom could not be determined (Kim *et al.*, 2005).

7.1.4 Gas Permeation Properties

The single gas permeation properties through the carbon membranes carbonised at different temperatures under vacuum were tested with an upstream pressure of 1 atm and the results are given in Table 7.2.

Table 7.2 Permeation properties of the carbon membranes

Sample ID	Permeance [10^{-10} mol/(m ² ·s·P _a)]				
	He	CO ₂	O ₂	N ₂	CH ₄
CM-V823	25.60	20.88	3.24	0.68	2.16
CM-V873	74.30	87.32	16.89	10.10	9.80
CM-V973	42.47	41.45	11.57	2.75	1.31
CM-V1073	18.22	8.03	4.75	0.30	0.27
CM-V1173	7.26	0.79	0.26	0.013	0.006
CM-V1273	0.78	0.041	0.015	0.007	0.004

The modification of gas permeation rate is an indication of the porous membrane structure resulting from the change in the carbonisation temperature. The order for the gas permeances is not always exactly in accordance with the order of the kinetic gas diameter, for instance, some samples giving higher permeances for CO₂ than He although He has a smaller molecular size. The higher permeation rate of CO₂ over He indicates that the transport of CO₂ through these carbon membranes may be aided by a surface diffusion mechanism besides the usual molecular sieving action. For the samples tested in Table 7.2, a carbonisation temperature of 873 K yielded the highest permeation rates for all the gases tested. Beyond 873 K, increasing carbonisation temperature resulted in decreasing gas permeances. When the carbonisation temperature was higher than 1073 K, the membrane samples exhibited very low permeances for all the gases tested, indicating that most of the pores were not permeable to the gases. This carbonisation temperature effect agrees with the results

from other researchers (Rao and Sircar, 1993b; Centeno and Fuertes, 1999). From Figure 7.6, CO₂ adsorption showed that sample CM-V1273 had the highest micropore volume whilst in Table 7.2 it produced the lowest gas permeances. Additionally, in Figure 7.7, N₂ adsorption showed that sample CM-V1073 had the lowest nitrogen uptake, even much lower than sample CM-V1273. However, sample CM-V1073 had much higher gas permeances than sample CM-V1273. Thus, it seemed that there were some inconsistencies between the results from the gas adsorption experiments and the gas permeation tests. Based on the N₂ adsorption experiments, the pores that were developed during carbonisation include micropores and mesopores; both of which would contribute to gas permeation. For instance, the total pore volume determined by the t-plot method to the N₂ adsorption isotherms in Figure 7.7 were 0.0509, 0.1065 and 0.0460 cm³/g for the samples CM-V823, CM-V973 and CM-V1173 whilst the micropore volumes for the three samples were 0.0308, 0.1003 and 0.0357 cm³/g, respectively. Therefore, the fraction of mesopore volume constituted 39%, 6% and 22% of the total pore volume for the three samples CM-V823, CM-V973 and CM-V1173, respectively. Judging from the fact that CM-V823 showed the ideal separation factors of 37.59, 30.68, 4.77, and 9.67 for He/N₂, CO₂/N₂, O₂/N₂ and CO₂/CH₄ (based on the values given in Table 7.2), most of the mesopores might not exist as straight pores. Otherwise, the membranes would not give these separation factors (Zhou *et al.*, 2003). Therefore, it may be deduced that most of the mesopores in the carbonised membranes are connected through micropores, narrow channels between meso- and/or micropores, and the micropores predominantly control the transport properties of the membranes.

7.1.5 Gas Separation Properties

The O₂/N₂ separation properties of the membranes carbonised at 873-1273 K under vacuum are shown in Table 7.3.

Table 7.3 Separation properties of the carbon membranes

Sample	O ₂ /N ₂ selectivity
CM-V873	4.84
CM-V973	6.48
CM-V1073	11.46
CM-V1173	5.43
CM-V1273	3.18

It could be observed that the carbon membranes obtained exhibited certain molecular sieving properties. With increasing carbonisation temperature, the selectivity for a gas mixture of O₂/N₂ gradually increased and reached a maximum value at a temperature of 1073 K. Further increases in the temperature beyond 1073 K resulted in decreasing selectivities. Since the decomposition of Kapton® 100HN commenced around 773 K and the rate of weight loss reached a maximum value around 825 K (Figure 7.1), the pores created by the evolution of the gaseous products generated during the pyrolysis process started to form during this early stage of decomposition. Sample CM-V873 which showed high gas permeances but low selectivities, provided an indication of the pore structure development and the formation of comparatively large pores with respect to gas permeation. With increasing carbonisation temperature from 873 to 1073 K under vacuum, the selectivity increased (Table 7.3) accompanied by decreasing gas permeation rate (Table 7.2). Since the weight change after 973 K was marginal (Figure 7.1), it could be surmised that the modification of the molecular sieving effect resulted mainly from the shrinkage of existing pores. Therefore, the more serious shrinkage of large pores than small pores was the reason for the increased O₂/N₂ selectivity of CM-V1073. The very low permeances for the gas species (Table 7.2) and small values of selectivity (Table 7.3) for O₂/N₂ shown by

CM-V1173 and CM-V1273 might be attributed to the overall shrinkage of the pore structure and the more serious shrinkage of small pores. This trend is different from that reported by Suda and Haraya; the carbon membranes carbonised at 1273 K showed the highest selectivity than those carbonised at lower temperatures (Suda and Haraya, 1997).

7.2 CARBON MEMBRANES FROM DIFFERENT ATMOSPHERES

7.2.1 Thermogravimetric Analysis

Figure 7.9 shows the weight change of the Kapton® polyimide during heat treatment under argon, helium and nitrogen atmospheres. The relationship of thermal conductivity for the three gases in the temperature range of 873-1073 K is $\lambda_{He} \gg \lambda_{N_2} > \lambda_{Ar}$, and the thermal conductivity of helium increases more significantly with increasing temperature than those of nitrogen and argon (Jacobsen *et al.*, 2003).

Figure 7.9 TG data of Kapton® 100HN under argon, helium and nitrogen atmospheres

As observed in the TG tests, the temperatures of the sample under argon, helium and nitrogen atmospheres were 858, 875 and 863 K, respectively, when the programmed

temperature was 873 K and 1049, 1072, and 1055 K, respectively, when the programmed temperature was 1073 K. Corresponding temperatures are 818 and 1027 K for vacuum atmosphere as determined in the pyrolysis system (Figure 3.1). Under the argon atmosphere, the largest temperature difference between the sample and the furnace was observed during the whole heating process. By comparison, the pyrolysis under helium proceeded at the highest temperature among the three atmospheres and gives the lowest amount of residue.

In Figure 7.9, the decomposition of the Kapton® polyimide under different atmospheres commences around 773 K and the sample weight decreases significantly within a narrow temperature range of 773-923 K. The TG curves under different atmospheres are quite identical before 873 K, but start to differ from each other at higher temperatures. At the final temperature of 1073 K, the weight loss under argon atmosphere was the least whilst the largest weight loss occurred under helium atmosphere. It has been reported that CO and CO₂ are the main gaseous products evolved during this temperature range, beyond which the weight change eases, resulting in gradual decreases with increasing temperature due to the evolution of CH₄, H₂ as well as N₂ (Hatori *et al.*, 1996; Konno *et al.*, 1997, 2001). However, the decomposition rate under helium atmosphere was still significant beyond 923 K. At the end of the heat treatment for a programmed temperature range of 673-1073 K, the weight loss during the pyrolysis under argon, helium and nitrogen atmospheres were 44.30%, 53.79% and 46.29%, respectively.

The apparent activation energy for the pyrolysis of the Kapton® polyimide under different atmospheres was determined using the Coats-Redfern equation (Coats and Redfern, 1964):

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2 (1-n)} \right] = \ln \left[\left(\frac{A_0 R}{\beta E} \right) \left(1 - \frac{2RT'}{E} \right) \right] - \frac{E}{RT} \quad (7.1)$$

where T' is the mean experimental temperature and the rest of the parameters are defined in Chapter 4. For the pyrolysis processes carried out under argon, helium and nitrogen atmospheres at a specified temperature program up to 1073 K, the values for the apparent activation energy estimated using equation (7.1) were 395.01, 196.35 and 237.25 kJ/mol, respectively.

7.2.2 X-ray Diffraction Patterns

Figure 7.10 shows the XRD spectra for the Kapton® polyimide and the carbon membranes obtained under different carbonisation atmospheres. The label of the carbon membrane specified the pyrolysis atmosphere, temperature and hold time. For instance, CM-Ar873H2 denotes carbon membrane which was pyrolysed under argon atmosphere at 873 K for 2 h.

Figure 7.10 XRD spectra of the precursor (1) and the carbon membranes (2-9: CM-Ar873H2, CM-He873H2, CM-N873H2, CM-V873H2, CM-Ar1073H2, CM-He1073H2, CM-N1073H2, and CM-V1073H2)

In order to clearly show the X-ray diffraction patterns, the profiles were shifted accordingly without affecting the diffraction angles. After the Kapton® film had been carbonised under various atmospheres, the spectra of the carbon membranes showed an intense broad peak around $2\theta \approx 24^\circ$. This peak is typical of amorphous carbon and may be assigned to the disordered graphitic (002) planes.

Figure 7.11 X-ray diffraction angle and d-spacing of the carbon membranes prepared at 873 K (1-4) and 1073 K (5-8) under argon (3.66 Å), helium (2.6 Å), nitrogen (3.64 Å) and vacuum atmospheres

Increasing the carbonisation temperature from 873 K to 1073 K, the diffraction angle for the carbon membranes obtained under each carbonisation atmosphere increases as shown in Figure 7.11. Carbonisation under argon, helium, nitrogen and vacuum results in the average d-spacing of 4.04, 3.91, 3.98 and 3.91 Å, respectively, for the temperature of 873 K and 3.75, 3.72, 3.72 and 3.68 Å, respectively, for the temperature of 1073 K (Figure 7.11). Clearly, the increase in the carbonisation temperature for each atmosphere resulted in appreciable development toward a more ordered carbon structure. However, the effect of carbonisation atmosphere on the

average d-spacing was less significant. The narrow d-spacing shown by the samples carbonised under helium was attributed to the fact that the decomposition proceeded at a higher temperature compared to argon and nitrogen atmospheres for the same heating program. Another very weak peak appears around $2\theta \approx 43^\circ$ (Figure 7.10) with an average d-spacing of 2.10 Å; the same d-spacing as the (100) plane in graphite.

7.2.3 Raman Spectra

Figure 7.12 shows the Raman spectra for the carbon membranes prepared under different carbonisation atmospheres. These carbon membranes are amorphous based on the Raman spectra patterns because the D mode is invisible in perfect graphite and only becomes active in the presence of disorder (Ferrari and Robertson, 2000). The intensities of the G-peak (I_G) and the D-peak (I_D) were estimated from the two-peak Gaussian curve fitting.

Figure 7.12 Raman spectra for the carbon membranes (1-8: CM-Ar873H2, CM-Ar1073H2, CM-He873H2, CM-He1073H2, CM-N873H2, CM-N1073H2, CM-V873H2 and CM-V1073H2)

In Figure 7.12, the adsorption intensity of the D-peak around 1350 cm^{-1} decreases when the carbonisation temperature is increased from 873 K to 1073 K for each atmosphere. Similarly, the adsorption intensity of the G-peak around 1580 cm^{-1} also decreases with increasing carbonisation temperature. The change in the G-peak with temperature was contrary to the result reported by Kim *et al.* (Kim *et al.*, 1998) which showed increasing G-peak intensity for the carbon films from Kapton® with a thickness of $125\text{ }\mu\text{m}$.

Fig 7.13 Plot of the intensity ratio of D-peak and G-peak for the membranes carbonised under argon, helium, nitrogen and vacuum; on the right scale, the intensity ratio R is related to the crystallite size L_a

For the carbon membranes obtained from each atmosphere in Figure 7.13, the intensity ratio (I_D/I_G) of the D-peak and the G-peak decreases for increasing carbonisation temperature from 873 K to 1073 K. The I_D/I_G ratio is a typical parameter to quantify the degree of disorder in carbon materials, and the decrease of the I_D/I_G ratio indicates that the degree of graphitisation increases (Ko, 1996). The

resulting in-plane sizes of the graphitic clusters (L_a) determined using equation (3.5) are also given in Figure 6.13. Increasing the carbonisation temperature from 873 K to 1073 K, the values of L_a increase from 3.29, 3.29, 3.30 nm and 3.19 to 3.32, 3.40, 3.36 and 3.31 nm for argon, helium, nitrogen and vacuum atmospheres, respectively.

7.2.4 Pore Structure Analysis

Pore structural parameters including BET surface area, micropore volume and total pore volume determined from N₂ adsorption at 77 K are given in Table 7.4.

Table 7.4 Effect of the carbonisation atmospheres on the membrane structure

Sample	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Percentage of micropore (%)
CM-Ar873H2	466.2	0.2356	0.1569	66.59
CM-Ar1073H2	318.19	0.1527	0.1389	90.96
CM-He873H2	573.92	0.3363	0.2167	64.44
CM-He1073H2	359.61	0.1856	0.1525	82.16
CM-N873H2	497.61	0.2354	0.1974	83.86
CM-N1073H2	334.29	0.1823	0.1464	80.31
CM-V873H2	332.96	0.1674	0.1330	79.45
CM-V1073H2	25.95	0.0175	0.0099	56.57

The increase in the carbonisation temperature from 873 to 1073 K resulted in decreased BET surface area, total volume and micropore volume for all the atmospheres tested. For the two carbonisation temperatures, the carbon membranes obtained under helium atmosphere show the highest BET area, the total volume and the micropore volume. The most significant change in the total volume also comes from the helium pyrolysis: from 0.3363 cm³/g for CM-He873H2 K to 0.1856 cm³/g for CM-He1073H2. The reason for these patterns might be that the thermal degradation under helium always proceeded at a higher temperatures as compared with the other three atmospheres due to the excellent heat transport properties of helium. For carbonisation at 873 K, the nitrogen and argon atmospheres produced approximately the same total volume whilst the former yielded higher BET area and

micropore volume. Table 7.4 also showed that carbonisation atmosphere at 873 K had more significant influence on the pore size distribution (micropore or non-micropore) than the total pore volume. The samples obtained from vacuum pyrolysis produced the lowest BET area, total pore volume and micropore volume. According to Geiszler and Koros (1996), the mechanism of carbonisation may be changed by varying the atmosphere from vacuum to inert gas flow. Under vacuum atmosphere, the polyimide probably degrades via a unimolecular degradation mechanism. However, the carbonisation reaction under nitrogen flow may be accelerated due to increased gas phase heat and mass transfer which is favourable to create a more open porous matrix in the resulting carbon membranes. Thus, it may be deduced that the gaseous products (CO, CO₂, CH₄, H₂ and N₂) under vacuum pyrolysis are slowly and uniformly released to create a more compacted carbon structure (Hatori *et al.*, 1996; Konno *et al.*, 1997, 2001). The extremely low BET area and micropore volume of CM-V1073H2 might be an evidence of this deduction.

7.2.5 Gas Permeation Properties

The effect of carbonisation atmosphere on the permeation properties is shown in Figures 7.14 and 7.15. Compared with the membranes carbonised under inert atmospheres, the membranes carbonised under vacuum produce lower gas permeances for He, CO₂ and O₂ (Figure 7.14). For the gases N₂ (3.64 Å) and CH₄ (3.8 Å) with larger molecular sizes, the difference in the gas permeances is nearly negligible. This verifies that the ultra-micropores predominantly control the transport properties of the membranes. The gas permeances of the membranes subjected to various atmospheres decrease with increasing carbonisation temperature from 873 to 1073 K, indicating that the influence of the atmosphere is more significant at the lower temperature. At a carbonisation temperature of 873 K, the influence of different

Figure 7.14 Effect of carbonisation atmosphere on the gas permeances

Figure 7.15 Effect of carbonisation atmosphere on the ideal selectivity (1-8: CM-Ar873H₂, CM-He873H₂, CM-N873H₂, CM-V873H₂, CM-Ar1073H₂, CM-He1073H₂, CM-N1073H₂, and CM-V1073H₂)

inert atmospheres on the gas permeances is only distinguishable for He (2.6 Å) and CO₂ (3.3 Å). The permeances of the samples carbonised at 873 K under argon, helium and nitrogen are 2.97×10^{-8} , 2.50×10^{-8} and 2.68×10^{-8} mol/(m²sPa) for He and 3.93×10^{-8} , 3.08×10^{-8} , and 3.62×10^{-8} mol/(m²sPa) for CO₂, respectively. As discussed in section 7.2.4, the highest pore volume of CM-He873H2 would mean that the membranes carbonised at 873 K under helium were more porous than the membranes carbonised under argon and nitrogen for the same temperature. However, the membrane carbonised under helium atmosphere produced lower permeances for He and CO₂ than those under argon and nitrogen atmospheres. The reason for the comparatively lower gas permeances could be that some pores within CM-He873H2 were dead pores which were amenable for gas to adsorb but not for the gas to permeate through. For the carbonisation temperature of 1073 K, the membranes obtained from different inert atmospheres yield similar gas permeances except for He while the difference in the gas permeances between vacuum and the various inert atmospheres is still appreciable.

The ideal selectivities of O₂/N₂ and CO₂/CH₄ are shown in Figure 7.15. All the carbon membranes tested show higher selectivities for CO₂/CH₄ than for O₂/N₂. Increasing the carbonisation temperature from 873 to 1073 K, the membranes for all atmospheres show improved ideal selectivities for O₂/N₂ and CO₂/CH₄. The membranes carbonised at 873 and 1073 K under vacuum show the highest ideal selectivities of 9.37 and 17.76, respectively, for O₂/N₂. This is consistent with the results from the XRD analysis; the vacuum pyrolysis is favourable to create uniformly distributed narrow pores due to the moderate thermal degradation. The membranes carbonised at 873 and 1073 K under argon atmosphere give the highest selectivities of 93.35 and 476.74, respectively, for CO₂/CH₄. Consequently, carbonisation under

argon atmosphere is beneficial to form adsorptive carbon membranes. Based on the ideal separation factors shown in Figure 7.15, the larger pores detected through N₂ adsorption (Table 7.4) may be connected through micropores or narrow channels between meso- and/or micropores. Otherwise, the carbon membranes cannot give too low gas permeances for N₂ and CH₄ (Figure 7.14) (Zhou *et al.*, 2003).

7.3 CARBON MEMBRANES WITH DIFFERENT THICKNESSES

7.3.1 X-ray Diffraction Pattern

The X-ray diffraction profiles for the carbon membranes from Kapton® films with different thicknesses are shown in Figure 7.16. The samples CM-30, CM-50, CM-100, CM-200 and CM-500 were prepared from the Kapton® films with thicknesses of 7.6, 12.7, 25.4, 50.8 and 127 μm , respectively. The values of the X-ray diffraction angle and the average d-spacing are shown in Figure 7.17.

Figure 7.16 X-ray diffraction profiles of the Kapton® polyimide film (insert) and the carbonised membranes with different thicknesses

The XRD profiles for CM-30 and CM-50 are identical, but the XRD profiles for CM-100, CM-200 and CM-500 are quite different. However, all the profiles show an intense broad peak around $2\theta \approx 24^\circ$ and a very weak peak appears around $2\theta \approx 43^\circ$. Judging from the different full widths at half maximum value of (002) peaks, the membrane samples have different porous structures. The diffraction angles for CM-30, CM-50, CM-100, CM-200 and CM-500 are 25.24, 25.18, 23.84, 23.88, and 23.90°, respectively, as shown in Figure 7.17. The corresponding values for the average d-spacing are 3.526, 3.534, 3.729, 3.723 and 3.721 Å, respectively. Therefore, an increase in the precursor thickness from 7.6 to 25 µm (CM-30 to CM-100) could give rise to a more open carbon structure. However, carbonisation of the precursors with thicknesses beyond 25 µm does not change the carbon structure anymore.

Figure 7.17 XRD parameters of carbon membranes obtained from Kapton® films with different thicknesses

7.3.2 Pore Structure Analysis

The CO₂ adsorption isotherms for the membranes with different thicknesses are shown in Figure 7.18. The pore size distributions determined from the CO₂ adsorption isotherms are shown in Figure 7.19. The carbon membranes CM-30 and CM-100 obtained from Kapton® 30HN (7.6 µm) and 100HN (12.7 µm) show nearly the same amount of CO₂ uptake which is higher than those of the other membrane samples. Compared to CM-100, CM-30 has lower volume of pores in the range of 4.0-7.0 Å but higher volume of pores in the range of 7.1-8.5 Å (Figure 7.19). The membrane CM-200 obtained from Kapton® 200HN (50.8 µm) shows lower CO₂ uptake than those of CM-30, CM-50 and CM-100 but higher CO₂ uptake than that of CM-500. The CO₂ adsorption isotherm CM-500 is nearly linear and the CO₂ uptake is very low.

Figure 7.18 CO₂ adsorption isotherms for the carbon membranes with different thicknesses

Figure 7.19 Pore size distributions obtained from CO₂ adsorption isotherms

The volume of the pores in the range of 4.0-6.0 Å in CM-200 is comparable to those of CM-30, CM-50 and CM-100 but its volume of the pores in the range of 6.1-8.5 Å is apparently lower than CM-30, CM-50 and CM-100. CM-500 contains very little detectable pores as shown in Figure 7.19. An interesting finding was that the surface of CM-50 was not flat; carbonisation corrugated the film. Although the precursor for CM-50 was Kapton® 50 HN (12.7 µm) which had a less thickness more than that of the precursor for CM-30, a more serious deformation of CM-50 was observed after carbonisation. As shown in Figure 7.19, CM-50 and CM-100 have almost the same amount of pores in the range of 4.0-7.0 Å but CM-50 contains lower volume of pores in the range of 7.1-8.5 Å than that of CM-100.

7.3.3 Pure Gas Permeation

The single gas permeation properties of carbon membranes with different thickness were tested. Due to the low permeation rates shown by these membranes, only the permeances of He and CO₂ are given in Figure 7.20.

Figure 7.20 Permeances of He and CO₂ through carbon membranes with different thicknesses

The gas permeances for He and CO₂ increase as the membrane thickness increases from 7.6 to 12.7 μm . Further increases in the membrane thickness result in decreasing He and CO₂ permeances. The gas permeances determined are the overall permeances of the pure gases through the carbon membrane under a pressure gradient across the membrane. The structural parameters such as the membrane porosity, the tortuosity of the pores within the membrane and the pore connectivity are not considered. Therefore, the gas permeance through varying thickness membranes may not be simply defined to be inversely proportional to the membrane thickness. Due to the uncertainty of such membrane structural parameters, the thickness effect can be correlated to time-lag and diffusion coefficient (Crank, 1980)

$$D = \frac{l^2}{6t_l} \quad (7.2)$$

where D is the diffusion coefficient, l is the membrane thickness and t_l is the time-lag. Figure 7.21 is an example of the pressure changes at the permeate side with time.

Figure 7.21 Example of pressure changes in the permeate side for He and CO₂ permeation through CM-50

Table 7.5 Time-lag of carbon membrane with different thicknesses

Carbon membrane	CM-30	CM-50	CM-100	CM-200	CM-500
Thickness of the precursor (μm)	7.6	12.7	25.4	50.8	127
Time lag (min)	46	17	28	40	147
Diffusion coefficient (m^2/s)	3.49×10^{-15}	2.64×10^{-14}	6.40×10^{-14}	1.79×10^{-13}	3.05×10^{-13}

The permeation of He through the carbon membranes shows insignificant time-lag (Figure 7.21). However, the permeation rate of CO₂ is very low at the beginning of the test and remains unchanged after a certain time. Adsorption of CO₂ into the carbon pores could be the reason for the delay in permeation. The carbon membranes with different thicknesses need different times for the permeation of CO₂ to become stable. Table 7.5 shows that CM-50 has the shortest time-lag. Increasing membrane thickness beyond CM-50 results in increasing time-lag. The diffusion coefficients determined from equation (7.2) increased with increasing membrane thickness, and the variation of diffusion coefficient is quite large. Based on the fact that the diffusion

coefficient of a penetrant through a porous media is related to the porosity as well as the tortuosity of the pores, it can be surmised that the carbonisation of Kapton® films with different thicknesses would yield about different membrane structural properties. Not only the pore volume and pore size distribution would be affected, the characteristics of the inter-connected pores and the tortuosity of the pores would also be affected.

7.4 CORRELATION OF METHANE DIFFUSION AND PORE SIZE

Rao and Sircar (1996) reported a simple method to estimate the average pore size of a carbon membrane. This method is based on the correlation of methane diffusivity and pore size using published data for diffusion of methane through well calibrated zeolite pore entrances. A reference plot of methane diffusivity at 295 K through micro- and meso-pores in the size range of 4-10000 Å was constructed. The reference plot showing the relationship between the methane diffusivity and the pore size in the micropore range is shown in Figure 7.22.

Figure 7.22 Correlation of CH_4 diffusivity and pore dimension

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An equation deduced from the reference plot to describe the diffusivities in the low pore size range ($<12.6 \text{ \AA}$) is

$$D = \exp \left[-6.31 - 91.82e^{-0.49d_p} - 4.17e^{-3.34d_p} \right] \quad (7.3)$$

where D is the methane diffusivity and d_p is the pore size ($\text{\AA}$). For non-adsorbable gases, the gas diffusivity D can be correlated with the gas permeance by the following equation:

$$D = \left(\frac{\tau}{\varepsilon} \right) RTlP \quad (7.4)$$

where τ is the tortuosity of the pore network, ε is the porosity of the membrane, R is the gas constant, T is the temperature, l is the membrane thickness and P is the gas permeance. For porous materials, a common approximation is to take $\tau \approx 1/\varepsilon$ due to the great uncertainty to determine tortuosity. The micropore volume was determined by CO_2 adsorption as shown in Table 7.1. The true density (ρ_t) of the sample was measured by helium displacement with an ultra-pycnometer (upy-1000, Quantachome) instrument and is given in Table 7.6.

Table 7.6 Density, porosity, methane diffusivity and mean pore size of the carbon membranes prepared at different temperatures

Sample	True density (g/cm^3)	Apparent density (g/cm^3)	Porosity (%)	Diffusivity (cm^2/s)	Mean pore size ($\text{\AA}$)
CM-V823	0.97	0.84	13.41	7.36×10^{-6}	5.74
CM-V873	1.16	0.93	20.38	1.45×10^{-5}	6.01
CM-V973	1.29	0.97	24.34	1.36×10^{-6}	5.20
CM-V1073	1.30	1.00	22.99	3.13×10^{-7}	4.82
CM-V1173	1.27	0.98	22.54	7.24×10^{-9}	4.08
CM-V1273	1.21	0.86	29.16	2.88×10^{-9}	3.93

The apparent density (ρ_p) is thus calculated from the micropore volume and the true density:

$$\rho_p = 1 / (V_t + 1/\rho_t) \quad (7.5)$$

Hence, the porosity (ε) can be determined from ρ_t and ρ_p :

$$\varepsilon = 1 - (\rho_p / \rho_t) \quad (7.6)$$

The mean pore sizes of the carbon membranes are estimated and shown in Table 7.6. The change in the mean pore size with the carbonisation temperature is consistent with that given by the average d-spacing as determined from the XRD profiles although the latter has lower values. As shown in Figure 6.16, the diffusivity of methane decreases significantly with decreasing the pore size in the range of 4-12.6 Å. A slight change in the pore size by a few angstroms will lead to a marked change in the diffusivity by several orders of magnitude, and as a consequence, the gas permeation rate (Shiflett and Foley, 2000). This fact reflects the great effect of small changes in pore size on the gas permeance and it shows the way to prepare CMSM with higher permeances without loss of molecular sieving properties (Hatori *et al.*, 1996).

7.5 ANALYSIS OF GAS PERMEATION RESULTS

In order to test the consistency and reliability of single gas permeation rates, the permeation of He through CM-V1073H2 is shown here as an example. Table 7.7 gives the results of repeating He permeation for 3 times through one membrane sample and Table 7.8 gives the results of He permeation through three different batches of membrane samples. The standard deviations and coefficients of variation of He permeances are determined. Standard deviation, being considered as a measure of dispersion or variation about the mean, can be expressed as:

$$S = \sqrt{\frac{1}{N-1} \left(\sum_{i=1}^N (x_i - \bar{x})^2 \right)} \quad (7.7)$$

The coefficient of variation can be expressed as:

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$$CV = \frac{S}{\bar{x}} \times 100\% \quad (7.8)$$

where S = standard deviation,

CV = coefficient of variation,

N = the amount of the observations,

x_i = the value of the observations, and

$\bar{x}$ = the mean of the observations, can be expressed as $\frac{\sum x_k}{N}$.

Table 7.7 Repeatability of He permeation through one sample

Order of test	1 st	2 nd	3 rd
Permeance [mol/(m ² sPa)]	8.29×10 ⁻¹⁰	8.17×10 ⁻¹⁰	8.05×10 ⁻¹⁰
Average deviation	1.46%	0.04%	1.42%
Standard deviation		1.18×10 ⁻¹¹	
Coefficient of variation		1.44%	

Table 7.8 Repeatability of He permeation through different samples

Sample	1#	2#	3#
Permeance [mol/(m ² sPa)]	8.21×10 ⁻¹⁰	8.29×10 ⁻¹⁰	7.59×10 ⁻¹⁰
Average deviation	2.21%	3.23%	5.44%
Standard deviation		3.80×10 ⁻¹¹	
Coefficient of variation		4.74%	

The average deviations of He permeances (shown in Table 7.7) for the three tests are 1.46%, 0.04% and 1.42. The coefficient of variation for repeating the gas permeating experiments on one membrane sample was 1.44%. The repeability for the permeation tests was good. For the three batches of carbon membranes prepared, the average deviations of He permeances (shown in Table 7.8) were 2.21%, 3.23% and 5.44%. The coefficient of variation for the He permeation tests was 4.74%. The reproducibility was good. Therefore, the results for the gas permeation experiments are typical and reliable.

CHAPTER 8

THEORETICAL STUDY OF GAS PERMEATION

8.1 THEORETICAL OUTLINE

Theoretical studies of single gas permeation and gas separation in carbon membranes have been carried out using different methods. In the published works, a model of a slit-shaped carbon pore is commonly used. Considered as a semi-infinite graphite slab, the carbon pore wall consists of parallel graphite planes with an interplanar spacing of 0.335 nm and with a carbon atom density of 114 nm^{-3} . The porous carbon membrane may contain a range of pore sizes from nano- to meso- to micropores. The main resistance to the gas permeation is offered by interconnected nano- and mesopores (Xu *et al.*, 2000). In the non-equilibrium dynamics (NEMD) simulation of H_2/CH_4 separation, Vieira-Linhares and Seaton (2003) observed that the pores between 6.3 and 10 Å showed selective adsorption of methane. Pores smaller than 6 Å showed molecular sieving effect whilst pores bigger than 10-12 Å showed poor selectivities. At a feeding pressure of 11.3 bar, a maximum selectivity around 170 of CH_4 over H_2 was obtained corresponding to a pore size of 7 Å. Xu *et al.* (2000) reported that the separation of CO_2/CH_4 was dependent on the porosity. Through molecular dynamics simulation, these researchers found that the adsorbed amounts of the gases increased with increasing porosity and reached a maximum at a porosity of 0.45-0.5 beyond which they both decreased with increasing porosity. The selectivity also increased with increasing porosity due to the improved CO_2 flux and nearly constant CH_4 flux and reached a maximum of about 14 at a porosity of 0.6. In the study of Furukawa and Nitta (2000), the carbon membranes were modelled with three different pore shapes, i.e., a diamond path (DP), a zigzag path (ZP) and a straight path

(SP). It was observed that the permeation resistances inside the DP and ZP membranes were significant but the resistances of the SP membrane were localised at the membrane exit. For the separation of $\text{CH}_4/\text{C}_2\text{H}_6$ using the three carbon membranes, the selectivities of C_2H_6 over CH_4 were higher than the ideal separation factors derived from single gas permeation but lower than the adsorption equilibrium separation factors.

MacElroy and Boyle (1999) simulated the transport of binary mixtures of H_2 and CH_4 through carbon membrane with varying thickness using NEMD technique. If the pores controlling the separation process were short, the pore entrance/exit resistances to the mass transfer would be significant. The transport of strongly adsorbing CH_4 molecules was nearly not affected by the cross-coefficient of diffusion. Strano and Foley (2003) considered the membrane permeability as the contribution of highly selective membrane pores in conjunction with less selective cylindrical defect pathways. By applying the model to the published results, these researchers found that the carbon membranes having high numbers of defects showed a quadratic dependence of flux on pressure and the O_2/N_2 selectivity varied with O_2 permeability. According to Gilron and Soffer (2002), the pure gas permeance through the carbon membranes displayed the molecular weight and temperature dependence expected from Knudsen diffusion even though the pore size distribution was below 0.55 nm.

8.2 THEORETICAL MODELS

The transport properties of gas molecules in microporous membranes may be represented by Knudsen, configurational diffusion and/or surface diffusion. Therefore, the gas permeation rate may be a function of both diffusion coefficient and the

concentration of the penetrant. The total concentration of the gas molecules inside the membrane may be determined as (Shelekhin *et al.*, 1995)

$$C_T = C_g + C_a \quad (8.1)$$

where C_T , C_g and C_a are the total, the gas-phase and the adsorbed-phase concentrations, respectively. If the concentration of the penetrant is primarily determined by the gas phase inside the membrane, then

$$C_T \approx C_g = \frac{p\theta}{RT} \quad (8.2)$$

where θ is the porosity of the membrane, p is the pressure, R is the gas constant and T is the temperature. If the concentration of the penetrant is determined by the concentration of the adsorbed phase, then

$$C_T \approx C_a = \frac{V\rho}{V_m} \quad (8.3)$$

where V_m is the molar volume of the penetrant in the adsorbed state (m^3/mol) and ρ is the density of the membrane (kg/m^3). The adsorption phenomena in microporous membranes may be described by the Dubinin-Radushkevich equation:

$$V = V_0 \exp \left[- \left(\frac{A}{\beta E} \right)^2 \right] \quad (8.4)$$

where V is the adsorption volume at temperature T (K) and relative pressure p/p_0 , V_0 is the limiting adsorption volume (cm^3/g), A is the sorption potential $[A = RT \ln(p_0/p)]$ (J/mol), β is the affinity coefficient, and E is the characteristic energy of sorption potential (J/mol).

If the pores inside the carbon membrane are straight pores, the diffusion coefficient may be expressed as

$$D = \lambda \rho_{\lambda} \bar{u} \quad (8.5)$$

where ρ_{λ} is the probability that the gas molecule make a jump whose length is λ , and $\bar{u}$ is the molecular mean velocity (m/s). The probability ρ_{λ} is a combination of geometrical and energetical probabilities

$$\rho_{\lambda} = \rho_g \rho_E = \rho_g \exp\left(-\frac{\Delta E}{RT}\right) \quad (8.6)$$

where ρ_g is the geometrical probability or the probability that the gas molecules jump in the desired direction and ρ_E is the energetical probability or the probability that the gas molecules have sufficient kinetic energy to surmount the energy barrier ΔE . The energetical probability ρ_E is expressed as

$$\rho_E = \exp\left(-\frac{\Delta E}{RT}\right) \quad (8.7)$$

If the obstruction in the way of the diffusant molecule is rigid, the diffusant will bounce off during the collision. Therefore, the geometrical probability ρ_g may be expressed as

$$\rho_g = \frac{1}{3} \left[\frac{(\pi d_n^2/4)}{(\pi d_p^2/4)} \right] = \frac{1}{3} \frac{d_n^2}{d_p^2} \quad (d_n < d_p) \quad (8.8)$$

Substituting expressions for the energetical probability ρ_E and the mean free velocity $\bar{u} = \sqrt{8RT/(\pi M)}$ (Bhave, 1991) into equation (8.5) and taking $\lambda = d_p$ (pore diameter), the diffusion coefficient can be expressed as

$$D = \rho_g d_p \left(\frac{8RT}{\pi M} \right)^{1/2} e^{-\frac{\Delta E}{RT}} \quad (8.9)$$

where M is the molecular mass of the diffusant.

The permeability coefficient in straight membrane pores is defined as

$$\bar{P}_s^0 = \frac{J_s \cdot l}{\Delta p} \quad (8.10)$$

where $\bar{P}_s^0$ is the permeability coefficient J_s is the transmembrane flux in straight pores, Δp is the pressure difference between the upstream and the downstream side, and l is the membrane thickness. The driving force for gas permeation is the gradient of the chemical potential

$$J_s = -Bc \frac{\partial \mu}{\partial x} \quad (8.11)$$

where B is the mobility [$\text{mol} \cdot \text{m}^2 / (\text{J} \cdot \text{s})$], c is the concentration and μ is the chemical potential (J/mol). So, the diffusion coefficient becomes

$$D_F = BRT \frac{d \ln(p)}{d \ln(c)} = D_c \frac{d \ln(p)}{d \ln(c)} \quad (8.12)$$

where D_c is the corrected diffusivity that may or may not be dependent on the concentration, and D_F is Fickian diffusivity. For the adsorbed phase, the derivative is

$$\frac{d \ln(p)}{d \ln(c)} = \frac{1}{2[(RT)/\beta E]^2 \ln(p_0/p)} \quad (8.13)$$

where

$$\ln(c) = \ln\left(\frac{V}{V_0}\right) = -\left(\frac{A}{\beta E}\right)^2 = -\left[\frac{RT \ln(p_0/p)}{\beta E}\right]^2 \quad (8.14)$$

The corrected diffusivity in the adsorbed phase is determined by

$$D_{ads} = \frac{D_{c,ads}}{2[(RT)/\beta E]^2 \ln(p_0/p)} \quad (8.15)$$

For the gas phase, the derivative is

$$\frac{d \ln(p)}{d \ln(c)} = 1 \quad (8.16)$$

and the corrected diffusivity in the gas phase is independent of the pressure

$$(D_{c,gas} = D_{gas}).$$

Accounting for the differences between the transmembrane flux in membranes with random porous structures and the flux in straight channels, a correction coefficient should be included in equation (8.10). Therefore, the flux in the porous membrane becomes

$$\frac{J_s}{J} = \frac{\tau}{\theta} \quad (8.17)$$

where θ is the porosity and τ is the tortuosity. The total transmembrane flux is thus written as

$$J = - \left(D_{ads} \frac{dC_{ads}}{dp} + D_{gas} \frac{dC_{gas}}{dp} \right) \frac{\theta}{\tau} \frac{dp}{dx} = - \left(D_{c,ads} \frac{d \ln(p)}{d \ln(C_{ads})} \frac{dC_{ads}}{dp} + \frac{D_{c,gas}}{RT} \right) \frac{\theta}{\tau} \frac{\Delta p}{l} \quad (8.18)$$

where $D_{c,ads}$ and $D_{c,gas}$ are the corrected diffusion coefficients (m^2/s) in the adsorbed and gas phases, and J is the flux across the membrane. Since that $D_{c,ads}$ and $D_{c,gas}$ are governed by the geometrical and energetical probabilities, the permeability coefficient can be presented as

$$\bar{P}^0 = D_{c,ads} \frac{d \ln(p)}{d \ln(C_{ads})} \frac{\theta}{\tau} \frac{dC_{ads}}{dp} + \frac{\theta}{\tau} \frac{D_{c,gas}}{RT} \quad (8.19)$$

$$D_{c,ads} = \rho_g d_p \left(\frac{8RT}{\pi M} \right)^{1/2} e^{-\frac{\Delta E_{ads}}{RT}} \quad (8.20)$$

$$D_{c,gas} = \rho_g d_p \left(\frac{8RT}{\pi M} \right)^{1/2} e^{-\frac{\Delta E_{gas}}{RT}} \quad (8.21)$$

The characteristic energies ΔE_{ads} and ΔE_{gas} result from the interaction between the carbon pore wall and the fluid. Figure 8.1 shows a schematic diagram of the slit-shaped carbon pore model.

Figure 8.1 Schematic diagram of the slit-shaped pore model

The pore width, H , is the internuclear distance (along the z -axis) between carbon atoms in opposite walls. Each pore comprises n parallel layers of carbon atoms separated by an internuclear distance, Δ , and each layer plane has an atom density ρ_a .

The fluid-fluid interaction is modelled by a Lennard-Jones (LJ) pairwise interaction potential:

$$u_{ff}(r) = 4\varepsilon_{ff} \left[\left(\frac{\sigma_{ff}}{r} \right)^{12} - \left(\frac{\sigma_{ff}}{r} \right)^6 \right] \quad (8.22)$$

where r is the distance between fluid molecules, ε_{ff} is the depth of potential and σ_{ff} is the collision diameter. The total interaction potential between a nitrogen molecule and one wall of the model pore is given by [Mays, 1996]:

$$u_{sf}(z) = 2\pi\rho_a\varepsilon_{sf}\sigma_{sf}^2 \left\{ \sum_{j=0}^{n-1} \left[\frac{2}{5} \left(\frac{\sigma_{sf}}{z+j\Delta} \right)^{10} - \left(\frac{\sigma_{sf}}{z+j\Delta} \right)^4 \right] \right\} \quad (8.23)$$

where $\rho_a = 38.18 \text{ nm}^{-2}$ is the surface number density of carbon atoms in a graphite layer, $\Delta = 0.335 \text{ nm}$ is the separation between graphite layers, z is the internuclear separation between the fluid molecule and the carbon atoms in the nearest carbon layer and n is the number of carbon layer planes in the pore wall. σ_{sf} and ε_{sf} are solid-fluid LJ collision and well-depth parameters. The values for σ_{sf} and ε_{sf} can be calculated according to Lorentz-Berthelot rules:

$$\varepsilon_{sf} = (\varepsilon_{ss}\varepsilon_{ff})^{1/2} \quad (8.24)$$

and

$$\sigma_{sf} = (\sigma_{ss} + \sigma_{ff})/2 \quad (8.25)$$

where ε_{ss} and σ_{ss} are the solid parameters. The total fluid-solid interaction in the pore described as the interaction, $u_{sf}(z)$, is given by

$$u_{pore} = u_{sf}(z) + u_{sf}(H-z), \quad 0 < z < H \quad (8.26)$$

where H is the C centre - C centre separation across the pore. The Lennard-Jones parameters used in the calculation are given in Table 8.1.

Table 8.1 Lennard-Jones parameters used in the calculations

	$\sigma \text{ (\AA)}$	$\varepsilon/k_B \text{ (K)}$	
O ₂ -O ₂	3.46	118.00	Hirschfelder, 1964
N ₂ -N ₂	3.75	95.20	Steele, 1974
C-C	3.40	28.00	Steele, 1974
CH ₄ -CH ₄	3.82	148.12	Tanaka <i>et al.</i> , 2002

For nonadsorbable gases, the first term in equation (8.19) is negligibly small and the permeability of the penetrant is determined exclusively by the transport in the gas phase. Thus, the permeability of permanent gases such as CH₄, O₂ and N₂ is

$$\bar{P}^0 = d_p \rho_g \left(\frac{8}{\pi MRT} \right)^{1/2} \frac{\theta}{\tau} e^{-\frac{\Delta E_{gas}}{RT}} \quad (8.27)$$

The gas permeance for the nonadsorbable gases is

$$P = \frac{\bar{P}^0}{l} = \frac{d_p \rho_g}{l} \left(\frac{8}{\pi MRT} \right)^{1/2} \frac{\theta}{\tau} e^{-\frac{\Delta E_{gas}}{RT}} \quad (8.28)$$

8.3 GAS PERMEATION RATE OF NONADSORBABLE GASES

8.3.1 Theoretical Single Gas Permeance

Based on equation (8.28), the permeances of gases with different molecular masses through the carbon membranes were estimated. The gas permeances were calculated based on the following assumptions. Firstly, the adsorption of the penetrant was negligible. Secondly, the pores were a bundle of straight pores. These two assumptions are also applicable for the theoretical study presented in sections 8.3.2 and 8.3.3. Thirdly, the average pore diameter was 6 Å.

Figure 8.2 Theoretical permeances of gases with different masses

In Figure 8.2, the maximum permeance for each penetrant which can be accomplished in the carbon membrane is the line for $\Delta E_{gas} = 0$ kJ/mol. Essentially, it is the limit for the gas permeance determined by Knudsen diffusion mechanism. For each penetrant, the permeance decreases significantly as the apparent activation energy increases. Increasing apparent activation energy not only decreases the gas permeance, but also results in the molecular sieving effect for mixtures composed of different gases. When the apparent activation energy is higher than 10 kJ/mol, the permeance for all the gases is very low.

8.3.2 Potential Energy of Diffusion

In narrow membrane pores, overlapping of the fluid-solid interaction potential occurs. This interaction originates from the potential barrier which is characterised by the apparent activation energy required to overcome it.

Figure 8.3 Potential energy estimates of CH₄ in carbon membrane pores: (a) potential energy distribution (1-12 refers to the pore diameter of 3.9, 4.0, 4.5, 5, 6, 8, 10, 12, 14, 16, 18 and 20 Å); (b) average potential energy

Figure 8.4 Potential energy estimates of O_2 in carbon membrane pores: (a) potential energy distribution (1-12 refers to the pore diameter of 3.9, 4.0, 4.5, 5, 6, 8, 10, 12, 14, 16, 18 and 20 Å); (b) average potential energy

Figure 8.5 Potential energy estimates of N_2 in carbon membrane pores: (a) potential energy distribution (1-12 refers to the pore diameter of 3.9, 4.0, 4.5, 5, 6, 8, 10, 12, 14, 16, 18 and 20 Å); (b) average potential energy

The potential energy of CH₄, O₂ and N₂ in carbon membrane pores were estimated using Lennard-Jones (LJ) 12-6 potential (equation (8.22)) and May's potential model (equation (8.23)). The results are shown in Figures 8.3-8.5. For each gas, the lines showing the distribution of the potential energy between fluid and the carbon pore wall become lower with decreasing pore diameter. The values of potential energy for CH₄, O₂ and N₂ show similar distribution characteristics in the pores of 6-20 Å; the potential energy is strong when the gas molecules are near the pore surface while the potential energy is weak when the gas molecule is near the centre of the pore. The values of potential energy in the pores smaller than 6 Å show different distribution characteristics from those in the wider pores; the potential energy being strong near the pore centre and weak near the pore wall. Overlapping of the fluid-solid interaction potential from both pore walls may account for this phenomenon.

For N₂ and CH₄, the values of potential energy show similar distribution characteristics in the pores smaller than 6 Å; however, O₂ shows quite different potential energy distribution within the pores of the same diameters. This means that within very narrow pores, very small variations of the penetrant size will result in apparent change in the potential energy. The absolute values of the average potential energy for each gas increase significantly with decreasing pore diameter. For the same pore diameter and internuclear separation, the order of the average potential energy is O₂ < N₂ < CH₄ which is in accordance with the size of the gas molecules. The absolute values of the potential energy for O₂, N₂ and CH₄ decrease from 17.11, 18.03 and 23.64 kJ/mol, respectively, for the pore with a diameter of 3.9 Å to 1.95, 2.06 and 2.73 kJ/mol, respectively, for the pore with a diameter of 20 Å. The difference in the potential energy determines the amount of a gas species diffusing through the membrane at fixed conditions, thus resulting in the selectivity of gas separation.

8.3.3 Gas Permeances Through Carbon Membranes

Using equation (8.28) and the values of the average potential energy shown in Figures 8.3-8.5, the permeances of O₂, N₂ and CH₄ through the membrane pores with different diameters were calculated and shown in Figures 8.6, 8.7 and 8.8, respectively. With increasing pore diameter, the calculated permeances for the three gases increase sharply. The permeances for O₂ and N₂ are higher than that of CH₄ for the same pore size, and the difference is significant for the membrane pores smaller than 6 Å. The increase of O₂ permeance with increasing pore size is higher than that of N₂ in the pores of 3.9-6 Å, but their difference tends to decrease for larger membrane pores. For the pores of 3.9-10 Å, the increases of O₂ and N₂ permeances are always more significant than that of CH₄ (Figures 8.6-8.8).

Figure 8.6 Permeances of O₂ through the carbon membranes

Figure 8.7 Permeances of N_2 through the carbon membranes

Figure 8.8 Permeances of CH_4 through the carbon membranes

The experimental gas permeances of O_2 , N_2 and CH_4 are also shown in Figures 8.6, 8.7 and 8.8, respectively. Despite using a simple pore model (with regular, slit-shaped pores), the experimental results agreed reasonably well with the theoretical curve. For O_2 permeation through the membrane pores in Figure 8.6, the agreement between experimental and theoretical results is good for the narrow pores (3.9-4.5 Å), but some difference arise for the larger pores. The gas permeance was calculated for carbon membrane with regular, slit-shaped pores whilst the real carbon membrane had a pore size distribution. The pores with average diameters of 5.2, 5.74 and 6.01 Å corresponded to the samples CM-V973, CM-V823 and CM-V873, respectively, as given in Chapter 7. For these membranes, N_2 adsorption showed that they consisted of small amount of mesopores, with comparatively wide pore size distributions. The existence of these wide pores would result in significant increase in the O_2 permeance. Therefore, the straight slit-shaped carbon pore model will underestimate the contribution of such pores. For the permeation of N_2 and CH_4 , good agreement between experimental and theoretical results is shown in Figures 8.7 and 8.8, respectively.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

9.1 CONCLUSIONS

Carbon membranes were prepared from Kapton® polyimide films. The pyrolysis kinetics of Kapton® polyimide 100HN were studied. Fitting various reaction mechanisms to isothermal and nonisothermal TG data produced inconsistent values of Arrhenius parameters. Isoconversional method showed the dependence of the apparent activation energy on the degree of conversion but it could not give enough information for the study of pyrolysis kinetics. The mathematical treatment of the experimental data using different analytical models produced different results. The predicted TG curve using the kinetic parameters from the model proposed in this study matched the experimental TG data very well for a wide range of conversion, indicating its applicability for the study of pyrolysis kinetics.

The structural and transport properties of the intermediate state between polyimide and carbon were studied. The membranes heat treated at temperatures ranging from 673 to 748 K showed similar XRD patterns as that of the precursor. Two minimum ideal selectivities for O₂/N₂ and CO₂/CH₄ were observed for the samples heat treated at 673 and 723 K. The membranes heat treated at 773 K showed appreciably high gas permeances and comparable ideal selectivities with the membranes processed at lower temperatures. The comparatively high gas permeances resulted from the decomposition of the precursor, and the low selectivities were due to the underdeveloped carbon structure coupled with the remaining polyimide structure.

CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Heat treatment of the Kapton® film at 873 and 1073 K resulted in amorphous carbon as observed by the XRD and Raman analyses.

The influences of the carbonisation parameters on the gas transport properties of the carbon membranes were studied using statistical analysis. Carbonisation temperature had the strongest influence on the gas permeation properties. The carbonisation atmosphere and the thermal soak time had limited influences on the development of membrane transport properties, and the heating rate did not have any influence. Nitrogen atmosphere coupled with lower final temperature resulted in the highest gas permeation rate. The final temperature had a greater effect on the carbonisation subjected to the nitrogen atmosphere rather than the vacuum atmosphere. Lower carbonisation temperature coupled with longer thermal soak time resulted in decreased gas permeabilities. Vacuum atmosphere coupled with higher heating rate resulted in increased permeabilities, and prolonged thermal soak time coupled with lower heating rate decreased the permeabilities.

The development of membrane structure and transport properties during carbonisation were investigated. The average d-spacing of the carbon membranes gradually decreased with increasing carbonisation temperature. A large amount of pores were created during the early stages of carbonisation. The average pore sizes of the carbon membranes obtained at 823, 873, 973, 1073, 1173 and 1273 K under vacuum were 5.74, 6.01, 5.20, 4.82, 4.08 and 3.93 Å, respectively. With increasing carbonisation temperature from 823 K, the gas permeances increased and reached the maximum values at 873 K and thereafter the gas permeances gradually decreased. The membranes carbonised at 1073 K showed the highest O₂/N₂ selectivity of 11.46. For the same heating program for the furnace, the carbonisation under the helium

atmosphere proceeded at higher temperatures as compared to argon and nitrogen atmospheres. Comparing with argon, helium and nitrogen atmospheres, the vacuum atmosphere resulted in the lowest average d-spacing, the lowest in-plane size of the graphitic clusters and the lowest gas permeances. The membranes carbonised under helium atmosphere had the highest BET area, total pore volume and micropore volume which decreased from 573.92 m²/g, 0.3363 cm³/g and 0.2167 cm³/g to 359.61 m²/g, 0.1856 cm³/g and 0.1525 cm³/g with increasing the temperature from 873 K to 1073 K. The thickness of the precursor had significant influences on the pore structure and gas permeation properties of the resulting carbon membranes. With increasing precursor thickness from 7.6 to 25.4 µm, a more open structure was obtained. The time-lag determined by CO₂ permeation was 17 min for sample CM-50 (from Kapton® film 50HN) and its value increased with increasing membrane thickness. Sample CM-50 had the highest permeation rates of 1.39×10⁻⁹ and 1.81×10⁻¹⁰ mol/(m²sPa) for He and CO₂, respectively.

The diffusion of gas molecule through carbon membrane with regular pores showed an upper bound as determined by Knudsen diffusion mechanism. The potential energy for the diffusion increased significantly as the pore size decreased. For the membrane pores smaller than 6 Å, overlapping of the fluid-solid interaction potential occurred. The potential energy within pores larger than 6 Å showed similar distribution characteristics for O₂, N₂ and CH₄. The O₂ permeances from the theoretical model were in fairly good agreement with the experimental results for narrows pores, whilst the N₂ and CH₄ permeances showed good agreement between experiment and modelling results.

9.2 RECOMMENDATIONS

Some experimental and theoretical studies can be considered for further work. The recommendations are as follows:

1. Investigate the transport properties of the carbon membranes at different temperatures

The transport properties of the Kapton® based carbon membranes were studied at room temperature with a pressure difference of 1 atm between the feed side and the permeate side. Varying the temperature will allow for the determination of apparent activation energy of diffusion which apparently influences the permeation rate of both adsorbable and nonadsorbable gases.

2. Test the transport and separation properties of gas mixtures such as CO₂/CH₄ and H₂/N₂

Investigation of transport properties of single gases proved that the Kapton® based carbon membranes allowed the permeation of He and CO₂ and hindered the permeation of N₂ and CH₄. These results indicate that the pores applicable for the gases to permeate through are very small and are narrowly distributed. These characteristics make it possible to attain attractive permselectivities for CO₂/CH₄ and H₂/N₂ separations. It is therefore recommended to carry out such tests to determine the separation performance of these membranes.

3. Carry out CO₂ adsorption at different temperatures

The permeation experiments were performed around 295 K. For the permeation and separation of CO₂/CH₄, preferential adsorption and surface diffusion of CO₂ will also occur besides activated diffusion. Therefore, CO₂ adsorption at higher temperatures should be conducted in order to provide useful information to further understand the mechanism of CO₂/CH₄ separation.

4. Investigate the membrane structure

The pore structure of the resulted carbon membranes was investigated using CO₂ adsorption at 273 K. Due to the limitation of the instrument (ASAP2010, Micromeritics), the highest relative pressure is 0.03. In order to totally characterise the membrane structure resulting from carbonisation, CO₂ adsorption at room temperature and even higher temperatures are necessary. Transport properties of penetrants with different sizes can be used to determine the molecular sieving effect of the carbon membranes and the variations of the membrane structures as a result of carbonisation parametric effects. Combination of the results from CO₂ adsorption and gas permeation will be helpful to fully determine the critical pore size and effective porosity of the carbon membrane responsible for the molecular sieving nature.

5. Model the permeation and separation of CO₂/CH₄ through the carbon membranes

The potential energy for the diffusion of nonadsorbable gases (O₂, N₂ and CH₄) was determined and the single gas permeance was calculated. Using the same pore model, the permeation rate of CO₂ as a combination of the adsorbed phase diffusion and gas phase diffusion can be estimated. The CO₂/CH₄ separation properties of the carbon membranes are therefore determined. Correlation between experimental and theoretical results may help to further extend the understanding the resistance of diffusion in real carbon membranes, the interconnectivity of the pores and the contribution of pores with different sizes.

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APPENDIX A

DETERMINATION OF PORE SIZE DISTRIBUTION BY DFT

METHOD

When placing a membrane sample in an evacuated space at a fixed temperature and dosing nitrogen into the space, the pressure within the space will fall rapidly from its initial value and gradually approach the equilibrium value. In such a system, the nitrogen atoms that enter a pore space are influenced by the presence of the solid surface. The influence is that of an external attractive force which causes the nitrogen atoms to spend more time near the surface. As a result, at equilibrium the space near the surface has acquired a greater average density of nitrogen atoms than regions farther removed. For the equilibrium in a pore represented by two parallel walls separated by a distance H , the chemical potential at every point in the fluid equals to the chemical potential of the bulk fluid which is a homogenous system of constant density. The grand potential energy for the system is expressed as:

$$W[\rho(r)] = F[\rho(r)] + \int dr \rho(r) [V(r) - \mu] \quad (\text{A-2})$$

where $\rho(r)$ is the equilibrium density at a general 3-space coordinate r , $V(r)$ is the potential acting on a molecule at r , and μ is the chemical potential. $F[\rho(r)]$ is the Helmholtz free energy expressed as a function of the molecular density distribution $\rho(r)$ of the gas at equilibrium. The expression $F[\rho(r)]$ can be expended into two parts, one representing the free energy arising from the repulsive forces and a second reflecting the contribution from attractive forces:

$$F[\rho(r')] = F_{hs}[\rho(r')] + 1/2 \int dr \rho(r) U(r, r') \quad (\text{A-3})$$

where $F_{hs}[\rho(r')]$ represents the hard-sphere repulsive forces which cannot be exactly determined. An approximation

$$F_{hs}[\rho(r')] = \int dr f_{hs}[\rho(r)] \quad (A-4)$$

is frequently used where $f_{hs}[\rho(r)]$ is the Helmholtz free energy density of a uniform hard-sphere fluid. The far right term of equation (A-3) is the mean-field calculation of the attractive energy. $U(r, r')$ is the summation of the attractive part of the pairwise potential of a molecule at r with all other fluid molecules in the system at r' .

$U(r, r')$ is calculated from the Lennard-Jones 6-12 pairwise relation:

$$u(r) = -4\epsilon_{NN} \left[\left(\frac{\sigma_{NN}}{r'} \right)^6 - \left(\frac{\sigma_{NN}}{r'} \right)^{12} \right] \quad (A-5)$$

thus,

$$U(r, r') = \int dr' \rho(r') u(r) \quad (A-6)$$

Density functional theory describes the thermodynamic grand potential as a functional of the single-particle density distribution. Calculating the density profile that minimizes the grand potential energy yields the equilibrium density profile. The quantity adsorbed per unit area of surface is obtained by integrating the equilibrium density profile over the spatial coordinate r and subtracting the quantity of adsorptive that would be present in the absence of wall forces. Applying the above process to find the equilibrium density profile over an analytical pressure range from ultra low to saturation while maintaining a constant pore width is required to generate a single model isotherm for a specific pore size. For a range of pore size from the size of the gas molecule up to a free surface, a set of model isotherms should be generated and the series of calculations for each pore size over the pressure range should be repeated.

The total adsorption on the membrane sample is expressed by

$$Q(p) = \int dH q(p, H) f(H) \quad (\text{A-2})$$

where $Q(p)$ is the total quantity adsorbed per unit of weight at pressure p ,

$q(p, H)$ is the quantity adsorbed per unit of area or volume at pressure p in an ideal pore of size H . $f(H)$ is the total area or volume of pores of size H in the sample.

For the observed nitrogen adsorption isotherms, the pore size distribution $f(H)$ was calculated using the DFT software from Micromeritics Instrument Corporation.

APPENDIX B

UNCERTAINTY ANALYSIS OF PORE VOLUME

1. Methodology for the determination of uncertainty

For a general case in which an experimental result, r , is a function of N measured variables x_i :

$$r = r(x_1, x_2, \dots, x_N) \quad (\text{B-1})$$

The uncertainty in the result is given by (Coleman and Steele, 1999):

$$\frac{U_r^2}{r^2} = \left(\frac{x_1}{r} \frac{\partial r}{\partial x_1} \right)^2 \left(\frac{U_{x_1}}{x_1} \right)^2 + \left(\frac{x_2}{r} \frac{\partial r}{\partial x_2} \right)^2 \left(\frac{U_{x_2}}{x_2} \right)^2 + \dots + \left(\frac{x_N}{r} \frac{\partial r}{\partial x_N} \right)^2 \left(\frac{U_{x_N}}{x_N} \right)^2 \quad (\text{B-2})$$

During each CO₂ adsorption experiment, the final pore volume is determined as the sum of N values of single pore volume corresponding to N equilibrium points. For the I^{th} equilibrium point, the reduction of adsorbate (mole) in the manifold equals the amount of adsorbate in the sample tube plus the amount (mole) adsorbed onto sample.

$$V_{CUMI} = V_I \cdot D$$

$$\frac{\left[\frac{(P_{SYS,I} - P_{SYS,I})}{P_{STD}} \right] \left(\frac{V_{LOW}}{1000} \right)}{RT_{SYS}} = \frac{\left(\frac{P_{SAMI}}{P_{STD}} \right) \left(\frac{V_{FC}}{1000} \right)}{RT_{ABT}} + \frac{\left(\frac{V_{CUMI} W_{SAM}}{1000D} \right)}{22.4}$$

$$V_{CUMI} = \frac{22.4D}{RP_{STD}W_{SAM}} \times \left[\frac{(P_{SYS,I} - P_{SYS,I})V_{LOW}}{T_{SYS}} - \frac{P_{SAMI}V_{FC}}{T_{ABT}} \right]$$

$$(P_{SYS,I} - P_{SYS,I})V_{LOW} = \frac{P_{SAMI}V_{FC}T_{SYS}}{T_{ABT}} + \frac{V_{CUMI}RT_{SYS}P_{STD}}{22.4D}$$

For the I^{th} single pore volume determined by the instrument, the uncertainty can be expressed as:

$$\begin{aligned}
\left(\frac{U_{V_{CUMI}}}{V_{CUMI}}\right)^2 &= \left(\frac{W_{SAM}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial W_{SAM}}\right)^2 \left(\frac{U_{W_{SAM}}}{W_{SAM}}\right)^2 \\
&\quad + \left(\frac{T_{SYS}}{V_{SUMI}} \cdot \frac{\partial V_{CUMI}}{\partial T_{SYS}}\right)^2 \left(\frac{U_{T_{SYS}}}{T_{SYS}}\right)^2 + \left(\frac{P_{SYS_1I}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial P_{SYS_1I}}\right)^2 \left(\frac{U_{P_{SYS_1I}}}{P_{SYS_1I}}\right)^2 \\
&\quad + \left(\frac{P_{SYS_2I}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial P_{SYS_2I}}\right)^2 \left(\frac{U_{P_{SYS_2I}}}{P_{SYS_2I}}\right)^2 + \left(\frac{P_{SAMI}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial P_{SAMI}}\right)^2 \left(\frac{U_{P_{SAMI}}}{P_{SAMI}}\right)^2 \\
\left(\frac{W_{SAM}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial W_{SAM}}\right)^2 \left(\frac{U_{W_{SAM}}}{W_{SAM}}\right)^2 \\
&= \left\{ \frac{W_{SAM}}{V_{CUMI}} \cdot \frac{22.4D}{RP_{STD}} \cdot \left[\frac{(P_{SYS_1I} - P_{SYS_2I})V_{LOW}}{T_{SYS}} - \frac{P_{SAMI}V_{FC}}{T_{ABT}} \right] \left(-\frac{1}{W_{SAM}^2}\right) \right\}^2 \left(\frac{U_{W_{SAM}}}{W_{SAM}}\right)^2 \\
\left(\frac{T_{SYS}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial T_{SYS}}\right)^2 \left(\frac{U_{T_{SYS}}}{T_{SYS}}\right)^2 \\
&= \left[\frac{T_{SYS}}{V_{CUMI}} \cdot \frac{22.4D(P_{SYS_1I} - P_{SYS_2I})V_{LOW}}{RP_{STD}W_{SAM}} \cdot \left(-\frac{1}{T_{SYS}^2}\right) \right]^2 \left(\frac{U_{T_{SYS}}}{T_{SYS}}\right)^2 \\
\left(\frac{P_{SYS_1I}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial P_{SYS_1I}}\right)^2 \left(\frac{U_{P_{SYS_1I}}}{P_{SYS_1I}}\right)^2 \\
&= \left(\frac{P_{SYS_1I}}{V_{CUMI}} \cdot \frac{22.4DV_{LOW}}{RP_{STD}W_{SAM}T_{SYS}}\right)^2 \left(\frac{U_{P_{SYS_1I}}}{P_{SYS_1I}}\right)^2 \\
\left(\frac{P_{SYS_2I}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial P_{SYS_2I}}\right)^2 \left(\frac{U_{P_{SYS_2I}}}{P_{SYS_2I}}\right)^2 \\
&= \left(-\frac{P_{SYS_2I}}{V_{CUMI}} \cdot \frac{22.4DV_{LOW}}{RP_{STD}W_{SAM}T_{SYS}}\right)^2 \left(\frac{U_{P_{SYS_2I}}}{P_{SYS_2I}}\right)^2 \\
\left(\frac{P_{SAMI}}{V_{CUMI}} \cdot \frac{\partial V_{CUMI}}{\partial P_{SAMI}}\right)^2 \left(\frac{U_{P_{SAMI}}}{P_{SAMI}}\right)^2 \\
&= \left(-\frac{P_{SAMI}}{V_{CUMI}} \cdot \frac{22.4DV_{FC}}{RP_{STD}W_{SAM}T_{ABT}}\right)^2 \left(\frac{U_{P_{SAMI}}}{P_{SAMI}}\right)^2
\end{aligned}$$

For the experiment composed of N equilibrium points, the uncertainty of the final pore volume is the combination of every single pore volumes:

$$\left(\frac{U_{V_{CUM}}}{V_{CUM}}\right)^2 = \left(\frac{V_{CUM1}}{V_{CUM}} \cdot \frac{\partial V_{CUM}}{\partial V_{CUM1}}\right)^2 \cdot \left(\frac{U_{V_{CUM1}}}{V_{CUM1}}\right)^2 + \left(\frac{V_{CUM2}}{V_{CUM}} \cdot \frac{\partial V_{CUM}}{\partial V_{CUM2}}\right)^2 \cdot \left(\frac{U_{V_{CUM2}}}{V_{CUM2}}\right)^2 + \dots + \left(\frac{V_{CUMN}}{V_{CUM}} \cdot \frac{\partial V_{CUM}}{\partial V_{CUMN}}\right)^2 \cdot \left(\frac{U_{V_{CUMN}}}{V_{CUMN}}\right)^2$$

$$V_{CUM} = V_{CUM1} + V_{CUM2} + \dots + V_{CUMN}$$

where

V_{LOW} -lower manifold volume (cm³),

V_{FC} -volume of free space, cold (cm³),

V_{FW} -volume of free space, warm (cm³),

$P_{SYS,I}$ -system manifold pressure before Ith equilibrium (mmHg),

$P_{SYS,I}$ -system manifold pressure after Ith equilibrium (mmHg),

P_{SAMI} -sample pressure after Ith equilibrium (mmHg),

P_{STD} -standard pressure (760 mmHg),

T_{SYS} -system manifold temperature (K),

T_{ABT} -analysis bath temperature (K),

W_{SAM} -weight of sample (g),

R -gas constant (0.082 atm·l/(mol·K))

V_I -amount of gas adsorbed per gram of sample (cm³/g STP),

V_{CUMI} -pore volume of Ith equilibrium point (cm³/g STP),

V_{CUM} -final pore volume of a sample (cm³/g STP), and

D -density conversion factor (0.001831 cm³ liquid/cm³ STP).

2. Example for the calculation of uncertainty

The CO₂ adsorption results for a sample CM-V1073H2 were used to show the example of determining the uncertainty of pore volume. This sample was pyrolysed in vacuum at a final temperature of 1073 K with a hold time of 120 min and a heating rate of 0.5 K/min. For the 10th equilibrium point, the uncertainty of the weight of the sample is

$$\begin{aligned} & \left(\frac{W_{SAM}}{V_{CUM10}} \cdot \frac{\partial V_{CUM10}}{\partial W_{SAM}} \right)^2 \left(\frac{U_{W_{SAM}}}{W_{SAM}} \right)^2 \\ &= \left\{ \frac{0.0309}{0.0797} \times \frac{22.4D}{RP_{STD}} \times \left[\frac{36351.57}{298} - \frac{101.85 \times 18.3370}{273} \right] \left(-\frac{1}{0.0309^2} \right) \right\}^2 (0.03\%)^2 \\ &= 8.52 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} & \left(\frac{T_{SYS}}{V_{CUM10}} \cdot \frac{\partial V_{CUM10}}{\partial T_{SYS}} \right)^2 \left(\frac{U_{T_{SYS}}}{T_{SYS}} \right)^2 \\ &= \left[\frac{298}{0.0797} \times \frac{22.4D \times 36351.57}{RP_{STD} \times 0.0309} \times \left(-\frac{1}{298^2} \right) \right]^2 \left(\frac{0.02}{298} \right)^2 \\ &= 4.79 \times 10^{-6} \end{aligned}$$

$$\begin{aligned} & \left(\frac{P_{SYS10}}{V_{CUM10}} \cdot \frac{\partial V_{CUM10}}{\partial P_{SYS10}} \right)^2 \left(\frac{U_{P_{SYS10}}}{P_{SYS10}} \right)^2 \\ &= \left(\frac{1}{0.0797} \times \frac{22.4D \times 34.7898}{RP_{STD} \times 0.0309 \times 298} \right)^2 \left(\frac{0.052}{1} \right)^2 \\ &= 2.63 \times 10^{-6} \end{aligned}$$

$$\begin{aligned} & \left(\frac{P_{SYS210}}{V_{CUM10}} \cdot \frac{\partial V_{CUM10}}{\partial P_{SYS210}} \right)^2 \left(\frac{U_{P_{SYS210}}}{P_{SYS210}} \right)^2 \\ &= \left(-\frac{1}{0.0797} \times \frac{22.4D \times 34.7898}{RP_{STD} \times 0.0309 \times 298} \right)^2 \left(\frac{0.052}{1} \right)^2 \\ &= 2.63 \times 10^{-6} \end{aligned}$$

$$\begin{aligned}
& \left(\frac{P_{SAM10}}{V_{CUM10}} \cdot \frac{\partial V_{CUM10}}{\partial P_{SAM10}} \right)^2 \left(\frac{U_{P_{SAM10}}}{P_{SAM10}} \right)^2 \\
&= \left(-\frac{1}{0.0797} \times \frac{22.4D \times 18.3370}{RP_{STD} \times 0.0309 \times 273} \right)^2 \left(\frac{0.052}{1} \right)^2 \\
&= 8.71 \times 10^{-7} \\
& \left(\frac{U_{V_{CUM10}}}{V_{CUM10}} \right)^2 = 8.52 \times 10^{-5} + 4.79 \times 10^{-6} + 2.63 \times 10^{-6} + \times 2.63 \times 10^{-6} + 8.71 \times 10^{-7} \\
&= 9.61 \times 10^{-5}
\end{aligned}$$

$$\begin{aligned}
& \left(\frac{V_{CUM10}}{V_{CUM}} \cdot \frac{\partial V_{CUM}}{\partial V_{CUM10}} \right)^2 \cdot \left(\frac{U_{V_{CUM10}}}{V_{CUM10}} \right)^2 \\
&= \left(\frac{0.0797}{0.2024} \right)^2 \times (9.61 \times 10^{-5}) \\
&= 1.49 \times 10^{-5}
\end{aligned}$$

For the totally 53 equilibrium points, the final uncertainty of the final pore volume is:

$$\begin{aligned}
\left(\frac{U_{V_{CUM}}}{V_{CUM}} \right)^2 &= \left(\frac{V_{CUM1}}{V_{CUM}} \cdot \frac{\partial V_{CUM}}{\partial V_{CUM1}} \right)^2 \cdot \left(\frac{U_{V_{CUM1}}}{V_{CUM1}} \right)^2 + \left(\frac{V_{CUM2}}{V_{CUM}} \cdot \frac{\partial V_{CUM}}{\partial V_{CUM2}} \right)^2 \cdot \left(\frac{U_{V_{CUM2}}}{V_{CUM2}} \right)^2 + \dots \\
&\quad + \left(\frac{V_{CUMN}}{V_{CUM}} \cdot \frac{\partial V_{CUM}}{\partial V_{CUMN}} \right)^2 \cdot \left(\frac{U_{V_{CUMN}}}{V_{CUMN}} \right)^2 \\
&= 9.90 \times 10^{-7} + 2.07 \times 10^{-6} + \dots + 7.12 \times 10^{-5} \\
&= 2.17 \times 10^{-3}
\end{aligned}$$

$$\left(\frac{U_{V_{CUM}}}{V_{CUM}} \right) = 4.65\%$$

The uncertainty for the final pore volume $\left(\frac{U_{V_{CUM}}}{V_{CUM}} \right)$ is about 4.65%.

APPENDIX C

PUBLICATIONS ARISING FROM THIS RESEARCH

1. Lua Aik Chong and Su Jincai, Isothermal and non-isothermal pyrolysis kinetics of Kapton® polyimide, Polym. Degrad. Stab. 91 (2006) 144-153.
2. Su Jincai and Lua Aik Chong, Influence of carbonisation parameters on the transport properties of carbon membranes by statistical analysis, J. Membr. Sci. 278 (2006) 335-343.
3. Lua Aik Chong and Su Jincai, Effects of carbonisation on the pore evolution and gas permeation properties of carbon membranes from Kapton® polyimide, Carbon (in press).

APPENDIX D

SUMMARY OF EXPERIMENTAL RESULTS

Table 1 Application of proposed model to the pyrolysis of Kapton® 100HN

	Pyrolysis heating rate (K/min)				
	2	4	6	8	10
T _m (K)	849.3	861.9	872.8	880.2	887.3

Table 2 Pure gas permeances for the Kapton® membrane and the membranes heat treated at temperatures of 623-1073 K

Sample	Permeance [$\times 10^{-10}$ mol/(m ² sPa)]				
	He	CO ₂	O ₂	N ₂	CH ₄
Kapton	0.871	0.169	0.0605	0.0143	0.0142
Kp-N623	0.908	0.150	0.0521	0.0129	0.00946
Kp-N673	0.976	0.157	0.0634	0.0237	0.0192
Kp-N698	0.865	0.176	0.0630	0.0212	0.0103
Kp-N723	0.944	0.163	0.0608	0.0319	0.0139
Kp-N748	1.6	0.483	0.104	0.0468	0.026
Kp-N773	10.6	11	1.9	0.57	0.55
Kp-N873	268.	362	99.8	16.6	5.17
Kp-N1073	12.6	6.4	1.34	0.08	0.02

Table 3 Ideal selectivities for the Kapton® membrane and the membranes heat treated at temperatures of 623-1073 K

Temperature (K)	Ideal selectivities	
	O ₂ /N ₂	CO ₂ /CH ₄
295	4.23	11.90
623	4.04	15.86
673	2.68	8.18
698	2.97	17.10
723	1.91	11.73
748	2.22	18.58
773	3.33	20.00
873	6.01	70.01
1073	16.75	320

Table 4 Densities and specific volumes of the Kapton® membrane and the membranes heat treated at temperatures of 623-773 K

Temperature (K)	Density (g/cm ³)	Specific volume (cm ³ /g)
295	1.4348	0.6970
623	1.3789	0.7252
673	1.3201	0.7576
698	1.3683	0.7308
723	1.3396	0.7465
748	1.4187	0.7049
773	1.5266	0.6551

Table 5 Pure gas permeabilities for the carbon membranes carbonised at various parameters

Sample	Single gas permeabilities (Barrer)			
	He	CO ₂	O ₂	N ₂
CM1	563.90	1056.83	304.22	111.69
CM2	80.77	45.03	37.97	30.16
CM3	89.31	133.88	26.58	26.08
CM4	58.85	50.01	42.88	26.57
CM5	571.48	684.17	157.69	21.89
CM6	708.99	715.03	188.04	67.59
CM7	71.11	93.61	33.25	18.57
CM8	51.82	43.67	26.24	15.55

Table 6 X-ray diffraction angle and average d-spacing of the carbon membranes prepared at different temperatures under vacuum

Temperature (K)	Diffraction angle (degree)	d-spacing (Å)
823	23.06	3.85
873	23.50	3.78
973	23.66	3.76
1073	23.92	3.72
1173	24.04	3.70
1273	24.40	3.65

Table 7 X-ray diffraction angle and average d-spacing of the carbon membranes prepared at 873 K and 1073 K under argon, helium, nitrogen and vacuum

Sample	Diffraction angle (degree)	d-spacing (Å)
CM-Ar873H2	22.00	4.04
CM-Ar1073H2	22.70	3.91
CM-He873H2	22.32	3.98
CM-He1073H2	22.68	3.92
CM-N873H2	23.72	3.75
CM-N1073H2	23.92	3.72
CM-V873H2	23.92	3.72
CM-V1073H2	24.16	3.68

Table 8 Intensity ratio of D-peak to G-peak and size of graphitic clusters of the membranes carbonised under argon, helium, nitrogen and vacuum

Sample	I _D /I _G	Size of graphitic cluster (nm)
CM-Ar873H2	2.52	3.29
CM-Ar1073H2	2.49	3.32
CM-He873H2	2.52	3.29
CM-He1073H2	2.44	3.40
CM-N873H2	2.51	3.30
CM-N1073H2	2.46	3.36
CM-V873H2	2.59	3.19
CM-V1073H2	2.50	3.31

Table 9 Effect of carbonisation atmosphere on the gas permeances

Sample	Permeance [$\times 10^{-10}$ mol/(m ² sPa)]				
	He	CO ₂	O ₂	N ₂	CH ₄
CM-Ar873H2	297	393	88.1	12.9	4.21
CM-Ar1073H2	16	6.15	1.26	0.076	0.013
CM-He873H2	250	308	82.7	10.3	4.37
CM-He1073H2	14.6	6.31	1.18	0.088	0.018
CM-N873H2	268	362	99.8	16.6	5.17
CM-N1073H2	12.6	6.4	1.34	0.078	0.017
CM-V873H2	137	158	43.4	4.63	1.83
CM-V1073H2	8.19	0.98	0.37	0.021	0.0060

Table 10 Effect of carbonisation atmosphere on the ideal selectivity

Sample	Ideal selectivity	
	O ₂ /N ₂	CO ₂ /CH ₄
CM-Ar873H2	6.83	93.35
CM-Ar1073H2	8.03	70.48
CM-He873H2	6.01	70.01
CM-He1073H2	9.37	86.34
CM-N873H2	16.69	476.74
CM-N1073H2	13.39	356.50
CM-V873H2	17.11	374.27
CM-V1073H2	17.76	162.46

Table 11 XRD parameters of carbon membranes obtained from Kapton® films with different thickness

Sample	Precursor	Thickness of precursor (μm)	Diffraction angle (degree)	D-spacing (Å)
CM-30	30HN	7.6	25.24	3.526
CM-50	50HN	12.7	25.18	3.534
CM-100	100HN	25.4	23.84	3.730
CM-200	200HN	50.8	23.88	3.724
CM-500	500HN	127	23.90	3.721

Table 12 Permeances of He and CO₂ through carbon membranes with different thickness

Sample	Permeance [$\times 10^{-10}$ mol/(m ² sPa)]	
	He	CO ₂
CM-30	8.93	0.35
CM-50	13.9	1.81
CM-100	6.99	0.82
CM-200	5.50	0.73
CM-500	2.27	0.31

Table 13 Potential energy estimate of CH₄, O₂ and N₂ in carbon membrane pores

Pore size (Å)	Potential energy (kJ/mol)		
	CH ₄	O ₂	N ₂
3.9	-23.64	-17.11	-18.03
4.0	-23.43	-16.67	-17.74
4.5	-21.10	-14.42	-15.72
5.0	-18.39	-12.44	-13.65
6.0	-14.06	-9.54	-10.43
8.0	-9.15	-6.31	-6.82
10.0	-6.64	-4.65	-4.98
12.0	-5.20	-3.72	-3.90
14.0	-4.25	-3.01	-3.19
16.0	-3.58	-2.55	-2.70
18.0	-3.10	-2.21	-2.33
20.0	-2.73	-1.95	-2.06

Table 14 Theoretical permeances of CH₄, O₂, and N₂ through carbon membranes

Pore size (Å)	Potential energy (kJ/mol)		
	CH ₄	O ₂	N ₂
3.93	0.004	0.015	0.007
4.08	0.006	0.26	0.013
4.82	0.27	4.75	0.30
5.20	1.31	11.57	2.75
5.74	2.16	3.24	2.00
6.01	9.80	16.89	10.1