

CHAPTER 3 :EXPERIMENTAL

OVERVIEW

Chapter 3 constitutes of 5 main Sections namely, Membranes used (Section 3.1), Chemicals and gases used (Section 3.2), Experimental methodology (Section 3.3), Experimental design and planning (Section 3.4) and Analytical equipment (Section 3.5). Section 3.1 presents an outline of the membranes used, their respective properties and suppliers. Section 3.2 outlines the chemicals and gases used, the purpose of the chemicals and the respective suppliers. Section 3.3 outlines a stepwise description of the experimental route. Section 3.4 details the experimental bounds of manipulated variables based on the scope of the present investigation. Section 3.5 then presents a description of the analytical equipment utilized and allied calibration information.

3.1 MEMBRANES USED

Six commercial membranes were used, Udel Polysulfone, Hyflon M, Hyflon F and Halar acquired from Ajedum films Solvay (USA), Teflon AF 2400 from Biogeneral (USA) and Nafion 117 from Ion Power (USA).

Udel Polysulfone and Teflon AF2400 are commercially used gas separation membranes (Biogeneral, 2012; Solvay 2012). The remainder 4 membranes though not known to be used as gas separation membranes were employed in the present study so as to unearth unknown gas separation capabilities and also aid in generating a pool of data that would be compared to literature so as to validate the designed setup. Furthermore Halar and the perfluorosulfonic acid based Nafion 117 are highly resistant to acidic conditions as they find applications in fuel cells. Resistance to corrosive environments is a desirable feature in the present application as some SO_2 may be converted to sulphurous acid when subjected to humid conditions. The membranes in the present study were supplied as films with no support such that the overall film thickness is the thickness of the selective layer. Table 3.1 presents the mechanical properties of the membranes whilst Table 3.2 presents the thermal properties of the membranes.

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Table 3.1 Mechanical properties of membranes

FILM TYPE	SUPPLIER	USE AS A MEMBRANE	PROPERTIES		
			O ₂ permeability @ 25°C cm ³ .mm.m ² .day ⁻¹ .atm ⁻¹	Mechanical	
				Tensile Modulus @ 23 °C	Tensile Elongation at Break @ 23°C
Hyflon M series	Solvay ⁽¹⁾	-	300 ⁽¹⁾	500 - 600 MPa (ASTM D 1708) ⁽¹⁾	> 275% (ASTM D1708) ⁽¹⁾
Hyflon F series	Solvay ⁽²⁾	-	300 ⁽²⁾	400 - 500 MPa (ASTM D3307) ⁽²⁾	>300% (ASTM D3307) ⁽²⁾
Halar 500	Solvay ⁽³⁾	Fuel Cell membranes ⁽³⁾	9 ⁽³⁾	1400 - 2100 MPa (ASTM D638) ⁽³⁾	250-300 % (ASTM D638) ⁽³⁾
Udel Polysulfone	Solvay ⁽⁴⁾	Gas Separation, Reverse Osmosis & Hermodialysis ⁽⁵⁾	90.55 ⁽⁴⁾	2310 Mpa (MD) 2340 Mpa(TD) (ASTM D882) ⁽⁴⁾	50 % - 100 % (ASTM D882) ⁽⁴⁾
Nafion 117	Ion power/Dupont ⁽⁶⁾	Proton exchange membrane fuel cells ⁽⁶⁾	*70.92 ⁽⁷⁾	249 Mpa (@ 50% RH - ASTM D882) ⁽⁶⁾	225% (MD) 310% (TD) (%0% RH- ASTM D882) ⁽⁶⁾
Teflon AF 2400	Biogeneral/Dupont ⁽⁸⁾	Gas Separation Membranes ⁽⁸⁾	65007.36 ⁽⁸⁾	1540 MPa (ASTM D1708) ⁽⁹⁾	6.1 % (ASTM D1708) ⁽⁹⁾

(1) (Solvay, 2006a), (2) (Solvay, 2008), (3) (Solvay, 2006b), (4) (Solvay, 2011), (5) (Solvay, 2012), (6) (Dupont, 2009), (7) (Chiou & Paul, 1988:2163), (8) (Biogeneral, 2012), (9) (Koev, 2011), *Permeability of dry membrane, humidity dependent permeability given in Appendix E

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Table 3.2 Thermal properties of membranes

FILM TYPE	SUPPLIER	USE AS MEMBRANES	PROPERTIES		
			O ₂ permeability @ 25°C cm ³ .mm.m ⁻² .Day ⁻¹ .atm ⁻¹	Thermal	
				Tg °C	Thermal Expansion Coefficient ppm/°F
Hyflon M series	Solvay ⁽¹⁾	-	300 ⁽¹⁾	85 (DMTA) ⁽¹⁾	120-200 (ASTM D696) ⁽¹⁾
Hyflon F series	Solvay ⁽²⁾	-	300 ⁽²⁾	-	120-200 (ASTM E831) ⁽²⁾
Halar 500	Solvay ⁽³⁾	Fuel Cell membranes ⁽³⁾	9 ⁽³⁾	85 (DMTA) ⁽³⁾	90 (ASTM D696) ⁽³⁾
Udel Polysulfone	Solvay ⁽⁴⁾	Gas Separation, Reverse Osmosis & Hermodialysis ⁽⁵⁾	90.55 ⁽⁴⁾	190 (ASTM D3418) ⁽⁴⁾	31 (ASTM E831) ⁽⁴⁾
Nafion 117	Ion power/Dupont ⁽⁶⁾	Proton exchange membrane in fuel cells ⁽⁶⁾	*70.92 ⁽⁷⁾	125 & 195 ⁽⁸⁾	-
Teflon AF 2400	Biogeneral/Dupont ⁽⁹⁾	Gas Separation Membranes ⁽⁹⁾	65007.36 ⁽⁹⁾	240 (ASTM D3418) ⁽¹⁰⁾	-

(1) (Solvay, 2006a), (2) (Solvay, 2008), (3) (Solvay, 2006b), (4) (Solvay, 2011), (5) (Solvay, 2012), (6) (Dupont, 2009), (7) (Chiou & Paul, 1988:2163), (8) Jung & Kim, (2012:12580), (9) (Biogeneral, 2012), (10) (Koev, 2011), *Permeability of dry membrane, humidity dependent permeability given in Appendix E. MD-Machine direction, TD-Transverse direction

3.1.1 HYFLON PFA/MFA

Hyflon is a semi-crystalline void free (non-porous) polymer that can be used within service temperatures of cryogenic upto 250-260°C (Solvay, 2006a:12). It has excellent chemical resistance as such is not attacked by inorganic acids, strong mineral acids and inorganic oxidising agents (Solvay, 2006a:5). The applied pressure limit is dependent on the operation temperature. The Hyflon M (PFA) molecular structure is the same as that of Hyflon F (MFA) since Hyflon F (MFA) is regarded to belong to the perfluoroalkoxy class, the difference being melting point (Massey, 2003:91).

Figure 3.1 gives an image of the Hyflon molecular structure, whilst Figures A.2 and A.3 in Appendix A give SEM images with dimensions of both Hyflon F and Hyflon M respectively.

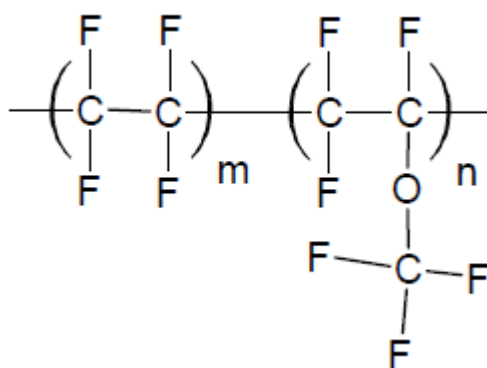


Figure 3.1 Molecular structure of Hyflon F (perfluoroalkoxy fluorocarbon)

3.1.2 HALAR ECTFE (ETHYLENE-CHLOROTRIFLUOROETHYLENE)

Halar is a semi-crystalline fluoropolymer that has a broad operating temperature range from cryogenic to 150°C depending on the grade and stresses applied (Solvay, 2006b:3). It has both excellent resistance to degradation by heat and chemicals such as strong acids and bases upto a pH of 14 (Solvay, 2006b:3). Just as with Hyflon and most polymeric materials, the applied pressure limit is dependent on the operating temperature. Figure 3.2 gives an image of the Halar ECTFE molecular structure, whilst Figure A.4 in Appendix A gives an SEM image with dimensions of Halar ECTFE.

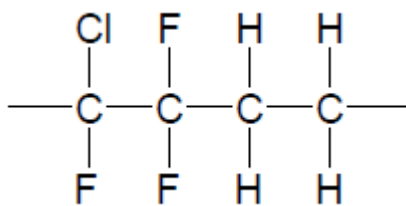


Figure 3.2 Molecular structure of Halar

3.1.3 UDEL POLYSULFONE

Udel polysulfone is a tough thermoplastic with a maximum service temperature range of 140°C - 160°C (Solvay, 2011:3). Udel Polysulfone is resistant to both acid and base attack, and is resistant to hot water hydrolysis, alcohols and aliphatic hydrocarbons (Solvay, 2011:32). However it does get attacked by polar organic and chlorinated solvents (Solvay, 2011:32). Figure 3.3 presents the Udel Polysulfone molecular structure, as Figure A.5 in Appendix A shows the corresponding SEM image with dimensions of the film.

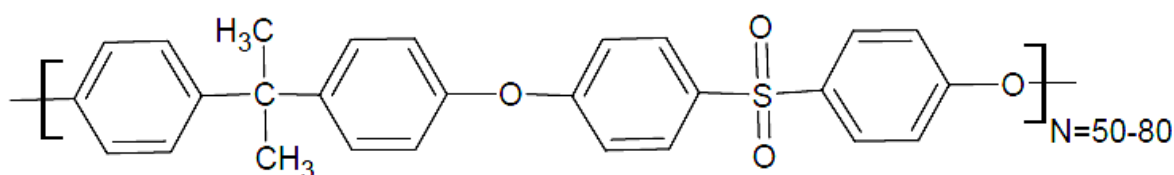


Figure 3.3 Molecular structure of Udel Polysulfone

3.1.4 TEFLON AF 2400

Teflon AF 2400 is an amorphous fluoro-polymer that finds use in high performance applications. It can be employed to temperatures of up to about 300°C (Dupont, 2011). Teflon AF 2400 remains intact despite undergoing thermal cycles (Dupont, 2011). The Teflon AF 2400 molecular structure is given in Figure 3.4, whilst Figure A.6 in Appendix A presents the respective SEM image with dimensions of Teflon AF 2400.

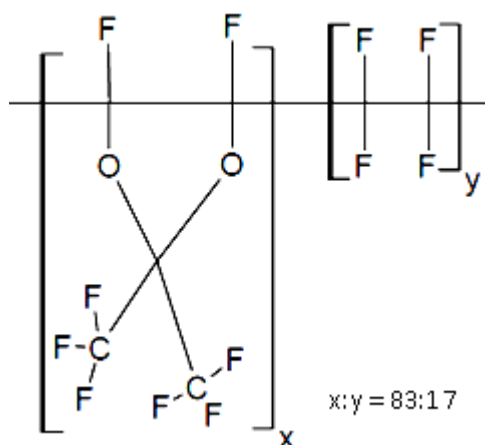


Figure 3.4 Molecular structure of Teflon AF 2400

3.1.5 NAFION 117

Nafion 117 is a non-reinforced film based on chemically stabilised perfluorosulfonic acid. The perfluorinated membrane finds applications in proton exchange applications and is chemically resistant and durable (Dupont, 2009). Figure 3.5 presents the molecular structure of Nafion 117 and the SEM image with dimensions of the film is given in Figure A.7 of Appendix A.

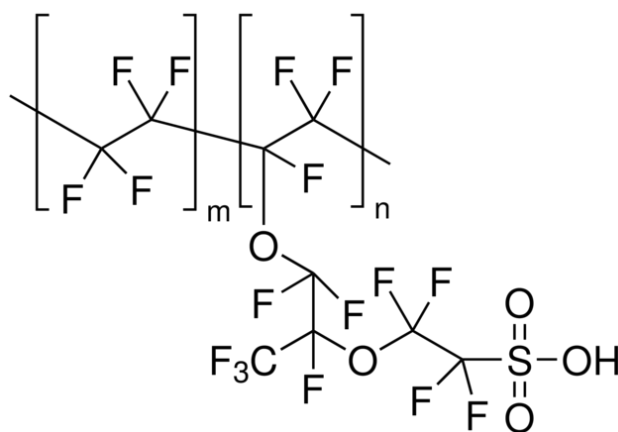


Figure 3.5 Molecular structure of Nafion 117

3.2 CHEMICALS AND GASES USED

Chemicals that were employed include sodium hydroxide pellets that were made into solution and used to absorb vented SO₂ in the cold trap, vacuum grease was used as a leak proof sealant and vacuum oil lubricated the vacuum pump internals. Table 3.3 presents the chemicals used and the respective supplier.

Ultra high purity oxygen supplied at 200 bar, carbon dioxide supplied at 50 bar, nitrogen supplied at 150 bar and sulphur dioxide at 3.9 Bar were employed for single permeation. Gas mixtures (SO₂:O₂, 25:75 wt %) supplied at 18 bar, (SO₂:O₂, 50:50 wt %) supplied at 7 bar and (SO₂:O₂, 75:25 wt %) supplied at 3.8 bar were used for binary permeation. Table 3.4 presents the gases used, the respective supplier, the purity and the supply pressure.

Table 3.3 Chemicals used

CHEMICAL	SUPPLIER
Sodium Hydroxide	C C Imelmann Pvt Ltd
Vacuum grease	Dow Corning
Vacuum pump oil	FUCHS

Table 3.4 Gases used

GAS	SUPPLIER	PURITY	SUPPLY PRESSURE
Sulphur dioxide (SO ₂)	Afrox	99.99 %	3.9 Bar
Oxygen (O ₂)	Afrox	99.99 %	200 bar
Carbon dioxide (CO ₂)	Afrox	99.99 %	50 bar
Nitrogen (N ₂)	Afrox	99.99 %	150 bar
SO ₂ /O ₂ (75:25) wt %	Afrox	-	3.8 bar
SO ₂ /O ₂ (50:50) wt %	Afrox	-	7.0 bar
SO ₂ /O ₂ (25:75) wt %	Afrox	-	18 bar
Air	Afrox	-	200 bar
Helium (He)	Afrox	99.99 %	200 bar

3.3 EXPERIMENTAL METHODOLOGY

3.3.1 INTRODUCTION

The determination of the permeability of polymeric films is often carried out through the use of one of the three (3) methods.

1. Constant pressure variable volume method, (Czichos, *et al.* 2006:378).
2. Constant volume variable pressure method, (Czichos, *et al.* 2006:378).
3. Mixed gas permeability method - a method using a special sensor for mixed gas permeation measurements, Czichos, *et al.* 2006:378).

Czichos, *et al.* 2006:378) presented the constant volume variable pressure method as having the capability to facilitate the measurement of low permeate fluxes yet measuring still high permeate fluxes. It is implied that the membrane that would offer the best SO₂/O₂ separation capability would present high SO₂ fluxes whilst simultaneously offering low O₂ fluxes. With the latter fact in mind, the ideal permeation method should have the capability of addressing both flux extremes in the single permeation experiments. Of the presented methods, the constant volume variable pressure method and the mixed gas permeability method were deemed proper candidates for the task. The constant pressure variable volume method is only limited to measurement of high permeate fluxes (Fluxes > 0.3 cm³.min⁻¹ (Czichos, *et al.* 2006:386)). The latter method was thus not ideal for the present study. The mixed gas permeability method ushers in complexity as the use of additional gases (sweep gas) and apparatus (gas chromatograph) would have to be considered. The constant volume variable pressure method was then the method of choice in the present study.

3.3.2 EXPERIMENTAL SETUP AND PROCEDURE

Table 3.5 gives a list of components and apparatus that were used to build the experimental setup. The supplier, specifications and the purpose of the individual apparatus are given. Shown in Figure 3.6 and Figure 3.7 are the schematic diagrams of the single and binary permeation experimental setups respectively. The process flows from left to right, starting off from the CO₂, N₂, SO₂ and O₂ gas cylinders on the extreme left for single permeation and SO₂/O₂ gas mixtures for binary permeation.

Table 3.5 Equipment list and specifications

EQUIPMENT	SUPPLIER	PURPOSE	SPECIFICATIONS				
				SO ₂	O ₂	CO ₂	N ₂
4 Pressure Regulators	Instrumentation Specialities & Afrox	Step down the supply cylinder pressure to the desired system pressure values.	Inlet	0-25 Mpa	0-25 Mpa	0-30 Mpa	0-25 Mpa
			Outlet	0-600 Kpa	0-6000 KPa	0 - 6000 Kpa	0-6000 Kpa
4 Mass Flow Controllers	Brooks Instruments	Control the gas flow into the system	0 - 1000 mln.min ⁻¹				
5 Non-Return Valves	Swagelok	Inhibit back flow of gases	7 Kpa crack pressure				
2 Pressure Transducers	Wika Instruments	Facillitate reading of pressure, both on the feed and permeate sides of the membrane	0 - 100 Bar				
1 Membrane Cell	N.W.U. Dpt Chem Eng	House the membrane	Stainless Steel				
1 Convection Oven	Labotec	Allow isothermal operation of the system	0 - 250°C Thermostated				
2 Thermocouples	Wika Instruments	Allow measurement of system temperature	Type T with potted seal, probe 3mm x 600mm				
1 Halogen Moisture Analyser	Mettler & Toledo	Determination of moisture content in membranes					
1 Back Pressure Regulator	Swagelok	Allow control of upstream pressure	0 - 500 Psig				
5 Valves	Swagelok	Isolate or connect different parts of the system	Stainless Steel				
1 Cold Trap	N.W.U. Dpt Instrument making	Trap acidic SO ₂ from damaging vacuum pump	Glass ware				
1 Vacuum Pump	Edwards	Evacuate the system					
Timer	Time me	Measure the rate of pressure build on the permeate					
Tubing	Swagelok	Offer a channel for gas flow	1/8 " stainless steel pipe diameter				

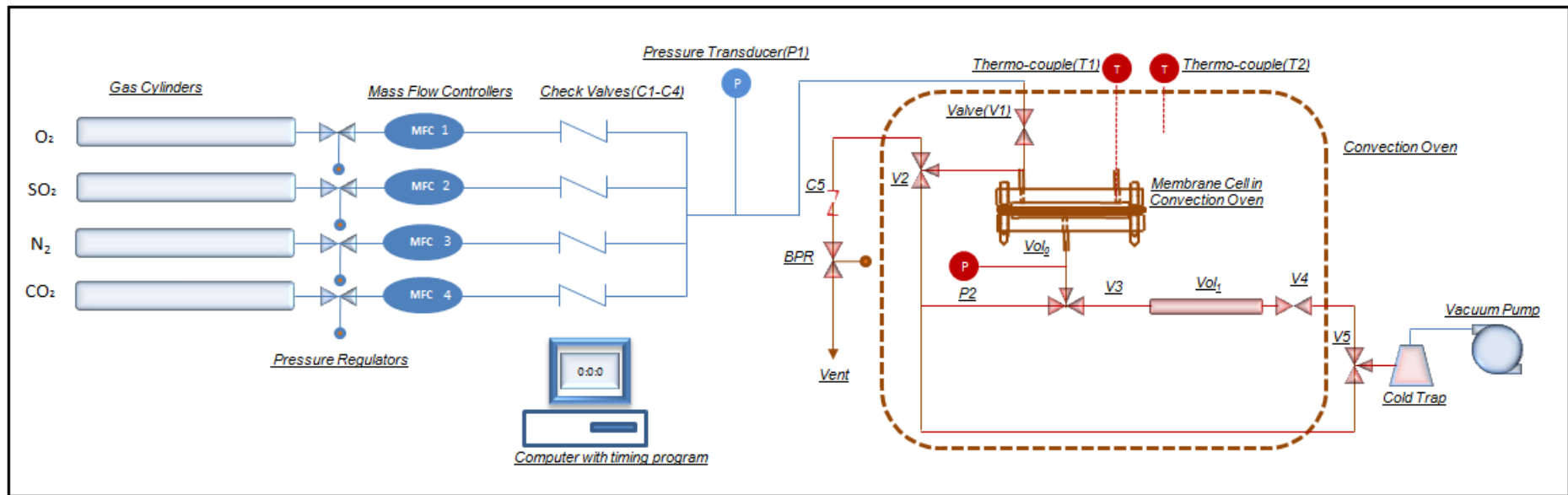


Figure 3.6 Experimental design setup – single permeation

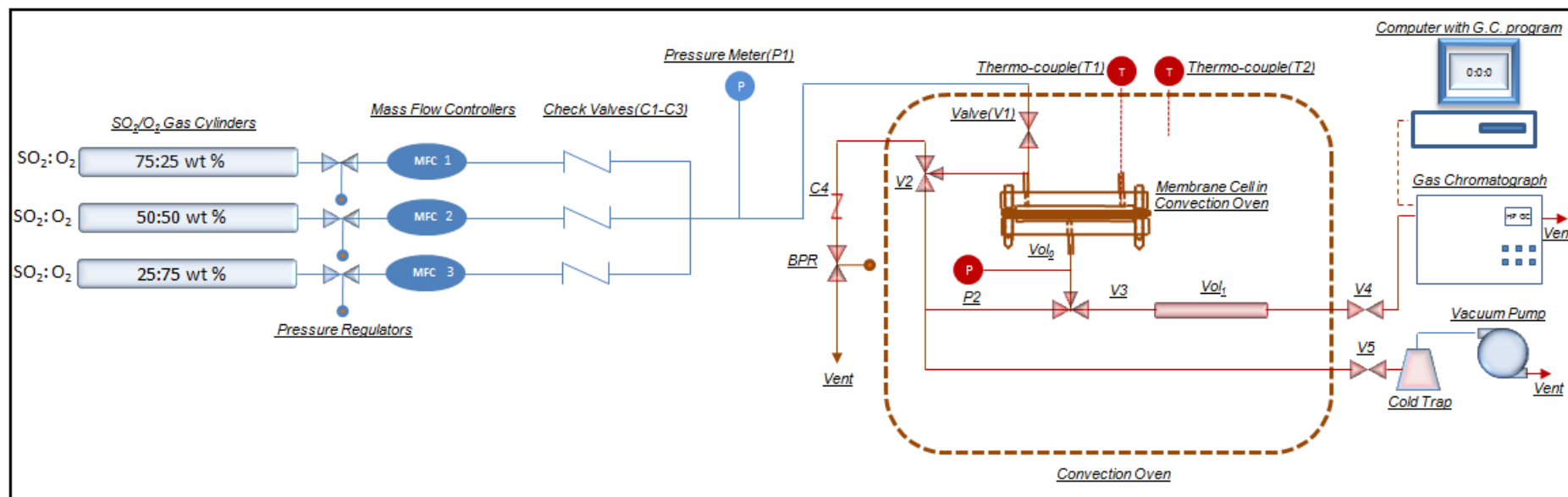


Figure 3.7 Experimental design setup – binary permeation

3.3.2.1 Determination of permeate side volume

Pure gas permeation and binary gas permeation experiments were performed through the constant volume-variable pressure method. Prior to experimentation, the constant volume of the permeate side had to be measured. The volume in question included the membrane cell permeate chamber volume, and the piping that connected the pressure transducer to the permeate chamber. To accurately determine this volume, the Burnett gas expansion method was employed (Czichos *et al.* 2011:434).

Burnett's method merely entails expanding a volume of inert gas such as helium from a chamber of unknown volume (to be determined through Burnett's method) into another chamber of known volume under isothermal conditions. Firstly, the permeate chamber in Figure 3.6 was isolated from the feed chamber through the use of an impermeable material. The downstream volume, that is, the volume of the permeate chamber plus the downstream tubing was connected to a pressure transducer. The downstream volume was first evacuated and then fed with inert gas (Helium) to a pressure that was sub-atmospheric and was recorded by the pressure transducer. Meanwhile, the volume of a separate chamber was measured through liquid filling and then completely dried. The chamber with the measured known volume was then evacuated whilst disconnected from the downstream volume by a valve. Connection was then made between the downstream volume and the chamber of known volume through a valve and the inert gas (Helium) was allowed to expand from the downstream volume to the chamber of known volume. It was only at equilibrium that the new pressure reading was recorded. Through the use of the ideal gas equation, the two pressure readings (before and after expansion) and the known chamber volume, the unknown downstream volume was then calculated. A series of gas expansions were performed in an effort to validate the resultant volume values. Once the downstream volume was known permeation experiments could commence. Calculations of the permeate volume are given in Appendix B.

3.3.2.2 Determination of leak rate

Prior to performing the permeation experiments, it was vital to first of all determine the rate of gas leakage into the isolated evacuated permeation cell so as to account for leaks in the final results. Determination of leak rate was performed thus.

The one-way valve (V1) shown in Figure 3.6 was initially closed. Two-way valve (V2) was then open to the configuration that connected the cell to the line leading to the cold trap and ultimately to the vacuum pump. Two way valve (V3) was open to a configuration that connected the cell to the line leading to the cold trap through valve (V2) and ultimately to the

vacuum pump. Two-way valve (V5) was open to a configuration that connected the cold trap to the cell through valves (V2) and (V3). The vacuum pump was switched on and allowed to evacuate both the feed and permeate sides of the cell for about 2 hours until the pressure value of transducer (P2) remained unchanged. Valve (V2) and valve (V3) were closed so as to isolate the membrane cell from the cold trap whilst timing was started immediately. Recording of the pressure build-up into the cell per given unit time was then done and the leak-rate determined.

3.3.2.3 Single permeation

It was vital that upon operation of the set up, safety was upheld, especially when working with the deadly SO_2 gas. A respirator, safety glasses, covered shoes and a dust coat were worn and all laboratory windows opened for adequate ventilation. It was important to ensure the cold trap had sufficient caustic soda solution to absorb SO_2 .

Once the leak-rate was known, with the membrane sample fitted into the cell, single permeation experiments were then performed.

With all valves closed in Figure 3.6. The back pressure regulator (BPR) was completely opened. Valve (V2) was opened to a configuration that connected the membrane cell to the vent through back pressure regulator (BPR). Valve (V1) was opened so as to connect the membrane cell to the mass flow controllers. The pressure regulator of the gas to be permeated was opened to a value slightly above the desired testing pressure so as to cater for pressure drops. The mass flow controller of the gas to be tested was opened so as to allow a gas flow rate of about 20 ml.min^{-1} to flow through to the cell and out through the vent to sweep out any contaminants for 2 minutes. The mass flow controller was then closed simultaneously with the back pressure regulator (BPR). Two-way valve (V3) was opened to the configuration that connected the membrane cell to the line leading to the cold trap through valve (V2) and ultimately to the vacuum pump. Two-way valve (V2) was slowly opened to the configuration that connected the membrane cell to the line leading to the cold trap and ultimately to the vacuum pump. Two-way valve (V5) was opened to the configuration that connected the cold trap and vacuum pump to the membrane cell through valves (V2) and (V3). The vacuum pump was switched on to allow evacuation of the feed line and the feed and permeate sides of the cell for about 2 hours until the pressure value of transducer (P2) remained unchanged. Within the two hours, valve (V2) was switched between the two configurations that allow connection of the closed back pressure regulator (BPR) to the membrane cell and the configuration that allowed connection of the membrane cell to the vacuum pump so as to evacuate the line between valve (V2) and back pressure regulator (BPR). With valve (V2) set in a configuration that connected the membrane cell to

back pressure regulator (BPR), the other valves were left to maintain their set configurations and the vacuum pump was also left on. The mass flow controller of the gas to be tested was opened and the pressure reading on pressure transducer (P1) was observed until it got to the desired feed value. Back pressure regulator (BPR) and the mass flow controller were opened or closed so as to control or maintain the value of the feed pressure on pressure transducer (P1). Once the feed pressure value on pressure transducer (P1) was almost constant ($\pm 20\text{mB}$) the oven temperature was set to 25°C for single permeation experiments with the help of thermocouple (T1) and thermocouple (T2). Two way valve (V3) was closed whilst simultaneously starting the timer and recording the pressure value on pressure transducer (P2). Permeation was allowed to occur into the known constant volume (Vol_0) and recording of the permeate pressure build up with time was done. As the experiment proceeded, the pressure value on the feed pressure transducer (P1) was kept almost constant. The vacuum pump was kept off as the experiment proceeded. In the event any significant deviations occurred on the feed pressure value, which would obviously be a decrease in pressure as pressure loss in the feed chamber was attributed to permeation, the mass flow controller was opened slightly to increase the feed pressure to the set experimental value. Care was exercised to curb overshooting the set experimental value during an experiment. Once recording was done (6- 8 plotting points), valve (V3) was opened to the configuration that connected the permeate volume Vol_0 to the vacuum pump through valve (V2) and the vacuum pump was switched on so as to evacuate volume Vol_0 . When the permeate pressure value was now identical to that of the previous experiment complete evacuation of Vol_0 had been done. The pressure build-up with time due to permeation was then recorded as was done in the previous experiment. The same procedure for permeate pressure measurement with time was performed on all single permeation experiments. In the event that the gas that was permeated, permeated so fast such that the pressure build up with time was too rapid to be accurately measured, a larger volume (Vol_1) was employed. The permeate total volume then became $\text{Vol}_0 + \text{Vol}_1$. With the latter configuration, an alternate procedure was followed. With all valves closed, back pressure regulator (BPR) was completely opened. Valve (V2) was opened to a configuration that connected the cell to the vent through back pressure regulator (BPR). Valve (V1) was opened so as to connect the membrane cell to the mass flow controllers. The pressure regulator of the gas to be permeated was opened to a value slightly above the desired experimental feed pressure so as to cater for pressure drops. The mass flow controller of the gas to be tested was opened so as to allow a gas flow rate of about $20\text{ ml}\cdot\text{min}^{-1}$ to flow through to the cell and out through the vent to sweep out any contaminants for 2 minutes. The mass flow controller and the back pressure regulator (BPR) were completely closed. The vacuum pump was switched on to allow evacuation of the permeate side volume ($\text{Vol}_0 + \text{Vol}_1$). Two-way valve (V5) was opened

to the configuration that connected the cold trap and vacuum pump to (Vol₁). One way valve (V4) was opened to allow evacuation of volume (Vol₁) for about 5 minutes. Two-way valve (V3) was opened to the configuration that connected the membrane cell to the line leading to volume (Vol₁) and ultimately to the vacuum pump. Evacuation of the permeate side of the cell for about 2 hours was done until the pressure value of transducer (P2) remained unchanged. Valve (V3) was closed whilst the configuration of valve (V5) was changed to that connecting the cold trap and vacuum pump to the feed side of the cell through valve (V2). Two-way valve (V2) was opened slowly to the configuration that connected the membrane cell to the line leading to the cold trap and ultimately to the vacuum pump and was left for 2 hours. Within the two hours, valve (V2) was switched between the two configurations that allowed connection of the back pressure regulator (BPR) to the membrane cell and the configuration that allowed connection of the cell to the vacuum pump so as to evacuate the line between valve (V2) and back pressure regulator (BPR). With valve (V2) set in a configuration that connected the membrane cell to back pressure regulator (BPR), the other valves maintained their set configurations and the vacuum pump was left on, the mass flow controller of the gas to be permeated was opened and the pressure reading on pressure transducer (P1) was observed until it got to the desired feed value. The back pressure regulator (BPR) and the mass flow controller were opened or closed so as to control or maintain the value of the feed pressure on pressure transducer (P1). Once the feed pressure value on pressure transducer (P1) was almost constant ($\pm 20\text{mB}$) the oven temperature was set to 25°C for single permeation with the help of thermocouple (T1) and thermocouple (T2). Valve (V5) was switched on to the configuration that connected the cold trap and vacuum pump to volume (Vol₁). Valve (V3) was opened to the configuration that connected the bottom of the cell to the cold trap and vacuum pump through volume (Vol₁) so as to polish up the downstream vacuum before conducting the experiment. Once evacuation was done, with the oven temperature still at 25°C and the feed pressure still at the set experimental value, the experiment could then commence. Valve (V4) was closed whilst starting the timer simultaneously and recording the pressure value on pressure transducer (P2). As permeation occurred into the known constant volume (Vol₀ + Vol₁) the permeate pressure build up with time was recorded. As the experiment proceeded, pressure values on the pressure transducer (P1) and temperature values on thermocouples (T1) and (T2) were monitored to ensure the pressure and temperature values did not deviate from the set values. The vacuum pump was switched off. In the event any significant deviations occurred on the feed pressure value, which would obviously be a decrease in pressure as pressure loss in the feed was attributed to permeation, the mass flow controller was used to slightly increase the feed pressure. Care was exercised so as not to overshoot the desired feed pressure value during an experiment. Once recording was done (6- 8 plotting points), valves

(V3) and (V4) were opened to the configurations that connected the permeate volume ($Vol_0 + Vol_1$) to the vacuum pump and the vacuum pump was switched on so as to evacuate the volume ($Vol_0 + Vol_1$). When done with evacuating to the initial pressure value identical to that of the previous experiment, the set up was ready for another experiment. Valve (V4) was then closed as the timer was started for the next experiment.

3.3.2.4 Binary permeation

It was vital that upon operation of the set up, safety was upheld, especially when working with the deadly SO_2 gas. A respirator, safety glasses, covered shoes and a dust coat were worn and all laboratory windows were opened for adequate ventilation. It was also crucial to ensure the cold trap had sufficient caustic soda solution to absorb vented SO_2 .

Valve (V4) of Figure 3.7 was set to a configuration that disconnected the gas chromatograph from Vol_1 and valve (V3) was set to a configuration that connected the permeate chamber of the membrane cell to the cold trap through valves (V2) and (V5). With back pressure regulator (BPR) completely closed, valve (V2) was set to connect the feed chamber of the membrane cell to the cold trap through valve (V5), and valve (V1) set to connect the mass flow controllers to the feed chamber of the membrane cell. With the gas cylinder valve completely closed, the pressure regulator and mass flow controller of the gas mixture to be investigated were set fully open. The vacuum pump was switched on, and after five minutes the whole experimental setup was connected to the vacuum pump through valve (V5). The vacuum pump was left on whilst (Vol_1) was evacuated by connecting the already evacuated permeate chamber to volume (Vol_1) through valve (V3). The gas from volume (Vol_1) that built up into the permeate chamber was then flushed out by re-connecting the permeate chamber to the vacuum pump through valves (V3), (V2) and (V5). (Vol_1) was continuously evacuated by repeating the procedure in the latter two statements until complete evacuation was achieved. In a similar manner, the line between valve (V2) and back pressure regulator (BPR) was evacuated by connecting the line through valve (V2) to the already evacuated feed chamber. The gas from the line that built up in the feed chamber was then flushed out by re-connecting the feed chamber to the vacuum pump through valve (V2) and valve (V5). The procedure in the two latter statements was repeated to ensure complete evacuation of the line between back pressure regulator (BPR) and valve (V2).

Once the readings on the two pressure meters (P1) and (P2) remained almost unchanged, complete evacuation would have been achieved. With back pressure regulator (BPR) completely closed and valve (V1) open, the gas cylinder valve was slowly opened. The feed chamber of the membrane cell was connected to the closed back pressure regulator (BPR) through valve (V2). Through the use of the mass flow controller and gas cylinder pressure

regulators, the upstream pressure was set to the working value. The back pressure regulator (BPR) would assist in venting gas in case the upstream pressure exceeded the working value. Once the upstream pressure was set, the oven temperature was set to the desired working value. Sub-ambient temperatures were achieved through placing ice in the oven and then setting the oven draft fan on so as to circulate the cold draft evenly. Valve (V5) was closed and the vacuum pump was switched off. The permeate chamber of the membrane cell was connected to volume (Vol₁) through valve (V3) with valve (V4) closed.

The permeate pressure was allowed to build up in both volumes (Vol₁) and (Vol₀) until it slightly exceeded atmospheric pressure. Carrier gases helium and air (not in diagram) were set open at 400 kPa and 200 kPa respectively and connected to the carrier gas lines of the gas chromatograph and the gas chromatograph was switched on. Once the gas chromatograph was ready, the gas chromatograph injection line was connected to the permeate chamber through valve (V4) and the permeated gas was allowed to flush the gas chromatograph injection line. A sample of the permeate gas was injected into the HP 6890 gas chromatograph through pressing the start button on the face of the gas chromatograph. The gas chromatograph results were then processed by a computer program (Agilent Chemstation (2001 – 2006)) that gave the peak areas representing the gas compositions.

The experimental procedure for the determination of the binary flux of the gases was identical to that of single permeation experiments and needed not be repeated.

3.3.3 VALIDATION OF EXPERIMENTAL METHOD

The constant volume variable pressure method is often expected to give permeate pressure – time plots of the form given in Figure 3.8. However in the current study, the transient permeation part of the graph was not included due to the accuracy limitations of the devices in use. Nonetheless, the steady state permeation region is good enough for attaining desired results (Dhingra, 1997:117). A study by Dhingra, (1997:117) proves that the use of the truncated steady state part of the pressure - time graph alone still gives acceptable results for the calculation of gas permeability (Dhingra, 1997:117). The straight region of the graph represents the steady state permeation region, several authors have indicated that. Stern *et al.* (1963:2047) term the linear section of the graph as the steady state region whilst Macchione *et al.* (2007:2624) refer to the tangent of the pressure-time graph as the steady state curve. Mohammadi *et al.* (1994:281) highlight that the change of pressure with time exhibits a linear form within the experimental range. The latter fact suggests that the range that covers the steady state range should generate a linear pressure – time graph.

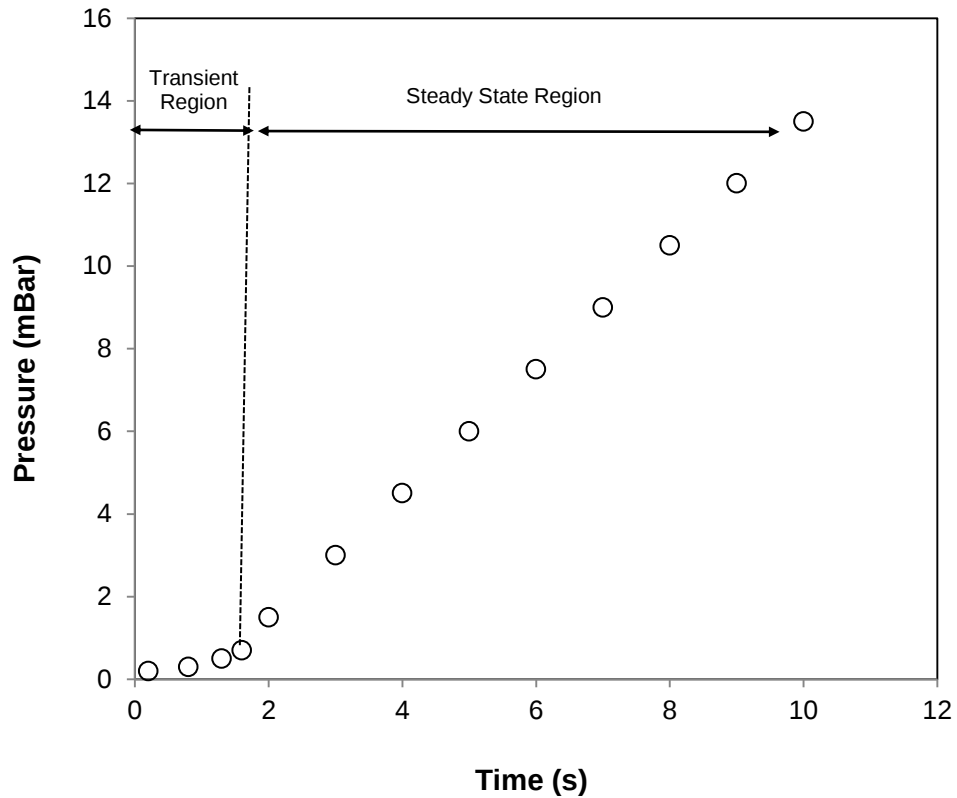


Figure 3.8 Pressure-Time graph for constant volume variable pressure method
(Adapted from Koros & Chern, (1987:890))

Czchios *et al.* (2006:379) state that the permeate pressure should be allowed to build up to as high as about 30 mBar for a feed pressure of about 4.4 Bar for flux measurement. The resultant feed pressure : permeate pressure ratio is about 150. A linear plot of the maximum allowable permeate pressure against feed pressure for flux measurement based on the 150 ratio is presented Figure 3.9.

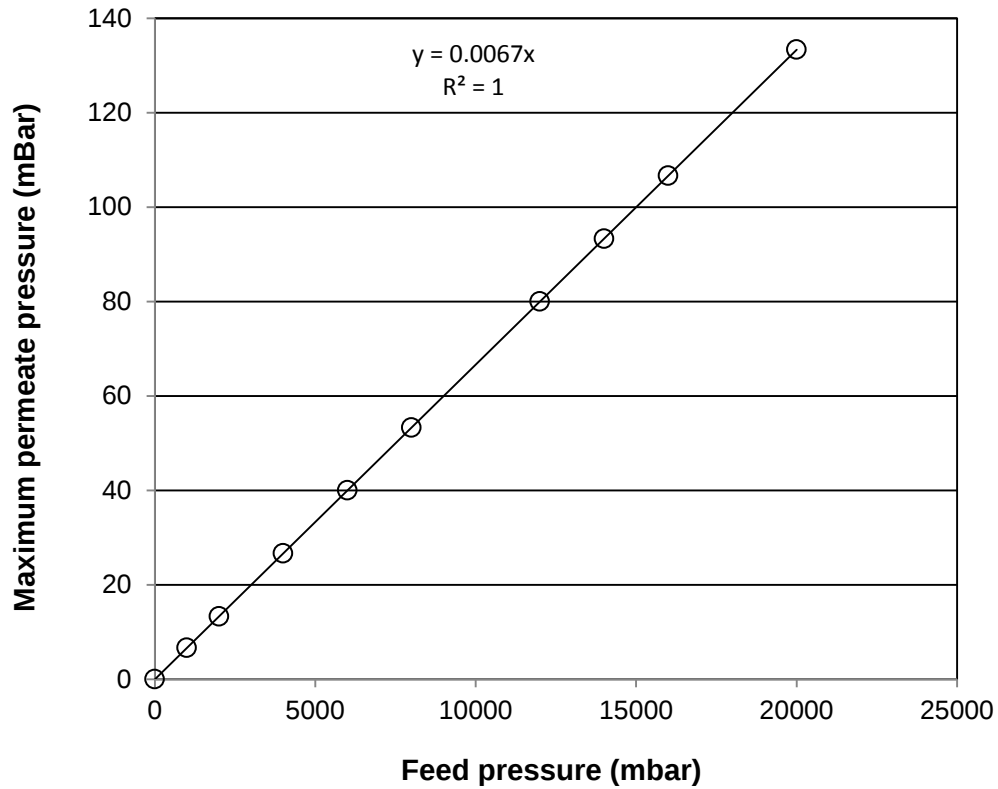


Figure 3.9 Maximum allowable permeate pressure

In the current study, the ratio suggested by Czchios *et al.* (2006:379) was violated only at the 1 bar feed pressure point which corresponds to a maximum allowable permeate pressure of 6.67 mbar, a maximum of 12 mbar was allowed instead. Results almost identical to literature where achieved despite the violation.

Furthermore, Macchione *et al.* (2007:2623) employed a feed pressure of 1 bar and a maximum allowable permeate pressure of 13.3 mBar. The effect of increasing the maximum allowable permeate pressure can be fatal as this may alter the trans-membrane pressure significantly and thus result in error. Figure 3.10 shows how the gradient of the permeate pressure – time graph changes as the maximum allowable permeate pressure is increased beyond stipulated proportions.

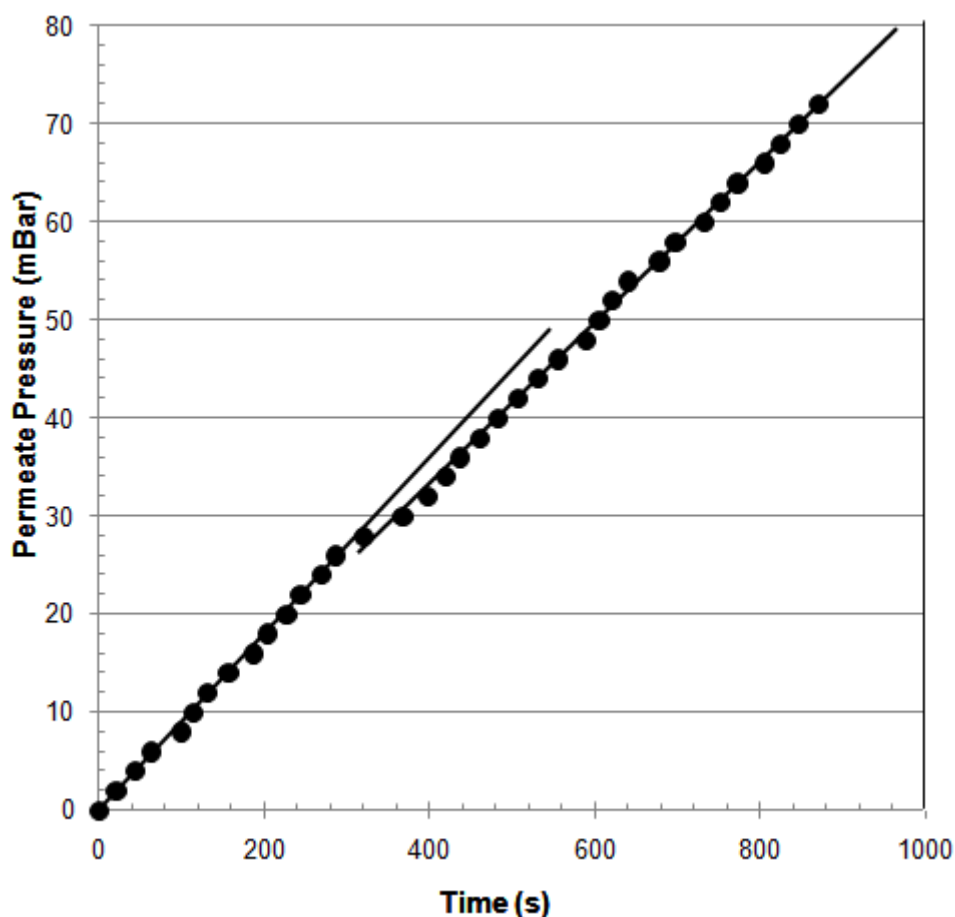


Figure 3.10 Change of dp/dt with increased maximum allowable permeate pressure

From Figure 3.10, there are two clear cut visible regions with differing gradients, however through calculation, the graph in Figure 3.10 can be divided into 4 regions with gradients of $0.08802 \text{ mBar.s}^{-1}$, $0.08419 \text{ mBar.s}^{-1}$, $0.08289 \text{ mBar.s}^{-1}$ and $0.08245 \text{ mBar.s}^{-1}$. The latter discourse emphasises the need to use an optimum permeate pressure experimental range as suggested by Czchios *et al.* (2006:379).

Authors inclusive of Massey, (2003:3), Stern & Fried, (2007:1036) and Fritzsche *et al.* (1990:564) have indicated that the permeation rates of permanent or supercritical gases such as O_2 , and N_2 through rubbery or glassy polymers are independent of upstream pressure at pressures close to standard. The latter fact nullifies the need to state the test pressure upon publication of permeability values in such a scenario. However then, in exceptions where pressure has a significant effect on permeability then the test pressure in question would have to be stated. Once the test pressure is not given, one may assume pressure independence of the permeability of the gases through the membrane in question.

Permeability results gotten from the current study were in close agreement with published data. A comparison of published data and data generated in the current study is given in Figure 4.2 of Section 4.1.3.

Hyflon M was used to investigate the repeatability of the single permeation results from the experimental setup. Three experimental runs were performed and the respective error calculated within a 95% confidence interval. An experimental error of 5.55 % resulted, signifying the reproducibility of the permeation experimental results gotten from the constant volume variable pressure permeation method. A much lower experimental error of 0.0212% for binary permeation composition experiments resulted, the latter being attributed to the accuracy of the GC compared to permeability results which were manually logged and thus ushered in human error. The error calculation procedure is presented in Appendix F. The error from three successive experimental runs producing dp/dt values, and also from the binary permeation composition experiments was below 10% in all experiments, proving the experiments to be repeatable.

3.4 EXPERIMENTAL DESIGN AND PLANNING

The experimental design is presented through an attempt to address the industrial requirements whilst bound by the feasible laboratory scale conditions.

3.4.1 PROCESS CONDITIONS IN THE HYBRID SULPHUR PROCESS

The ultimate objective of the study was to separate SO_2/O_2 gaseous mixtures in the Hybrid Sulphur process so as to recover O_2 as a by-product and recycle SO_2 back into the process. It is important to bear in mind that the use of membranes implies that the O_2 by-product stream would not be 100% pure through a single separation stage. A multistage system of membranes would be required to achieve high by-product purities. Based on the Hybrid Sulphur process flow sheet presented by Gorensek & Summers, (2009:4106) Table 3.6 presents all streams in need of SO_2/O_2 separation. These are process streams that converge at an absorber where O_2 is harnessed and recovered from the process as a byproduct. An individual treatment of the streams was done so as to ascertain the vapor liquid equilibrium nature of the streams. It is envisaged that of the diverse streams converging at the absorber, part of the streams would be combined and sent to the anolyte tank. The remainder would be combined into one main stream that would be fed to a membrane separator rather than the absorber proposed by Gorensek & Summers, (2009:4110).

Table 3.6 Process flow streams (Adapted from Gorensek & Summers, (2009:4108))

Stream Number	H ₂ O	H ₂ SO ₄	SO ₂	O ₂	H ₂	Total	Deg C	K	Bar
Kmol.s ⁻¹									
44	0.00059	0	0.06997	0.48988	0	0.560440	15.50	288.65	21
45	3.50E-06	4.30E-26	0.00025	0.00052	0	0.000774	40.99	314.14	21
46	6.90E-06	1.00E-25	0.00048	0.00098	0	0.001467	41.78	314.93	21
47	0.27692	1.30E-06	0.18854	0.00835	0	0.473811	233.42	506.57	21
66	3.20E-07	0.00E+00	0.00061	0.00116	0	0.001770	40.00	313.15	21
68	0.96665	6.60E-07	0.01365	6.10E-08	0	0.980301	40.31	313.46	21
75	0.28961	1.00E-07	0.00106	2.80E-11	0	0.290670	41.14	314.29	21
82	4.39285	0.00E+00	0.00185	4.90E-13	0	4.394700	40.21	313.36	21
94	2.90E-05	7.60E-16	0.00098	5.10E-04	0	0.001519	84.71	357.86	21

Prediction of vapor liquid equilibrium properties of the individual streams by the use of a process simulator Aspen Plus version 7.2 allowed determination of the quantity of vapor and liquid in the streams. Knowledge of the vapor/liquid quantities in-turn facilitated the determination of the destiny of the particular process stream, whether it should be sent to the anolyte tank or to the membrane gas separator. Vapor liquid equilibrium properties of the 9 streams are given in Appendix H (in hard copy and in CD). Table 3.6 indicates that there is negligible O₂ in streams 82, 75 and 68, moreover the vapor liquid equilibrium properties of streams 82, 75 and 68 presented in Appendix H indicate that there is negligible vapor in these streams as such can be sent directly to the anolyte tank. Figure 3.11 shows an extract of the process flow sheet proposed by Gorensek & Summers, (2009:4106) the streams in blue with negligible vapor are fed at the top of the absorber so as to counter currently meet the vapor filled streams that are in red and are fed from the bottom of the absorber.

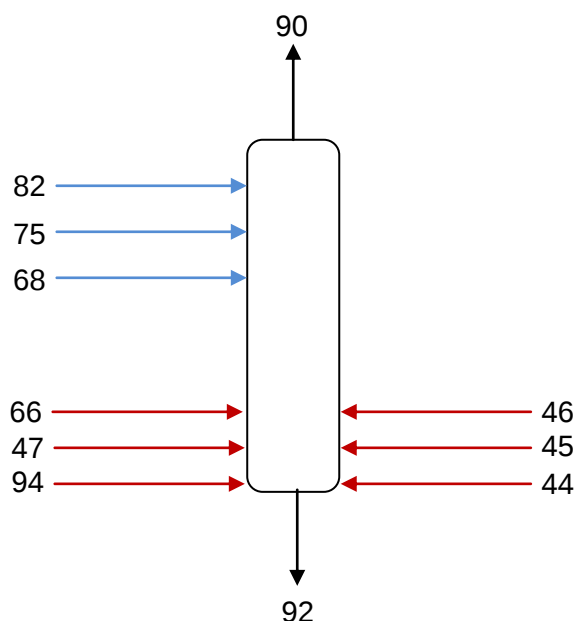


Figure 3.11 Flow sheet of streams converging on absorber (Adapted from Gorenssek & Summers, (2009:4106))

Of the six remaining streams that are to be sent to the membrane separator, stream 47 is at a temperature of 233.42 °C. There is a possibility of lowering the stream temperature of stream 47 through heat exchange so as to allow for further H₂O condensation and thus eliminate much of the H₂O from the vapor phase mixture. The latter would reduce the complexity of the vapor phase system from ternary (SO₂/O₂/H₂O) to binary (SO₂/O₂). H₂SO₄ may be regarded to be negligible in the streams. Hypothetical stream 47A was proposed, which is basically identical in total composition to the original stream (47) with the major exception being the temperature of the stream. It is envisaged that the temperature of stream 47 would be reduced to 93°C through heat exchange. Further temperature reduction below 93°C would result in the O₂ in stream 47 reporting to the liquid phase which is undesirable. Based on the latter statements, proposed streams to be sent to the membrane gas separator would be 44, 45, 46, 47A, 66, and 94. However, prior to introduction to the membrane gas separator, the streams would have to be fed through a phase separator so as to liberate the vapor phase from the liquid/aqueous phases. Assuming complete vapor liquid separation is performed, the liquid/aqueous phase would be sent to the anolyte tank whilst the vapor phase is directly fed into the membrane gas separator. The temperature and pressure of the mixed stream prior to phase separation is predicted by Aspen Plus version 7.2 to be

57.38°C and 21 bar respectively. However, a conclusion drawn in Appendix H suggests that flashing the mixture at a temperature range between 27.6°C and 57.38°C would be optimum. The compositions of the individual streams and the resultant combined stream to be fed to the phase separator and finally to the membrane gas separator are given in Appendix H (in hard copy and in CD).

3.4.2 EXPERIMENTAL RANGE

The ideal experimental ranges would envelope or include the combined vapor phase stream process conditions. Based on the predicted combined vapor phase stream process conditions presented in Appendix H, the laboratory experimental range was determined. Tables 3.7 and 3.8 present the experimental range for the single and binary permeation experiments respectively and an elaboration on the determination of the experimental range is presented thereafter.

Table 3.7 Single permeation experimental range and variables

SINGLE PERMEATION			
Manipulated variable	Range	Response variable	Calculation equation
Gas feed Pressure	1-3 bar ^(a)	Permeability ^(b)	$P = \frac{V_d l}{p_2 A R T} \left[\left(\frac{dp_1}{dt} \right)_{ss} - \left(\frac{dp_1}{dt} \right)_{leak} \right]$
Temperature	25°C	Flux ^(b)	$J = \frac{P \Delta p}{l}$
		Ideal Selectivity ^(b)	$\alpha_{A/B} = \frac{P_A}{P_B}$

^(a)Range for Hyflon F was 1.85 – 3.85 bar, ^(b) Parameters defined in Appendix C

Table 3.8 Binary permeation experimental range and variables

BINARY PERMEATION			
Manipulated variable	Range	Response variable	Calculation equation
SO ₂ feed partial pressure	1.1 - 2.4 bar	Pseudo permeability ^(a)	$\pi_{SO_2} = \frac{J_{SO_2} l}{\Delta p}$ $\pi_{O_2} = \frac{J_{O_2} l}{\Delta p}$
Temperature	15°C - 55°C	Flux ^(a)	$J_{SO_2} = \frac{V_d}{A R T} \left(\frac{dp_1}{dt} \right)_{SO_2}$ $J_{O_2} = \frac{V_d}{A R T} \left(\frac{dp_1}{dt} \right)_{O_2}$
Feed gas composition [SO ₂ :O ₂] = wt% (mol%)	25:75 (14.1:85.9) 50:50 (33.3:66.7) 75:25 (60:40)	Real selectivity ^(a)	$\alpha_{SO_2/O_2} = \frac{y(1-x)}{x(1-y)}$
		Permeate gas composition ^(b)	$\frac{A_{SO_2}}{A_{O_2}} = 0.857 \frac{W_{SO_2}}{W_{O_2}}$

^(a)Parameters defined in Appendix C, ^(b) Parameters defined in Appendix G

The binary permeation experimental range was determined in such a way as to at least include or envelope the predicted combined stream vapor phase process conditions comprising of the predicted optimum flash temperature range (27.6°C - 57.38°C) and the resultant predicted vapor phase process composition range (9.35 mol % – 18.16 mol %) SO₂ and (90.54 mol % - 81.23 mol %) O₂. The resultant SO₂ partial pressure range (1.96 bar – 3.81 bar) was gotten from the predicted SO₂ composition range and the total stream pressure of 21 bar. It is important to note that the maximum SO₂ partial pressure value used experimentally (2.4 bar) was limited by the cylinder supply pressure. An alternate purpose of the experimental ranges was to allow for fluctuations in process conditions and also determine the relationship between the manipulated and response variables.

With single permeation membrane screening experiments, process conditions were not very critical. Mere screening of membranes was the main objective in contrast to binary permeation experiments where the relationship between manipulated and response variables was crucial. Single permeation screening experiments were thus performed at ambient temperature and within a convenient pressure range that was identical in all gases used. Sulphur dioxide at 25°C was supplied at a pressure of about 3.9 bar and thus defined the upper limit for the single permeation experiments.

3.5 ANALYTICAL EQUIPMENT AND CALIBRATION CURVES

The sole analytical instrument employed in the present study was a Hewlett Packard 6890 gas chromatograph system that was responsible for analyzing both the composition of the feed and permeate gas streams.

3.5.1 GAS CHROMATOGRAPH SPECIFICATIONS

The HP 6890 GC made in Germany employed a thermal conductivity detector and was fitted with a metallic supelco 80/100 hayesep Q support capillary column with the dimensions 6ft x 1/8in x 2.1 mm coiled in the G.C. oven set at 35°C. With a Helium sweep gas flow rate of 30.1 ml.min⁻¹. The O₂ elution time was 0.91 ± 0.02 minutes whilst that of SO₂ was 8.5 ± 0.05 minutes as such the G.C. was automated to terminate an analysis run at 12 minutes when the gases of interest (SO₂ and O₂) had been detected. Figure 3.12 gives an imitation of the G.C. output image displaying the position of the O₂ and SO₂ output peaks at their respective elution times. Peak area calculations and the original output image with peaks were produced through a PC program Agilent Chemstation (2001 – 2006).

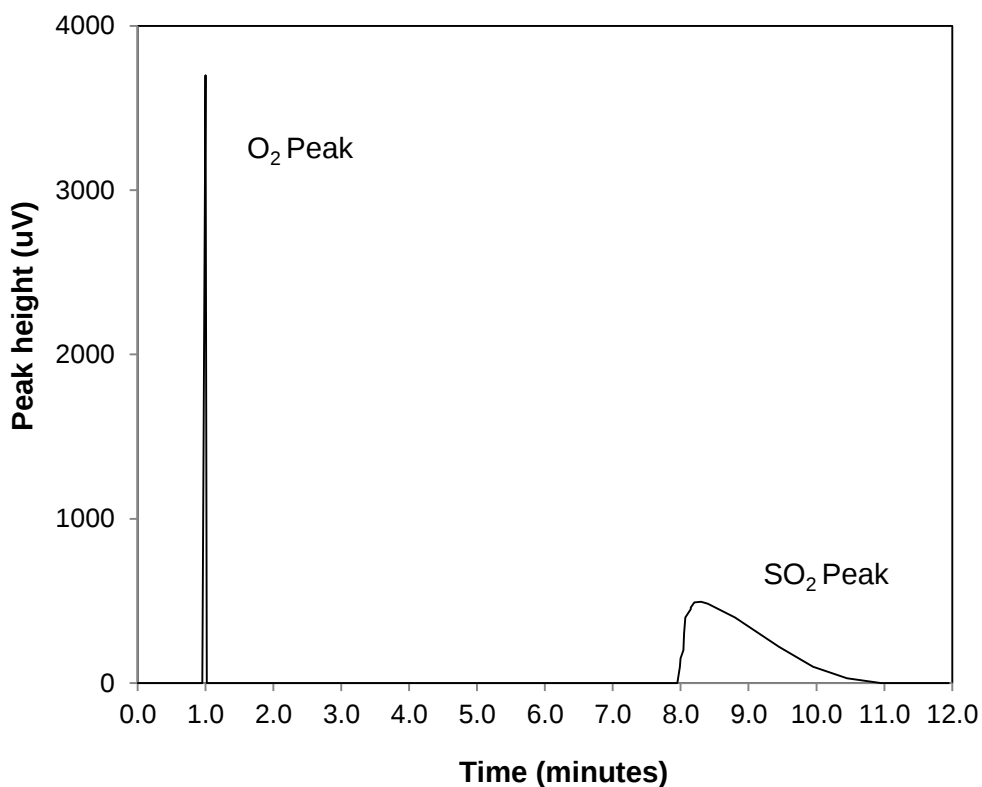


Figure 3.12 Typical G.C. Peak areas for a gas mixture constituting of more SO₂

3.5.2 GAS CHROMATOGRAPH CALIBRATION

The external standardization technique was employed for calibration (Grob, 2004:8). Gas mixtures (25:75 wt %, SO₂:O₂), (50:50 wt %, SO₂:O₂) and (75:25 wt %, SO₂:O₂) from Afrox were employed as calibration standards. A graph shown in Figure 3.13 was then plotted, relating the peak area ratios ($A_{\text{SO}_2}/A_{\text{O}_2}$) to the weight composition ratios ($W_{\text{SO}_2}/W_{\text{O}_2}$). The respective calibration information is given in Appendix G.

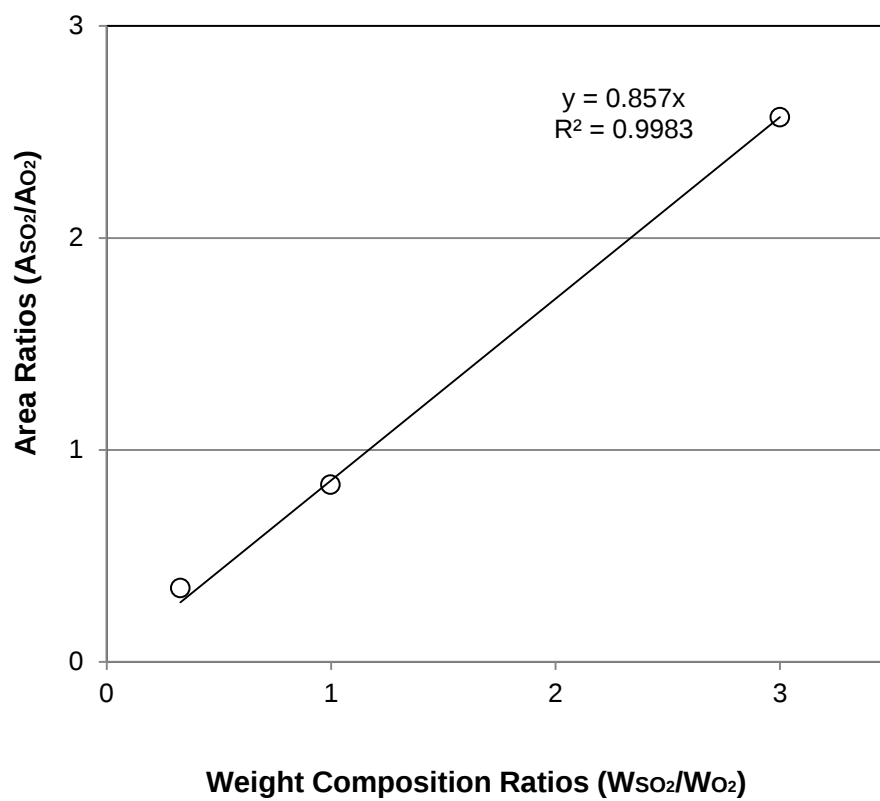


Figure 3.13 Gas chromatograph calibration curve

3.6 REFERENCES

- [1] BIOGENERAL. 2012a. Teflon AF Tubing and Membrane. <http://www.biogeneral.com/teflon.html>
Date of access: 28 May 2012.
- [2] CZICHOS, H., SAITO, T. & SMITH L. 2006. Springer Handbook of Materials Measurement Methods. Germany: Springer. http://books.google.com/books?id=8lANaR-Pqj4C&printsec=frontcover&source=gbs_ge_summary_r&cad=0#v=onepage&q=permeability&f=false .
Date of access 8 Nov 2011.
- [3] CZICHOS, H., SAITO, T. & SMITH L. 2011. Springer Handbook of Metrology and Testing. Germany: Springer.
<http://books.google.co.za/books?id=fpTE1Z5UfsQC&pg=PA433&lpg=PA433&dq=constant+volume+method,+gas+permeation&source=bl&ots=CTmQBaCc0B&sig=VcqKNabimsq2MNkl07PuoOqqDQY&hl=en&sa=X&ei=WG-3UljyMYGHhQeiyYH4Bg&ved=0CDEQ6AEwAA#v=onepage&q=constant%20volume%20method%20%20gas%20permeation&f=false> . Date of access 11 Nov 2011.
- [4] CHIOU, J.S. & PAUL, D.R. 1988. Gas permeation in a dry nafion membrane. *Ing. Eng. Chem. Res*, 27:2161-2164, 15 Aug
- [5] DHINGRA, S.S. 1997. Mixed Gas Transport Study through Polymeric Membranes: A Novel Technique. Blacksburg, Virginia:V.P.I.S.U. (Dissertation – Phd) 173p.
- [6] DUPONT. 2009. Dupont Fuel Cells, Dupont Nafion PFSA Membranes.
http://www2.dupont.com/FuelCells/en_US/assets/downloads/dfc101.pdf - Date of access: 21 May 2012.
- [7] DUPONT. 2011. Unique properties of Dupont Teflon AF.
http://www2.dupont.com/Teflon_Industrial/en_US/products/product_by_name/teflon_af/properties.html - Date of access: 22 Nov 2011.
- [8] FRITZSCHE, A.K. & KURZ J.E. 1990. The Separation of Gases by Membranes. (*In* Porter, M.C., ed. Handbook of Industrial Membrane Technology. New Jersey: Noyes publications. p.559-593.)
- [9] GORENSEK, M.B. & SUMMERS, W.A. 2009. Hybrid sulphur flowsheets using PEM electrolysis and a bayonet decomposition reactor. *International Journal of Hydrogen Energy*, 34:4097-4114, 9 Aug.
- [10] GROB, R.L. 2004. Introduction. (*In* Grob, R.L. & Barry, E.F., eds. Modern Practice of Gas Chromatography. New Jersey: John Wiley & Sons. p.1-21.)
- [11] JUNG, H. & KIM, W.J. 2012. Role of the glass transition temperature of Nafion 117 membrane in the preparation of the membrane electrode assembly in a direct methanol fuel cell. *International Journal of Hydrogen Energy*, 37:12580-12585, 26 Jun.

- [12] KOEV, I.L. (ikoev@biogeneral.com) 2 Nov. 2011. Data Sheet – Teflon AF 2400. Email to: Hlabano-Moyo, B.M. (22656227@nwu.ac.za).
- [13] MACCHIONE, M., JANSEN, J.C., LUCA, G.D., TOCCI, E., MARCELLO, L. & DRIOLI, E. 2007. Experimental analysis and simulation of the gas transport in dense Hyflon AD60X membranes: Influence of residual solvent. *Polymer*, 48:2619-2635, 3 Mar.
- [14] MASSEY, L.K. 2003. Permeability Properties of Plastics and Polymers. New York: Plastics Design Library. 585p
- [15] MOHAMMADI, A.T., MATSUURA, T. & SOURIRAJAN, S. 1994. Design and construction of gas permeation system for the measurement of low permeation rates and permeate compositions. *Journal of Membrane Science*, 98:281-286, 5 Sep.
- [16] SOLVAY. 2006a. Hyflon PFA Perfluoroalkoxy Fluorocarbon Resins Design and Processing Guide. http://www.solvaysolexis.asia/static/wma/pdf/9/2/2/1/BR_Hyflon.pdf Date of access: 7 Jun 2011.
- [17] SOLVAY. 2006b. Halar ECTFE Ethylene-Chlorotrifluoroethylene Design and Processing Guide http://www.solvaysolexis.asia/static/wma/pdf/9/2/1/9/BR_Halar.pdf Date of access: 7 Jun 2011.
- [18] SOLVAY. 2008. Design and Processing Guide Hyflon MFA. http://www.solvaysolexis.asia/static/wma/pdf/1/6/4/7/1/Y42E002_Hyflon_MFA_Design_Processing_Guide_2009.pdf _Date of access: 28 Dec 2011.
- [19] SOLVAY. 2011. Design Guide Udel Polysulfone. http://www.solvayplastics.com/sites/solvayplastics/EN/Solvay%20Plastics%20Literature/DPG_Udel_Design_Guide_EN.pdf Date of access: 28 May 2012.
- [20] SOLVAY. 2012. Sulfone polymers for membranes. http://www.solvayplastics.com/sites/solvayplastics/EN/specialty_polymers/Markets/Membranes/Pages/sulfone-polymers-membranes.aspx _Date of access: 13 Nov 2012.
- [21] STERN, S.A., GAREIS, P.J., SINCLAIR, T.F. & MOHR, P.H. 1963. Performance of a versatile variable-volume permeability cell. Comparison of gas permeability measurements by the variable-volume and variable-pressure methods. *Journal of Applied Polymer Science*, 7:2035-2051. 28 Aug.
- [22] STERN, S.A. & FRIED, J.R. 2007. Permeability of Polymers to Gases and Vapours. (In Mark. J.E., ed. *Physical Properties of Polymers Handbook*. New York: Springer. p.1033-1045.)