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POLY (2,6-DIMETHYL-1,4-PHENYLENE OXIDE) HOLLOW FIBRES FOR GAS SEPARATION

By
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**Submitted in Partial Fulfillment
of the requirements of the degree of
DOCTOR OF PHILOSOPHY**

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ABSTRACT

Hollow fibres used for gas separation applications need to have good mechanical strength and excellent gas separation properties. The production of hollow fibres by the dry-wet spinning process involves many variables, each having the potential to affect these properties.

This is a systematic study of the effect of several variables in the spinning process on the dimensions, morphology and CO₂/CH₄ gas separation performance of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Hollow fibres were prepared by the dry-wet spinning method from solutions of PPO in trichloroethylene using the non-solvent methanol as the bore liquid and for the gelation bath. The variables studied were the length of the air gap, the flowrates of the bore liquid and polymer solution and the presence of 2-ethyl-1-hexanol in the polymer solution used for spinning. A one-factor-at-a-time approach was used to show how these variables affected the outer diameter; wall thickness and carbon dioxide and methane permeate flux of the hollow fibres. A factorial design was used to determine which of the effects were significant and if there were any interactions between the variables that also affected the hollow fibre properties. The results were used to develop models for each of the five response variables as a function of those spinning variables that were found to significant.

The outer diameters of the fibres produced within the constraints of the factorial design ranged from 0.39–0.6 mm, and the wall thickness from 0.018–0.045 mm. The outer diameter of the fibres was found to decrease with increasing air gap, decreasing polymer solution flowrate and decreasing bore liquid flowrate. The wall thickness was found to increase with increasing polymer solution flowrate, and decreasing bore liquid flowrate. The interaction between the presence of 2-ethyl 1-hexanol and the bore liquid flowrate had a significant effect

on the hollow fibre wall thickness. None of the interactions between the other variables were found to have a significant effect on the hollow fibre dimensions.

The methane permeate flux for the hollow fibres produced within the constraints of the factorial design ranged from 1.52×10^{-11} - 4.8×10^{-11} mol/m².s.Pa, and the carbon dioxide permeate flux from 3.52×10^{-10} - 1.25×10^{-9} mol/m².s.Pa. The ideal separation factor varied between 23.2 and 27.9. Some of the hollow fibres tested were able to withstand an applied bore side pressure of more than 800 psig (5.52×10^6 Pa).

The carbon dioxide and methane permeate flux were found to increase with decreasing polymer solution flowrate, increasing bore liquid flowrate and with the presence of 2-ethyl-1-hexanol in the polymer solution. The length of the air gap had a complex effect on the permeate flux. The presence of 2-ethyl 1-hexanol, the bore liquid flowrate and the two-way interaction between the presence of 2-ethyl 1-hexanol and the polymer solution flowrate were found to have a significant effect on the on the ideal separation factor.

Hollow fibres of both an asymmetric and a homogeneous structure were produced. Scanning electron microscopy was used to show the morphology of the hollow fibres varied with the composition of the polymer solution and the variables used in the spinning process. Atomic force microscopy work was able to show the fine structure of the hollow fibres and how this varied across the walls of the fibre and with the conditions used in the spinning process.

RÉSUMÉ

Les fibres creuses utilisées pour les applications de séparation de gaz requièrent une solidité mécanique et d'excellentes propriétés de séparation de gaz. La production de fibres creuses par le processus de filage sec-humide apporte plusieurs variables, chacune ayant le potentiel d'affecter ces propriétés.

Ceci est une étude systématique de l'effet de plusieurs variables du processus de filage sur les dimensions, morphologie, et performance de séparation des gaz CO₂/CH₄ du poly(2,6-diméthyl-1,4-phenylene oxide) (PPO). Des fibres creuses furent préparées par le processus de filage sec-humide à partir de solutions PPO sur trichloroéthylène utilisant du méthanol non-dissolvant comme liquide d'alésage et bain de congélation. Les variables étudiées furent la longueur de l'intervalle d'air, les débits du liquide d'alésage et de solution polymère et la présence de 2-éthyl-1-hexanol dans la solution polymère utilisée pour le processus de filage. Une approche systématique de facteurs individuels fut utilisée pour démontrer l'effet de ces variables sur le diamètre extérieur, l'épaisseur des murs et le flux perméable d'anhydride carbonique et de méthane des fibres creuses. Une conception factorielle fut utilisée pour déterminer lesquels des effets étaient significatifs et s'il y avait une interaction quelconque entre les variables qui affectent également les propriétés des fibres creuses. Les résultats ont été utilisés pour développer des modèles pour chacune des cinq variables de réponses comme une fonction des variables de filage qui se sont avérés significatives.

Les diamètres extérieurs des fibres produites en tenant compte des contraintes de la conception fonctionnelle s'étendent entre 0.39 et 0.6 mm, et l'épaisseur des murs des fibres s'étend entre 0.018 et 0.045 mm.

Le diamètre extérieur des fibres s'est avéré à diminuer avec un intervalle d'air croissant, un débit décroissant de solution polymère et un débit décroissant de liquide d'alésage.

L'épaisseur des murs s'est avérée à croître avec une augmentation du débit de solution polymère, et un débit de liquide d'alésage diminué. L'interaction entre la présence de 2-ethyl 1 -hexanol et le débit du liquide d'alésage a eu un effet significatif sur l'épaisseur des murs des fibres creuses. Aucune interaction entre les variables n'a eu un effet significatif sur les dimensions des fibres creuses.

Le flux perméable pour les fibres creuses produites en tenant compte des contraintes de la conception factorielle s'étend entre 3.52×10^{-10} - 1.25×10^{-9} mol/m².s.Pa pour l'anhydride carbonique pur et de 1.52×10^{-11} - 4.8×10^{-11} mol/m².s.Pa pour le méthane pur. Le facteur de séparation idéal varie entre 23.2 et 27.9. Quelques unes des fibres testées purent soutenir une pression appliquée de côté d'alésage de plus de 800 psig (5.52×10^6 Pa).

Le flux perméable d'anhydride carbonique et de méthane se sont avérés à croître avec une diminution de débit de solution polymère, une augmentation de débit du liquide d'alésage ainsi que la présence de 2-ethyl-1-hexanol dans la solution polymère. La longueur de l'intervalle d'air a eu un effet complexe sur le flux perméable. La présence de 2-ethyl -1-hexanol, le débit du liquide alésage ainsi que la double interaction entre la présence de 2-ethyl -1-hexanol et le débit de la solution polymère s'est révélée avoir un effet significatif sur le facteur de séparation idéal.

Des fibres creuses de structure asymétrique et homogène furent produites. La microscope électronique à balayage fut utilisée pour démontrer que la morphologie des fibres creuses varie avec la composition de la solution polymère et les variables utilisées dans le processus de filage. La microscopie de force atomique a pu révéler la fine structure des fibres creuses et comment elle varie au travers des murs de la fibre et les conditions utilisées dans le processus de filage.

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ACKNOWLEDGMENTS

This research was made possible through support from a few organizations and key individuals. I would like to acknowledge the following:

Natural Science and Engineering Research Council and British Gas plc for providing funding through a scholarship.

Dr. T. Matsuura for his help and guidance.

Members of staff and colleagues at the Industrial Membrane Research Institute, in particular Mr. S. Deng and Dr. G. Chowdhury for their helpful technical discussions.

Dr. B. Lavery and Dr. C. Hamilton and other staff at British Gas Research Centre, Loughborough, UK for their helpful technical advice and kind hospitality during my working visit.

Mr. L. Tremblay and Mr. F. Ziroldo of Technical Services in the Department of Chemical Engineering for their practical help in building the experimental apparatus for this study.

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Chapter 1

INTRODUCTION

1.1. GOALS AND SCOPE OF THIS WORK

This research was sponsored in part by British Gas plc. As a large company involved in the supply of fuel gases, British Gas plc was keen to investigate technologies that could be used to enable more efficient and economic gas separation and purification. One area of particular interest was the removal of carbon dioxide from natural gas. It is important to remove carbon dioxide from natural gas to increase the heating value of the gas, prevent hydrate formation and corrosion of the pipeline, and reduce the volume of gas to be transported.

Membrane separation processes have emerged as a gas separation technique within the last twenty-five years and are competing with other gas separation techniques such as: adsorption, absorption and cryogenic fractionation. The competitiveness of membrane separation processes in the gas separation industry can be increased in part by the production of membranes with higher gas separation performance and increased flux. In order to achieve such enhanced performance a thorough understanding of the membrane formation process and how it affects the membrane morphology and gas separation is vital.

The goal of this research was to carry out a systematic study of the phenomenological

correlations between preparative conditions and the *morphology, dimensions* and *gas separation performance* of hollow fibre membranes. Although it has been increasingly common for researchers to investigate relationships between one or more of these areas of interest, there has not been a detailed study encompassing all these aspects for hollow fibre gas separation membranes of poly (2,6-dimethyl-1, 4-phenylene oxide) (PPO). The separation of carbon dioxide and natural gas was chosen as a basis for this research; however, many of the findings can be applied to other gas separation processes and are of importance to membranologists in general.

1.2. JUSTIFICATION FOR THIS STUDY

Fundamental studies like this one are valuable in increasing our understanding of the membrane formation process and the relationship between the parameters used in the preparation and the performance of the membrane. While there are many papers in the literature about the preparation of flat sheet membranes, little work has been published on the effect of spinning conditions on the gas separation performance of hollow fibre membranes. The reason is that while flat membranes are relatively easy to fabricate, the hollow fibre spinning process is more complex. The fabrication of a hollow fibre membrane with good gas separation performance is not a trivial process. It is not possible to simply adopt the process conditions used in the fabrication of a flat membrane. The spinning process is complex and there are many factors to consider during the formation process including mechanical, thermodynamic and kinetic considerations. There are also several interrelated hollow fibre properties that must be considered and established concurrently.

Figure 1 summarizes the correlations that are important in the development of hollow fibre membranes.

Figure 1.1. Important Correlations in the Development of Hollow Fibre Membranes.

There are a large number of variables involved in the spinning process; these include the composition of the polymer solution, the bore liquid and the gelation bath liquid. There are also rheological variables such as spinning velocity, extrusion rates of the polymer solution and bore liquid, and the spinneret design. Spinning rheology is very important; the rate of shear experienced in the spinneret and the amount of elongation of the fibre whilst in the air gap can affect on gas separation performance.

The spinning variables have the potential to affect any of the hollow fibre properties: dimensions, morphology and gas separation performance. The importance of these properties and their interrelation is discussed below.

Gas Separation Performance

The gas separation performance of a membrane is measured by the permeate flux through the membrane and the selectivity of the membrane towards those gases it is separating. It is dependant on the morphology and dimensions of the hollow fibre.

Fibre Dimensions

The dimensions of the hollow fibres are an important consideration because they have a direct effect on the productivity of the module. Module productivity ($\text{m}^3/\text{hr Pa}$) can be increased by

increasing the membrane surface area in a given module volume. Hollow fibres with small diameters have a higher surface area to volume ratio than larger diameter fibres and they can also be packed more efficiently in the module. Hence module productivity tends to increase with decreasing diameter of the hollow fibres. However there is a limit to this increase; at very small fibre diameters the pressure drop along the fibre becomes excessive and this reduces the module productivity. So the diameter of the hollow fibre must be optimized for the best performance.

The dimensions of the hollow fibres are also an important consideration because the mechanical strength of the hollow fibre not only depends on the inherent mechanical properties of the membrane material but also on the wall thickness and outer diameter. A hollow fibre membrane must have enough mechanical strength to be self-supporting and also to withstand the pressure differential when in use for gas separation applications.

Fibre Morphology

The fine structure or morphology of the fibre directly affects the gas separation performance of the hollow fibre. In an asymmetric membrane the morphology of the skin layer is the dominant factor affecting the selectivity of the membrane. It should have a dense structure and be free of defects. To maximize permeate flux through the membrane, the dense skin layer should be as thin as possible and the porous sublayer should have an open structure with as little resistance to permeate flow as possible while still providing adequate mechanical support for the skin layer. There are many factors controlling fibre morphology during the spinning process and it is necessary to balance the polymer solution composition and spinning and coagulation conditions to ensure the desired morphology of the fibre is achieved.

The spinning parameters and their correlation with various hollow fibre properties are discussed in more detail in section 1.8 which is a synopsis of work that has been carried out by others which is relevant to this study. The section includes further discussion about how this study differs from others and why it is important. The remainder of this chapter discusses

the gas separation processes and the use of membrane technology and focuses on the fabrication process for hollow fibre membranes and the material that was used in this study.

1.3. GAS SEPARATION AND MEMBRANE TECHNOLOGY

The production of a gas at a specific purity from a multi-component gas mixture can be achieved using gas separation techniques such as: adsorption, absorption and cryogenic distillation. In gas separation using membranes, the gases are separated on the basis of differences in their solubility and diffusivity in the membrane; typically a driving force of pressure differential of between 1×10^5 - 1×10^7 N/m² is used.

Selection between the various gas separation processes is dependent upon the particular application. The choice is strongly influenced by factors such as: feed and permeate pressure, feed composition, plant capacity and operating costs. Typically membrane separation gives medium purity products and is usually more competitive for low to medium scale production.

Details about the conditions under which membrane gas separations are best suited can be found in the 'Membrane Handbook' (Ho and Sirkar, 1992).

The main areas of membrane gas separation are:

Hydrogen Recovery

- recovery of hydrogen from streams in the production of substitute natural gas
- refinery hydrogen recovery
- recovery of hydrogen from the purge gas in ammonia synthesis

Helium Recovery

- recovery of helium from contaminated diving gas, CO₂/He separation
- recovery of helium from natural gas

Oxygen- Nitrogen Separation

- production of oxygen enriched gas for improved combustion and healthcare
- nitrogen production for use in nitrogen blanketing

Dehydration

- air dehumidification
- natural gas dehydration

Carbon Monoxide Recovery

- recovery and purification of CO from water-gas

Exhaust Gas Treatment

- removal of carbon dioxide, sulfur and nitrous oxides from exhaust gases

Acid Gas Removal

- removal of HCl from exhaust gas
- removal of H₂S from natural gas

Carbon Dioxide Removal

- removal from natural gas
- landfill gas upgrading

The separation of carbon dioxide and natural gas is of major importance in the natural gas industry and was chosen as a basis for this research. More details about separations in the natural gas industry are given below.

1.4. SEPARATIONS IN THE NATURAL GAS INDUSTRY

As environmental regulations favour cleaner burning fuels, natural gas is replacing the use of coal and oil in the power generation and other markets. Natural gas is the fastest growing energy source and this trend is expected to continue in the future. By 2020 the world's consumption of natural gas is expected to equal 162 trillion cubic feet ($4.59 \times 10^{12} \text{ m}^3$), almost double the 1999 level. With an average annual growth rate of 3.2 percent, the share of natural gas in total primary energy consumption is projected to grow to about 28 percent in 2020 from 23 percent in 1999 (DOE / EIA, 2000). The Canadian Gas Association expects strong growth in Canadian natural gas consumption in the power generation sector. Overall, consumption in Canada is expected to grow from 3.1 trillion cubic feet ($8.78 \times 10^{10} \text{ m}^3$) in

1999 to 4.3 trillion cubic feet ($12.2 \times 10^{10} \text{ m}^3$) in 2020, an annual increase of 1.5%. Canada was reported to have 63 trillion cubic feet ($1.8 \times 10^{12} \text{ m}^3$) of proven natural gas in reserves in 1999. Canada was the world's third largest natural gas producer in 1999 with annual production of about 6 trillion cubic feet ($1.7 \times 10^{11} \text{ m}^3$) and this is likely to increase as more gas resources are discovered (DOE / EIA, 2000).

Natural gas is predominantly methane and contains small quantities of some higher alkanes and traces of cyclic hydrocarbons. It also contains various quantities of non-hydrocarbons such as water, HCl, H_2S , CO_2 , N_2 and other inert gases. It may also contain minor amounts of COS, CS_2 , mercaptans and trace metals such as sodium, mercury and iron rust. To meet transmission specifications some of these components must be removed or reduced. Natural gas sweetening is the removal of acid gases such as carbon dioxide, hydrogen sulfide and other organic sulfur compounds. They must be removed for reasons of health, safety and corrosion reduction during transmission. Dehydration is also an essential step in the processing of natural gas to meet pipeline specifications, since the water could condense and lead to hydrate formation and corrosion of the pipeline. Carbon dioxide in the presence of water can form carbonic acid, which can cause corrosive damage to pipelines. Some gas fields can contain up to 50% carbon dioxide and 20% nitrogen. It is important to remove carbon dioxide and nitrogen because they reduce the calorific value of the gas. Removal at the well is preferential, since it reduces the volume of gas to be transported.

The book "Natural Gas Engineering" (Katz et al., 1990) is an excellent source of information about natural gas. It discusses the occurrence of natural gas in the earth, its properties and details the stages of its production, treatment, storage and transport.

Membrane separation processes are competing with other gas separation techniques in the natural gas industry. They can be particularly competitive in offshore installations since they are compact and lightweight. Spillman (1989) and Ghosal et al. (1994) give an overview on gas separation membranes; they have compared them to other gas treatment technologies

such as pressure swing adsorption, cryogenic fractionation and absorption and found the membrane processes to be quite competitive under certain conditions. Spillman found membranes for acid gas removal to be very cost effective for a range of feed gas compositions, particularly when used for low to medium gas flow rates and when the pressure of the feed gas or product gas was high. Other researchers have also directly compared membrane processes with amine treatment and found the membrane processes to be more competitive (Babcock et al., 1988, Lee et al., 1994). In a gas separation study conducted by the British Government's Department of Energy (UK Offshore Supplies Office, Report GEL 1419, October 1998) membrane technology was compared to traditional solvent treating. The requirement of each technology was to reduce the CO₂ content in 97 Mmscfd (31m³/s) of natural gas containing 15.8% CO₂ to a product gas with 2% CO₂. In terms of capital cost, weight, space and operating cost, membrane technology proved superior.

With the discovery of new natural gas sources of low quality gas and the possibility of reopening old wells that have been closed down due to their production of low quality gas, the upgrading of low quality natural gas is an area gaining interest. Membrane processes have been shown to be competitive in the upgrading of low quality natural gas (Bhide et al., 1993, Lee et al., 1995). There has also been a growing interest in the upgrading of low quality natural gas produced by fermentation of biomass and in the refining of landfill gases. Such gases can contain substantial amounts of acid gases; landfill gas can contain 40-60% CO₂ with trace contaminants and the remainder methane. There have been studies on the use of membranes to upgrade low quality natural gas from biomass fermentation and landfills (Schell et al., 1983, Rautenbach et al., 1993).

Natural gas / carbon dioxide separation is also important in the field of enhanced oil recovery. The effluent gas from a stream undergoing carbon dioxide flooding for enhanced oil recovery may contain 20 - 80% carbon dioxide in methane. The separation of this gas is valuable, since the hydrocarbons can be recovered as one stream and the other stream, which is rich in carbon dioxide, can be re-injected into the well. Membranes have been used commercially for the

removal of carbon dioxide from the gases released from enhanced oil recovery processes. The Cynara Company installed units containing membranes manufactured by Dow Chemicals at the SACROC tertiary oil recovery project in West Texas (Parro, 1984).

1.5. HISTORY OF GAS SEPARATION MEMBRANES

Membrane gas separation techniques began with the work of J.K. Mitchell in 1831 who measured the rates of escape of ten different gases through natural rubber balloons (Mitchell, 1831). Also in the 1830's, Fick studied gas transport across nitrocellulose membranes and formulated his Law of Diffusion (Fick, 1855). In 1866, Thomas Graham discovered that rubber showed different permeabilities to different gases according to their molecular size (Graham, 1866).

It was not until the 1940's that a membrane separation process was used on a large scale. Membranes were used for the concentration of uranium 235; the process was based on differences in molecular weight and involved a large number of stages, making the process costly. Despite more early work on gas separation membranes they failed to become commercially popular in other industries until much more recently. The reason for this was the early membranes had low flux and poor separation. While the development of asymmetric cellulose acetate membranes using a phase inversion method (Loeb et al., 1962) in the late 1950's made a big impact in the liquid separation field, these membranes could not be used for gas separation. The main problem was whilst drying the membranes to be used in the dry gas environment, the pores collapsed and the membranes lost their separating properties. In the late 1960's, Vos and Burris (1970) overcame the problem by adding surfactant before drying the membranes. This reduced the interfacial tension inside the membrane and allowed the water to be evaporated without pore collapse. Cellulose acetate membranes dried using this technique were used by Gantzel and Merten (1970) to separate hydrogen / nitrogen mixtures.

During the 1970's, Dupont and Dow began to develop large-scale gas separation modules. There were several breakthroughs for the gas separation field during this time, including the introduction of the composite membrane by General Electric (Ward et al. 1976). This membrane has a thin selective layer bonded to a porous supporting layer usually of a different polymer. Also the coating technique developed by Henis and Tripodi (1980) allowed selectivity of membranes to be improved without reducing permeability significantly by plugging large pores and defects using a highly permeable rubbery material. In 1979 Monsanto commercially produced gas separation membrane modules. These PRISM modules contained polysulfone hollow fibres with a thin dense skin on the outside surface, covered by a coating of a highly permeable rubber. The recovery of hydrogen from ammonia plant purge gas was one of the first widespread uses of the PRISM system. Shortly after its introduction it was used in more than 100 installations worldwide. The system has since been used for hydrogen separation processes in oil refinery and petrochemical industries, and for hydrocarbon/carbon dioxide and oxygen/nitrogen separations.

In 1985 Dow Chemical developed the Generon hollow fibre module, which was used to recover nitrogen from air. Monsanto also produced an air separation membrane in the mid 1980's called the PRISM Alpha. The membrane was made of the same polymer as the first PRISM but had a thinner active layer. As a result of the improved morphology, there was a two- to three-fold increase in productivity over the original. In 1986, a new division called Permea Inc was formed as a subsidiary of Monsanto. In the late 1980's Permea developed a new membrane for the dehydration of compressed air, called the PRISM Cactus.

Permea, now a division of Air Products and Chemicals, continues to produce membranes. Applications include hydrogen recovery from ammonia purge gas, petrochemical off gases and refinery fuel streams and the dehydration and removal of carbon dioxide from natural gas. Generon, now MG Generon of the Messer Group continues to produce membranes for air separation. Applications include the production of nitrogen for use during the drilling oil and gas wells, in enhanced oil recovery operations and for controlled atmosphere storage.

Gas separation membranes have continued to replace more traditional methods of gas separation. At the Chiba Refinery of the Cosmo Oil Company in Japan, Separex^R cellulose acetate spiral wound membrane systems are used to recover hydrogen from the off gas from an absorption column (Kesting et al., 1993). Gas separation membranes have also been used alongside other traditional separation methods in hybrid systems. The first hybrid system of this kind combined the benefits of pressure swing adsorption with PRISM separators. The system was built in Alabama, USA, in 1990, and is used to recover 97% of the hydrogen from a low pressure, steam reformed methane feed gas at a hydrogen purity in excess of 99.99 mol%.

Some gas separation data for commercially available membranes used for carbon dioxide/methane separations are given in Table 1.1.

Table 1.1 Gas Separation Data for Commercially Available Membranes Used for Carbon Dioxide/Methane Separations (Matsuyama et al., 1994)

Manufacturer	Membrane	CO ₂ Permeate Flux ($\times 10^{-11}$ Kmol/m ² sPa)	Separation Factor
Separex/Delta	Cellulose acetate/triacetate	3.3-5.0	26-30
Monsanto	Polysulfone/silicone rubber	1.4	17-24
General Electric	Polyetherimide	0.3	18
General Electric	Silicone rubber/polycarbonate	30	10

1.6. HOLLOW FIBRE SPINNING

Membranes can be fabricated in the form of flat sheets, hollow fibres and tubular membranes. The hollow fibre configuration was chosen in this study because when packed efficiently in a module, hollow fibres provide a much larger surface area for separation per unit volume than spiral wound or tubular membranes. Estimates for the membrane surface packing density for

a tube in shell hollow fibre module are 16000-32000 m² surface area / m³ internal module volume, and for a spiral wound module approximately 300-900 m² surface area / m³ internal module volume (Wakeman, 1986).

Hollow fibre membranes are fine cylindrical tubes with diameters less than 1.0mm. Hollow fibres are produced by a process called spinning, in which a solution or melt of the polymer is extruded through a die called a spinneret, which has an inner tube through which gas or liquid is co-extruded to give the fibre its hollow shape. Typically the fibres are wound or drawn to reduce their diameter after extrusion.

There are four main processes for spinning hollow fibre membranes:

Melt Spinning

In melt spinning the polymer is extruded through the spinneret in molten form. The emerging fibres are usually cooled by air where they solidify.

Dry Spinning

In dry spinning a solution of the polymer in a solvent is extruded into air, or an inert gas stream, flowing either co-currently or counter-currently to the fibres. The fibres solidify on evaporation of the solvent.

Wet Spinning

In wet spinning a polymer solution is extruded into a gelation bath containing liquid, which causes solidification or gelation of the polymer. The gelation can be caused by precipitation of the polymer in a liquid, which is a non-solvent for the polymer, or by a chemical reaction with the liquid, which causes gelation of the polymer.

Dry-Wet Spinning

Dry-Wet spinning is similar to wet spinning except before passing into the gelation bath, the fibre is passed through an air gap, where some solvent evaporation and stretching of the fibre takes place.

Melt spinning and dry spinning are not typically used to produce gas separation membranes

because they tend to produce fibres with a dense wall structure and hence give low permeate flux. In order to achieve better permeate flux with dense membranes it is necessary to use very thin films; this is not possible for the hollow fibre configuration because very thin walled fibres would be too weak to be self supporting or may not be able to withstand the high differential pressures required in gas separation processes.

For hollow fibres the ideal structure is an asymmetric one, with a very thin defect free layer ($< 0.5 \mu\text{m}$) and a porous sub-layer (thickness 50-200 μm) to provide the necessary support. This structure combines the good selectivity of a dense membrane with the high flux usually seen in much thinner membranes. Wet spinning and dry-wet spinning can form asymmetric membranes. In this research the dry-wet spinning process was used. One benefit of using this technique is that while the fibre passes through the air gap solvent evaporation can initiate the formation of a dense highly selective skin, which is completed in the quench environment in the gelation bath. The spinning of an integral asymmetric membrane in a single step is advantageous and may be less costly than the preparation of composite membranes, in which an additional coating step is required after spinning the porous sublayer (which is usually of a different material).

The fundamental details for each of the four hollow fibre spinning processes are discussed in a paper by P.S. Puri (1990). The book, 'Hollow Fibres', by J. Scott (1981) is an excellent practical source for details about the large-scale manufacture of hollow fibres. The book also contains several chapters about the fabrication of hollow fibre modules and the sealing of hollow fibres within the modules. For hollow fibre membranes a tube in shell module is typically used. These modules can be operated with the feed on either the shell or the tube (bore) side. It is usually desirable for membrane modules to be as compact and lightweight as possible. This is of particular importance for membrane applications in the natural gas industry, where the gas separations may be carried out on oilrigs.

1.7. SYNOPSIS OF RESEARCH RELEVANT TO THIS STUDY

Although there are many papers about hollow fibres and their use in many applications such as reverse osmosis, ultrafiltration and gas separation, there have been few systematic studies on the exact effects of the variables used in the spinning process. This is largely due to the complex nature of the spinning process and the inter-dependence of the spinning variables.

There have been systematic studies on the preparative conditions for flat membranes, but it is not usually possible to adopt these conditions for the spinning process in the fabrication of hollow fibre membranes. Membrane formation in hollow fibres is more complex than that in flat membranes, because there are two coagulation processes taking place, one on the inside and one on the outside of the fibre. In dry-wet spinning the internal coagulation process starts immediately after extrusion from the spinneret, while the external coagulation process is delayed to some extent as the fibre passes through the air gap.

Work that has been reported on the effect of spinning conditions on hollow fibre characteristics tends to focus on the coagulation conditions during spinning (Chung et al., 1992, Lee et al., 1993, Li et al., 1994, Wienk et al., 1994, Lee et al., 1995).

There have been some studies on the rheological aspects of spinning, such as shear and elongation and their effect on the gas separation properties of hollow fibres (Shilton et al., 1994, Ismail et al., 1996, 1997). By altering the polymer solution flowrate and the rate of drawing, Shilton et al. (1994) found that the rate of shear experienced in the spinneret and the amount of elongation of the fibre whilst in the air gap had an effect on gas separation performance. They modelled the shear rate in the annulus and found it to have a parabolic form, with the shear rate highest at the walls and lowest in the centre. The higher shear rates near the walls increased the molecular alignment and this could be frozen into the structure. They found the effect could be particularly pronounced at the inner wall where coagulation was immediate because of the contact with the nonsolvent bore liquid and relaxation from

shear did not have enough time to occur. They found the outer wall of the hollow fibre was not in highly oriented state because as the fibre passed through the air gap before entering the gelation bath, there was enough time for relaxation from the shear experienced in the spinneret.

Ismail et al. (1997) used polarised infra red spectroscopic techniques to directly measure molecular orientation in flat sheet polysulfone membranes prepared under different levels of shear. Their results indicated the polymer backbone aligned in the shear direction. They also studied hollow fibre membranes and found that increasing the polymer solution flowrate from 1 to $2.5\text{cm}^3\text{min}^{-1}$ caused an increase in the permeability of carbon dioxide and the selectivity of CO_2/CH_4 . There was more molecular orientation in the membranes produced at high shear, and increasing shear tended to produce fibres with enhanced pressure normalized flux and selectivity. The rheological conditions during membrane fabrication have utmost importance in enhancing membrane selectivity it can even surpass the intrinsic selectivity of membrane.

The rheology of melt hollow fibre spinning using a liquid bore fluid was modelled by Lipscomb (1994) using a thin filament approximation. He found the fibre geometry was directly controlled by the mass flowrates of the polymer melt and the bore fluid.

There have been several studies on the design of the spinneret and its effect on hollow fibre characteristics (Qin et al., 2000, Chung et al., 1998). Qin et al. (2000) studied the effect of shear stress in the spinneret on performance of ultrafiltration hollow fibre membranes and Chung et al. (1998) on polyethersulfone hollow fibres for gas separation. The latter group spun the hollow fibres using the wet phase-inversion process to reduce the effect of gravity (elongational stress) on fibre formation and attempted to freeze the orientation induced by shear stress within the spinneret into the wet-spun fibres. They used a constant bore fluid to polymer solution flow rate ratio and a spinneret with a die length to flow channel gap ratio of 17.5 that is much higher than the conventional spinneret. Their results suggested that hollow fibre membranes spun from this type of spinneret with high shear have a tighter molecular

packing structure and therefore a higher selectivity that surpasses the intrinsic value but a lower permeance.

The effect of spinning parameters on the *macroscopic dimensions* of polysulfone hollow fibres has been studied by McKelvey et al. (1997). The paper includes a table that summarises the main effects of various spinning parameters on the hollow fibre dimensions. The paper not only discusses the outer and inner diameter of the fibres but also fibres with irregular or non-concentric bores and fibres with varying diameters.

The effect of spinning parameters on *both* the macroscopic dimensions and permeation performance of polysulfone *ultrafiltration* hollow fibre membranes has been reported in several papers (Kim et al., 1995, Liu et al., 1992 and Lee et al., 1995). The latter used a factorial design to study the effects of various spinning parameters and reports optimal spinning conditions for ultrafiltration performance.

For *gas separation* hollow fibres, there have been a few systematic studies on the effect of spinning parameters on *both* the macroscopic dimensions and permeation performance. One studied these effects on silicone rubber coated polyimide hollow fibres (Chung et al., 1992), another on silicone rubber coated polyetherimide hollow fibres (Kneifel and Peinemann, 1992). In another study the effect of spinning parameters on hollow fibres made from modified PPO was studied, however these fibres did not have an effective integral skin and had to be coated with silicone rubber for gas separation testing (Nardella et al., 1995). The only systematic study, found in the literature, on the effect of spinning conditions on *integrally skinned* hollow fibre membranes was a 2^4 factorial design examining the effects of spinning conditions on the morphology and gas permeation properties of polysulfone hollow fibres (Pesek and Koros, 1994). The spinning conditions investigated were: convective evaporative humidity, fibre take-up rate, polymer solution flowrate and salt concentration in the bore fluid. The paper reports the conditions for these variables for optimum gas separation performance.

There have been many studies on the morphology of hollow fibres but few relate systematically the spinning conditions to the morphology of the hollow fibres. The effect of spinning conditions on the anisotropy of pore size (the change in pore size across the fibre wall) has been systematically studied for the formation of microporous fibres using the thermally induced phase separation method (Batarseh, 1999). Other researchers have investigated the effect of membrane preparation conditions on the nodular structure of membranes. Nodular structures have been observed in hollow fibre membranes prepared from a variety of different polymers. Fuji et al. (1992) studied the morphology of nine ultrafiltration hollow fibre membranes prepared from different polymers. They observed nodules, which ranged in size from 25-166nm.

Poly (2,6-dimethyl-1, 4-phenylene oxide), subsequently referred to as PPO, was the material used for the fabrication of the hollow fibres in this research. The general properties of PPO are given in Appendix A. PPO has a high glass transition temperature (205-210 °C). It has a rigid structure with low chain mobility and motion within the structure is largely vibratory. PPO can be formed into tough, moisture resistant membranes and in comparison with other glassy polymers such as polycarbonate, polysulfone and cellulose acetate it gives high gas permeability (Toi et al., 1991, Aguilar-Vega et al., 1993). It was chosen as the polymer material in this study because it has excellent thermal and chemical stability and has good carbon dioxide/ methane gas separation properties, as shown in Table 1.2.

Table 1.2 Carbon Dioxide/Methane Gas Separation Data for PPO Membranes

Reference	CO ₂ Permeability (Barrer*)	CO ₂ /CH ₄ Pure Gas Permeation Rate Ratio
Aguilar-Vega and Paul (1993)	65.5	16
Story and Koros (1991)	45	15
Ghosal and Chern (1992)	52	14
Alentiv et al. (1998)	27	10

* 1 Barrer = $0.76 \times 10^{-17} \text{ m}^3(\text{STP}).\text{m.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$

Some researchers have attempted to improve the gas separation performance of PPO by modifying its structure through substitutions of various functional groups. Whilst not directly related to the research carried out in this thesis (in which unmodified PPO was used), the findings are nonetheless useful since they show how polymer structure tailoring can affect gas separation performance not only by changing the solubility of gases in the polymer material, but also their diffusivity. The addition of functional groups can affect the free volume in the membrane and the packing and rotational motion of the polymer chains and depending on their size and position on the PPO backbone, can affect the gas separation performance in various ways. Several researchers have prepared membranes from PPO modified at the ring position by bromination (Chern et al., 1987, Story et al., 1992) and by sulfonation (Kruczek et al., 1998) and showed them to have increased carbon dioxide permeability compared to unmodified PPO membranes, with little loss in CO₂/CH₄ selectivity. Membranes prepared from PPO modified by the substitution of carbonyl-containing derivatives at the methyl side chain showed lower carbon dioxide permeability and a slightly higher selectivity for CO₂/CH₄ (Story and Koros, 1991). An excellent source of information on the use of PPO and modified PPO for gas separation applications is found in the book "Polyphenylene Oxide and Modified Polyphenylene Oxide Membranes" (Edited by Chowdhury et al., 2001).

PPO membranes can be prepared using various solvent/non solvent systems and several researchers have investigated the effects of coagulation conditions on the membranes characteristics. Broens et al. (1978), studied the formation of PPO ultrafiltration membranes prepared using 10% PPO in trichloroethylene with methanol as a coagulant. They added octanol as a non-solvent additive to the polymer solution in an attempt to introduce a grainy texture in the skin layer. Smid et al. (1991) produced hollow fibre membranes from PPO using trichloroethylene as a solvent, methanol as a coagulant and they studied the effect of adding the nonsolvent 2-ethyl-1-hexanol to the polymer solution used in spinning. They also studied the effect of the intrinsic viscosity of the polymer on the gas separation properties of the hollow fibres. They found by using PPO with a higher intrinsic viscosity for spinning the fibres produced had an increased permeation towards O₂/N₂, while maintaining selectivity.

Whereas decreasing the viscosity of the polymer solution (using the same intrinsic viscosity of the polymer) gave increased permeate flux. A study by Bauer et al. (1991) using plasma etching showed that the sublayer of PPO gas separation hollow fibre membranes had a lower selectivity than the intrinsic selectivity of the membrane and that it could have a large affect on the overall O_2/N_2 selectivity of the membrane. They also showed that the resistance of sublayer decreased markedly with increasing intrinsic viscosity of PPO. One explanation for this was given by Wijmans et al. (1985); PPO is a semi-crystalline polymer and the degree of crystallinity and the nucleation rate increases as the molecular weight decreases, so it can be expected that a large amount of nuclei are formed in the case of low molecular weight PPO and this would produce a network with a small mesh size, resulting in a high resistance to gas transport. For high molecular weight PPO, on the other hand, relatively few nuclei will render a network with larger meshes and hence lower resistance to gas. Another explanation for the different sublayer resistances found in membranes produced from various molecular weight PPO could be due to differences in mobility during the coagulation process. Lower molecular weight polymers have a shorter relaxation time than higher molecular weight polymers and due to higher mobility a more organized, denser structure may result.

Tsujita et al. (1991) attempted to control the macrovoid content of PPO gas separation membranes by quenching from a holding temperature above the glass transition temperature to one below. They found that specific volume was higher for films quenched at higher holding temperatures because the unrelaxed volume of quenched PPO films increased with increased holding temperature. Both carbon dioxide sorption and diffusivity were higher for the quenched films than for those films slowly cooled, because quenching from a higher temperature caused a much larger free volume to be frozen into the structure. Hence quenching increased the permeability of the membrane and the permeability of quenched films increased with holding temperature, while quenching only slightly reduced selectivity.

Some researchers have investigated the morphology of PPO membranes, in some cases nodular structures have been reported (Broens et al., 1978). Khulbe et al. (1997) studied the

relationship between morphology and gas separation performance for dense flat PPO membranes made from using different solvents. Membranes prepared using carbon disulfide as a solvent had supernodular aggregates (about 43nm in size) and this membrane had better gas separation performance than the membranes prepared from other solvents (benzene, toluene, trichloroethylene, chlorobenzene and bromobenzene) that had no supernodular aggregates. They found permeability increased and selectivity decreased with increase in boiling point of the solvent. Also using AFM, they concluded that the roughness parameter increased with an increase in the boiling point of the solvent. Khulbe et al. (1995) studied the morphological differences between asymmetric and homogeneous flat PPO membranes. They used electron spin resonance and Raman spectroscopy to show that the morphology of the skin layer was different for asymmetric and homogeneous membranes of PPO. Another paper (Khulbe et al. 1995) reported on the use of tapping mode atomic force microscopy to investigate the surface morphology of flat asymmetric and homogeneous PPO gas separation membranes. They found the top surface of the asymmetric membrane was made up of nodules of 62nm diameter, while the lower surfaces were much rougher than the top surfaces (two orders of magnitude higher) and had a microporous structure made up of supernodular aggregates. They found the top surfaces of the homogeneous membranes were also made up of nodules of 62nm diameter, whereas the nodules on the lower surface were almost double the size. Bauer et al. (1991) studied PPO gas separation hollow fibre membranes and found that the top layer of the asymmetric PPO hollow fibre they produced was not homogeneous, but consisted of two layers, a compact top layer and a transition layer underneath.

There has been little research on the effect of the spinning conditions used for the fabrication of PPO hollow fibre membranes. Bauer et al. (1991) found that by varying the length of the air gap they were able to produce hollow fibres with skin layers of various thickness and they discovered a relation between the reduced permeability of the sublayer and the thickness of the skin layer. They found the resistance of the sublayer and the thickness of the skin layer decreased with decreasing length of air gap.

Although a moderate amount of research has been carried out which is relevant to this study, much of the research has concentrated on only certain aspects of the hollow fibre fabrication process, and it is difficult to combine and utilize information from many different studies in which different conditions have been used. There have been few systematic studies on the phenomenological correlations between preparative conditions and the morphology and performance of hollow fibre membranes and the triadic relationship between structure, property and function or application. There has been no such systematic study for these relationships for PPO gas separation hollow fibres.

Detailed information about these correlations has importance to membranologists in general. A basic understanding of the hollow fibre membrane formation process is important because it can lead to the production of hollow fibre membranes with increased performance of the membrane. Advances like this have been seen in the past. For example “first generation” gas separation membranes were selected on the basis of convenience and availability. Later, it was discovered that by changing the preparative conditions the thickness of the skin layer could be reduced which led to a threefold increase in productivity using the same polymer. With the introduction of many membranes made from new and modified polymers any information which helps in the prediction of spinning conditions to use to give the optimum performance, will save a great deal of time and effort. It is difficult to establish firm cause and effect relationships between the spinning parameters and membrane morphology and performance because of complexity of the phenomena. Therefore, a factorial design approach is adopted in this work. The objectives and experimental methodology are discussed in the next section.

1.8. OBJECTIVES AND EXPERIMENTAL METHODOLOGY

The objective of this study was to:

Prepare hollow fibre membranes from poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) by the wet-dry spinning method and investigate the spinning process to elucidate relationships between the spinning parameters, fibre dimensions, morphology and the carbon dioxide/methane gas separation performance of the fibres.

Specific tasks required to achieve this objective were:

- Design and fabrication of a laboratory scale hollow fibre spinning system
- Design and fabrication of gas testing modules and testing equipment
- Fabrication of hollow fibres using various bore liquid flow rates, length of air gap, polymer solution concentration and flowrates and in presence and absence of the additive 2-ethyl-1-hexanol
- Measurement of fibre dimensions, morphology and gas separation performance
- Comparison and analysis of data
- Elucidation of correlations between fabrication conditions, fibre dimensions, morphology and the carbon dioxide/methane gas separation performance of the fibres.

At the beginning of the experimental study it was necessary to plan the experiments to ensure that the right type of data, and enough of it, were available to answer the questions of interest as clearly and efficiently as possible. In this study a factorial design was used so that the effects of the variables used in the spinning process could be evaluated simultaneously. Some general information about the use of factorial designs is given in Appendix B. Experimental designs have conventionally used a one-variable-at-a-time approach, in which one varies a single variable at a time and observes the effects. Factorial designs have the advantage over the one-variable-at-a-time approach in that they require fewer experiments to be carried out and can be used to determine any interaction between the variables. In addition to those

experiments required for the factorial design, some extra experiments were also carried out using the traditional one-variable-at-a-time approach to allow some of the effects to be shown in plots.

The methods used to carry out the experiments in this study are detailed in the following chapter.

Chapter 2

MATERIALS AND METHODS

2.1 MATERIALS USED

Poly(2,6-dimethyl-1,4-phenylene oxide) Blendex Modifier Resin BHPP 820 (CAS# 25134-01-4) obtained as a complimentary sample from General Electric Plastics, Washington, West Virginia.

Methanol, BDH Assured, (ACS 531-56), purchased from B.D.H. Inc.

Trichloroethylene, BDH Assured, (ACS 945-82), purchased from B.D.H. Inc.

Chloroform, Omnisolv, B90077-81, purchased from B.D.H. Inc.

2-Ethyl-1-Hexanol, purchased from Kodak

5-Minute epoxy, from Devcon Corporation (comprises two parts: a resin (Bisphenol A diglycidyl ether) and a hardener (2,4,6 tri-(dimethylaminoethyl)-phenol)

2.2 PREPARATION OF THE POLYMER SOLUTIONS

The poly (2,6-dimethyl-1, 4-phenylene oxide) (PPO) powder was dried in a vacuum oven at 60 °C for 48 hours. The PPO polymer solutions were prepared on a weight percentage basis. The weight of PPO polymer needed for the required concentration was measured directly into a glass screw top bottle. The required weights of trichloroethylene solvent and 2-ethyl-1-

hexanol additive were added to the bottle along with a stirring bar, and the bottle was well sealed. The solution was stirred with a magnetic stirrer in a water bath for several days until the entire polymer had dissolved. The solution was then filtered through a 3 μm teflon Millipore filter in a cartridge using nitrogen gas under pressure at 100 - 170 KPa. The polymer solution was then left for two days to de-gas before being used for spinning, as tiny bubbles in the solution could cause defects in the hollow fibre.

2.3 SPINNING APPARATUS AND PROCEDURE

2.3.1 Spinning Apparatus

For safety reasons, the spinning of PPO fibres could not be carried out in the open laboratory, because of the large quantities of methanol used for the gelation bath and bore liquid. A walk-in fume hood (Microzone MC-60-WD-SD) was purchased, and the spinning apparatus was built into a frame with wheels so it could be wheeled in and out of the fume hood. A schematic diagram of the apparatus used for spinning hollow fibres is shown in Figure 2.1.

The tank that was used to hold the polymer solution was made of two parts. The body of the tank and the base were separate pieces that were clamped together. An o-ring was used to form a tight seal between them. The polymer solution was contained within a heavy-duty polyethylene bag, which was held inside the tank. The bag was clamped in place between the tank and its base in such a way that the polymer solution could flow out of the tank through the valve, while the bag provided a seal between the polymer solution and the water filling the rest of the tank.

Figure 2.1 Schematic Diagram of the Apparatus used for Spinning Hollow Fibres

This arrangement had several advantages over simply having the polymer solution contained within a tank with no polyethylene bag. One practical advantage was that only the tank base required cleaning of the polymer solution after the run. Also by filling the remainder of the tank (above the polyethylene bag containing the polymer solution) with water and directly connecting to a height adjustable column of water, the water head could be used as the driving force for the polymer solution to flow through the spinneret. In addition, a rotameter placed in this water line could be used to measure the flowrate of water during the spinning process. The flowrate of the water was the same as that of the polymer solution because as

the polymer solution flowed out of the tank, the polyethylene bag collapsed and the space was replaced by water flowing in from a water tank held above the polymer solution tank. If higher polymer solution flowrates were required or when using a more viscous polymer solution a nitrogen gas cylinder could be used to replace the water head. But for the low flowrates and the less viscous solutions used in this experimental design, the water pressure head gave a more stable flowrate and was the preferred method. Peristaltic and syringe pumps were also investigated as a means of providing polymer solution flow, but these were found to be unsuitable. The peristaltic pump (Watson Marlow 101U) was found to be unsuitable because it gave a pulsing flow. The syringe pump (Sage Instruments, 341B) gave problems with the syringe plunger sticking as the solvent from the polymer solution evaporated and the polymer hardened around it.

A syringe pump (LabCor Inc. dual syringe pump H-74900-10) was used to provide the driving force for the low bore liquid flowrates (<10ml/min). For higher flowrates an adjustable methanol pressure head was used as a driving force for the flowrate. The rotameters used for measurement of the bore liquid and polymer solution flowrates were calibrated before running the experiments.

The spinneret was clamped at a fixed position above the gelation bath. The depth of gelation liquid in the bath was kept constant. The length of the air gap between the spinneret and the top of the gelation liquid in the bath was varied by raising and lowering the gelation bath.

The dimensions of the spinneret were:

Bore Fluid Tube Inner Diameter: 0.53mm

Polymer Solution Annulus Inner Diameter: 0.81mm

Polymer Solution Annulus Outer Diameter: 2.09mm

A schematic diagram of the spinneret design is shown in Figure 2.2

Figure 2.2 Schematic Diagram of Spinneret

Figure 2.3 Schematic Diagram of Cross Section of Spinneret Orifice

2.3.2 PROCEDURE FOR SPINNING

The polymer solution was placed in the polymer tank as follows. The tank was inverted and a polyethylene bag placed inside with the edge of the bag pulled down over the sides of the tank. The polymer solution was carefully poured into the bag. The tank base was then bolted in place; an o-ring between the base and the tank ensured a good seal. The valve in the tank base was opened and with the tank still inverted it was filled from the bottom with water, displacing any air in the bag. When all the air was displaced and the polymer solution began to emerge, the valve was closed and the tank was placed the right way up, with the tank base at the bottom. The tank was put in the fume hood and the connections were made from the side and top of the polymer tank to the ¼ inch polyethylene tubes connected to the water column and the spinneret. The spinneret was clamped into place and the gelation bath filled to a depth of 28 cm with methanol and set directly below it at the desired air gap. The syringe pump was filled with methanol and connected to the spinneret using ¼ inch polyethylene tubing. The bore liquid flow was started by turning on the syringe pump at the required flowrate. The valve below the polymer solution tank was opened to start the polymer solution flowing and the emerging fibre was guided into the gelation bath. Fibre was collected from the gelation bath under the set of conditions being studied and placed in a labelled container filled with methanol. Any fibres formed while conditions were being changed and before steady state had been reached were discarded.

The following data were recorded for each spinning:

- Ambient temperature, pressure and humidity
- Polymer solution composition
- Length of air gap
- Bore liquid flowrate and rotameter reading
- Polymer solution pressure head and rotameter reading

When spinning was complete, the valve below the polymer tank was closed, and the bore liquid flow stopped. The polymer tank was disconnected and thoroughly cleaned. The spinneret was removed, taken apart and cleaned by soaking it in a bath of chloroform.

The hollow fibres were kept in methanol for 24 hours and then hung to dry in the fume hood. The dry hollow fibres were stored in labelled plastic bags to keep them dust free.

2.4 FIBRE DIMENSION MEASUREMENT

The diameter and wall thickness of the hollow fibres were measured using an optical microscope. To mount the cross-section of a fibre for viewing, one end of the hollow fibre was placed in a 1 mm diameter hole drilled in a 3 mm thick Plexiglas disc and a razor blade was used to cut the fibre flush with the surface of the Plexiglas disc. The fibre was then viewed through the microscope and the measurements taken. The dimensions of the fibre were measured at 12 to 15 random points along the length of the hollow fibre and the mean of values calculated. In cases where the fibres were not circular the smallest and largest diameters were measured. In cases where the bore was not central the smallest and largest wall thicknesses are measured. A 95% confidence interval for the mean value of the measurements was calculated (Taylor, 1990); a sample calculation is given in Appendix C.

2.5 LEAK TESTING

Prior to gas permeation testing, all hollow fibres were tested for leaks. The fibres were submerged under distilled water, one end of the fibre was blocked and nitrogen gas at 55-70 KPa was introduced into the bore of the fibre at the other end. Bubbles indicated the presence of leaks. Any leaky sections are cut out and the remaining lengths of fibre were tested for further leaks. Dry leak-free sections were stored in plastic bags.

2.6 GAS PERMEATION TESTING

2.6.1 GAS PERMEATION TEST MODULE DESIGN

The design of the gas permeation test module allows hollow fibres to be tested with the feed on either the bore side or shell side. Figure 2.4 is a pictorial exploded assembly drawing of a test module. The module was made of 3/8 inch stainless steel tubing, 35 cm in length, with a side arm of 1/4 inch stainless steel welded 5 cm from one end. At either end of the module 5cm lengths of 1/4 inch polyethylene tube were connected to the module using a stainless steel 3/8 inch to 1/4 inch reducing male Swagelok connection

The hollow fibres to be tested (usually two or three lengths of fibre) were threaded through the module and sealed in place within the polyethylene tubes using epoxy. This sealing process is known as potting.

When potting the fibres the insides of the polyethylene tube were first scored to roughen the surface and provide a good adhesion with the epoxy. The epoxy was injected in the space around the fibres to seal them inside the polyethylene tube. Several epoxies were investigated for use. Devcon two-part 5-Minute epoxy gave the best results for good adhesion with no visible shrinkage and ease of use. This epoxy caused no damage to the fibres.

The epoxy came in a container with twin pack syringe that could dispense equal amounts of resin and hardener. A mixing tube fitted to the end of the syringe allowed the epoxy to be dispensed, mixed and injected around the hollow fibres in the tube in one step. While the epoxy was curing, a razor blade was used to cut through the polyethylene tubing, giving a neat end and exposing the fibre cross sections.

Figure 2.4 Schematic Diagram of a Test Module

For bore side feed, both ends of the fibres needed to be potted in the polyethylene tubes at either end of the module. Nylon ferrules placed around the tubes provided a tight seal when the 1/4 inch stainless steel Swagelok nuts are screwed in place.

For shell side feed, the fibres needed only be potted in the polyethylene tube at one end, the other end could be plugged with epoxy resin and lay suspended in the module.

The length of the exposed fibre was measured for each module and along with the diameter measurement used to calculate the surface area of the hollow fibres that was in contact with the feed gas.

2.6.2 GAS PERMEATION TESTING APPARATUS

Figure 2.5 is a schematic diagram of the apparatus designed for testing the gas permeation of hollow fibres. The apparatus had six hollow fibre modules of the design described above. Gas cylinders of pure methane and pure carbon dioxide were used to provide the feed gas. Feed pressure was recorded with a gauge (#31746-121 from VWR Scientific Canada). The tube leading from the gas cylinder was 1/8 inch stainless steel; all other high-pressure tubing in the system was 1/4 inch stainless steel. All high-pressure connections and valves were stainless steel Swagelok fittings, purchased from Ottawa Valve and Fitting. The connection from the stainless steel tube to the polyethylene tubing containing the potted fibres was made with a stainless steel fitting and 1/4 inch nylon ferrules. This connection was tested on demand at the laboratories at Ottawa Valve and Fitting. It was found to be leak-free and could withstand pressures up to 4.1×10^6 Pa. A bubble flowmeter was used to measure the permeation flowrate. It was connected to the permeate side of the module with 1/8 inch tygon tubing. Depending on the flowrate, either a 10ml or a 0.5 ml glass bubble flowmeter was used.

Figure 2.5 Schematic Diagram of the Gas Permeation Testing Equipment

2.6.3 PROCEDURE FOR GAS PERMEATION EXPERIMENTS

Pure carbon dioxide and pure methane gases were used for testing at a pressure of 100 psig (6.89×10^5 Pa); some experiments were repeated at 200 psig (1.38×10^6 Pa). The hollow fibre modules were used with the feed gas on the bore side of the fibres and the permeate was collected from the shell side. Each module contained one to three fibres about 35cm in length (the exact length of the fibre was measured for each module tested). Experiments were usually carried out with six modules, three modules containing fibres prepared under one set of conditions, and the other three containing fibres prepared under a different set of conditions.

With valve #1 fully open and valves #2 - 7 closed, the valve on the gas cylinder was opened and adjusted to give the desired pressure in the system. Valve #8 could be used to release excess pressure. Valves #2 - 7 were opened fully and then closed. Valves #9 - 14 were opened to release the gas in the modules; these valves were then closed. The last two steps

were repeated 5 times to ensure that the modules were completely flushed with the test gas. To start the experiment valves #2 -7 were opened and the time was recorded. Flowrates were measured using the bubble flowmeter every 30 minutes for the first two hours and hourly thereafter. The time and ambient pressure and temperature were recorded for each flowrate measured so that the flowrates could be corrected to standard temperature and pressure (a sample calculation is given in Appendix C). Flowrate measurements were taken until steady state was reached.

2.6.4 HIGH PRESSURE TESTING

Experiments designed to test the ability of some of the fibres to withstand bore side gas pressures of up to 1500 psig (10.3×10^6 Pa) were carried out using test modules containing a single hollow fibre. The test module containing the hollow fibre to be tested was placed behind a protective screen and the pressure on the bore side of the fibre was slowly increased in 100 psig (6.89×10^5 Pa) intervals, waiting for five minutes at each level. The pressure was increased to 1500 psig (10.3×10^6 Pa) or until the hollow fibre was destroyed. No permeation data was taken during these experiments and for safety reasons air was used rather than methane and carbon dioxide gases.

2.7 FACTORIAL DESIGN

A complete factorial experimental design was planned to investigate four factors at two levels. The factors chosen for the experimental design were:

Factors		Levels	
		-	+
A	Presence of Additive, 2-Ethyl 1-Hexanol in the Polymer Solution	absent	present
B	Length of Air Gap	low	high

C	Polymer Solution Flowrate	low	high
D	Bore Liquid Flowrate	low	high

The dependant variables (or responses) being studied at the various treatment combinations were:

1. Outer Diameter of the hollow fibre
2. Wall Thickness of the hollow fibre
3. Carbon Dioxide Permeation Flux of the hollow fibre
4. Methane Permeation Flux of the hollow fibre
5. Ideal Separation Factor of the hollow fibre (i.e. the ratio of the permeation fluxes for pure carbon dioxide and pure methane gas).

A 2^4 factorial design requires sixteen runs representing all combinations of the factors at the two levels.

In order to determine the appropriate levels of the factors that could be used to produce useful (i.e., uniform, strong, gas-testable) fibres at each of the treatment combinations it was necessary to carry out some preliminary experiments to target these levels. These preliminary experiments are discussed in the next chapter.

Initially there had been a plan to include the concentration of PPO in the polymer solution in the factorial design. However, while carrying out the preliminary experiments it was discovered there were difficulties in determining two levels of PPO concentration for which fibres could be produced at all the necessary treatment combinations; this is discussed further in Chapter 3. Since this problem was discovered quite early in the planned scheme of experimental runs, a decision was made to fix the PPO concentration and investigate the four remaining factors in the factorial design. However, some additional experiments were carried out to study the effect of the concentration of PPO in the polymer solution using a one-factor-at-a-time approach.

2.8 SCANNING ELECTRON MICROSCOPE WORK

A scanning electron microscope was used to study some of the hollow fibres and scanning electron micrographs (SEM's) were taken of the hollow fibre cross section. Some work was carried out through the Chemistry Department at the University of Ottawa. The bulk of the work was carried out with Ramendra Singh at the British Gas Research Institute, Loughborough, UK.

The fibres were prepared by plunging into liquid nitrogen and snapping to give a clean cross section. The fibres were then mounted on a plate by placing one end in a blob of epoxy, the fibre was held vertically until the epoxy hardened. Four fibres were mounted on each plate, clearly labelled and then gold sputtered.

2.9 ATOMIC FORCE MICROSCOPE WORK

An atomic force microscope (Burleigh Personal SPM with a ARIS 3005 5 micron scanning module) was used to study cross sections of hollow fibres. The work was carried out with Rob Judd at the British Gas Research Institute.

The fibre cross sections were prepared by applying a thick layer of epoxy around and in between a bundle of hollow fibres. The epoxy fibre bundle was cut across with a sharp scalpel when the epoxy had just hardened, to expose the fibre cross sections. The bundle was cut again about 5 mm from the first cut and mounted with double-sided sticky tape onto a disc with the clean cross sections facing up. The use of a microscope connected to a video camera mounted above the AFM, allowed the cantilever to be positioned directly above the fibre wall before it was lowered onto the sample. There were some problems when scanning directly at the edge of the fibre because of the height difference encountered. It was better to take several scans at each position, first scanning at the centre of the wall using a small scan size, then increasing the scan size incrementally until the fibre wall was encountered.

2.10 HOLLOW FIBRE PREPARATION AND TESTING METHODOLOGY

The steps involved in the preparation and testing of hollow fibres are summarized in Figure 2.6.

Figure 2.6 Steps in the Preparation and Testing of Hollow Fibres

Chapter 3

RESULTS: PRELIMINARY EXPERIMENTS

Before the effect of spinning conditions on the characteristics of hollow fibres could be adequately studied, it was necessary to carry out some preliminary experiments to overcome some of the practical hurdles in spinning. Several researchers have had difficulties in producing continuous, mechanically strong hollow fibres with concentric bores and a circular cross section. The economics of the spinning process depend in part on the rate of production of hollow fibres of uniform size and properties and in practice production can be limited by instabilities that arise in the process. Some of the difficulties that must be overcome are detailed by McKelvey et al. (1997) and are discussed in section 3.1.

Preliminary experiments were carried out to determine the appropriate range for the variables being studied in the spinning process and these are discussed in sections 3.2-3.7. From these ranges it is possible to determine the most suitable levels for the factors that could be used to produce useful (i.e., strong, gas-testable) fibres at each of the treatment combinations in the factorial design.

3.1 COMPLICATIONS THAT CAN ARISE IN THE SPINNING PROCESS

3.1.1 Hollow Fibres with Non-Concentric Bores

While a certain amount of non-concentricity of the bore of the hollow fibre can be tolerated, it will affect the performance of the membrane; McKelvey et al. (1997) stated the ratio of the maximum to minimum wall thickness should not be more than about 1.10 for well-made fibres. The dominant process variable affecting the attainment of hollow fibres with concentric bores is the design of the spinneret. Spinneret design is poorly documented in the literature and much design information remains proprietary, but several spinneret designs are given in the book 'Hollow Fibres' by Scott (1981). It is important that the spinneret is designed so that the flows of the bore liquid and polymer solution through it are axisymmetric and that the tube for the bore liquid is exactly in the centre to help avoid the production of hollow fibres with non-concentric bores.

The spinneret used in this study had a tube in orifice design and was fabricated from three parts in brass and stainless steel so it could be dismantled for easy cleaning. The parts were precisely machined so that the bore liquid tube always remained central. Ideally, the central tube for the bore liquid should have a streamlined design and be inserted in the spinneret in such a way that it does not unduly disturb the flow in the spinneret. The spinneret should always be cleaned immediately after spinning, by soaking and flushing with clean solvent. This is important because any polymer solution remaining in the spinneret will solidify and could block the fine bore liquid tube or cause problems with irregular bores in subsequent spinning. In the spinneret used in this study, the end of the bore liquid tube was flush with the bottom of the spinneret, this ensured no bore liquid could flow into the polymer solution channel of the spinneret and also ensured that the flow exiting the spinneret was not unduly disturbed.

Another factor that can affect whether the bore of the hollow fibre is central is uneven airflow around the hollow fibre as it passes through the gap. Some preliminary experiments produced hollow fibres that were striped, half the circumference was transparent and the other half opaque. There was also a slight difference in the wall thickness around the fibre (i.e. the bore was non-concentric). The cause was uneven airflow around the fibre in the air gap. The problem was overcome by rearranging the spinning apparatus in the fume hood. Any extraneous equipment in the fume hood was removed and the spinneret was positioned in the centre of the fume hood so allowing clear airflow around the fibre while spinning.

3.1.2 Non-Circular Hollow Fibres

Non-circular hollow fibres should be avoided because they can be more susceptible to failure during use because the stresses are not evenly distributed about the fibre wall. Ovality is generally more of a problem when the fibres are drawn and wound onto a drum and is usually a result of insufficient time in the first gelation bath before conveying over spin line guides. McKelvey et al. (1997) found that ovality increased as the concentration of solvent added to the nonsolvent bore liquid increased and this was because under these conditions vitrification occurred less quickly and the fibre was more susceptible to subsequent deformation. Similarly, in this study, ovality of hollow fibres was generally more prevalent when hollow fibres were spun using conditions for which vitrification of the hollow fibre tended to be slower (i.e. using high polymer flowrates, low bore liquid flowrates and short air gaps).

3.1.3 Diameter Variance

Any disturbances in spinning parameters can cause time-dependent variations in the outer diameter of the fibre. McKelvey et al. (1997) found the diameter variance was somewhat dependent on polymer solution composition and that increasing the polymer concentration in the polymer solution tended to dampen fibre diameter variability. In this study, *time-dependent* diameter variation during spinning was small. The only exception being at start-up when the fibre diameter was often variable until steady-state conditions were reached. However, for each experiment, the first few metres of fibre produced at the beginning of the

spinning process was discarded.

3.1.4 Polymer Solution Ageing

McKelvey et al. (1997) had complications during hollow fibre spinning arising from the ageing of the polymer solutions prior to spinning. They do not give specific details but state that if a polymer solution had been left to stand for more than several days or weeks before spinning, they had problems with fibre breakage during spinning; whereas an identical freshly prepared solution caused no problems during spinning. Even when no apparent degradation appeared to have taken place they found complexation and subtle ordering in solutions altered the rheology of the spin line and tended to cause fibre breaks. One explanation could be that the relaxation spectrums of polymer solutions shift as they age (Ziabicki, 1976). In this study, there were no apparent complications due to polymer ageing. The polymer solutions were prepared using the same timescale each time, the solutions being prepared, stirred for two days, filtered and then allowed to stand. The polymer solutions were used for hollow fibre spinning on the second day after degassing.

3.1.5 Bubbles in Polymer Solution

Bubbles of gas can become entrapped in the polymer solution while stirring the solution during its preparation. Failure to eliminate these bubbles prior to spinning can lead to fibre breaks and altered permeation properties. The polymer solutions used in this study were thoroughly de-gassed for two days before spinning to eliminate these small bubbles.

3.1.6 Fibre Breaks

A hollow fibre will break during the spinning process if the local tensile stress (i.e. tensile force/fibre cross sectional area) at some point in the spin line exceeds the local tensile strength. In particular, this can be a problem when the fibre is drawn during spinning, especially for large take-up rates.

The importance of the rheological behaviour of the spinning solution and stabilization issues is discussed in a paper by Puri (1990). Fibre breakage is very dependent on the viscosity of the polymer solution and therefore is also dependent on polymer solution composition. It is necessary for a polymer solution to have a high enough viscosity to enable it to be quickly stabilized on exiting the spinneret. Stabilization occurs a relatively short distance from the spinneret and always involves a rapid increase in viscosity of the polymer solution. Spinning with solutions of low viscosity tends to produce discontinuous strands.

The changes that promote stabilization also play a dominant role in determining the wall structure and the thin dense skin required for the asymmetric structure starts to form during this stabilization step. In melt spinning the extrusion into a cooler atmosphere promotes the necessary solidification. In dry-wet spinning the removal of a volatile solvent by evaporation as the fibre passes through the air gap promotes stabilization and the phase change occurring at the inner wall aids stabilization.

3.2 DETERMINING AN APPROPRIATE RANGE FOR PPO CONCENTRATION IN POLYMER SOLUTION

A range of polymer solutions of PPO in trichloroethylene were prepared containing from 20% to 25% PPO by weight. In each case the PPO could be dissolved in the trichloroethylene with some stirring and heating in a water bath at 60°C. The warm solutions were all transparent and yellow in colour and the intensity of the yellow colour increased with the PPO content. On cooling the solutions to room temperature, the solutions remained homogeneous and transparent except for the 25-wt% PPO in trichloroethylene solution, which became cloudy. The cloudiness or turbidity was a result of the formation of aggregates in the solution that scatter light and therefore indicated liquid-liquid phase separation had started to occur.

The solutions containing 25-wt% PPO in trichloroethylene were not used for the spinning of hollow fibres because the solutions were not in a stable condition at room temperature; the turbidity of the solution increased on standing and the solutions did not appear homogeneous.

They would not be suitable for use in experiments as part of a factorial design because it would be difficult to ensure that a series of batches of the same composition of polymer solution were at the same state of liquid-liquid phase separation. Cheng et al. (1995) also found that some of their polyamide solutions started to precipitate on standing and they stated “because of the inability to measure the exact aggregation state of the polymer in a poor solvent, precipitation to form uniform microporous membranes with reproducible properties becomes a very frustrating exercise”. Indeed, this may have been the reason that some researchers (e.g. McKelvey et al. (1997)) found it difficult to reproduce spinning experiments using polymer solutions that had been left to stand for different periods of time.

The solutions containing 20-24 wt% PPO were homogeneous at room temperature and potentially suitable for use in hollow fibre spinning. Table 3.1 is a summary of the hollow fibres prepared from these polymer solutions using a variety of spinning conditions. The table also shows for each set of spinning conditions whether or not the fibres produced were suitable for gas testing. For some sets of spinning conditions no fibres could be produced. In these cases either short discontinuous strands of fibre were formed or the hollow fibre shape did not form properly and the polymer solution formed a pool at the bottom of the gelation bath. In other cases fibres were formed but the coils of fibres stuck to one another in the gelation bath and they could not be separated for gas testing. In other cases the fibres were formed but they were too fragile or brittle to withstand the handling required to put them in gas testing modules. These problems are discussed in the remainder of this chapter and ranges are given for which useful (i.e., strong, gas-testable) fibres could be produced.

Table 3.1 Summary of Hollow Fibres Prepared using 20-24 wt% PPO Solution

Polymer Solution Flowrate (ml/min)	20%PPO 0%EH 60cm Air Gap		20%PPO 0%EH 80cm Air Gap		22%PPO 0%EH 60cm Air Gap		23%PPO 0%EH 80cm Air Gap		23%PPO 0%EH 60cm Air Gap		24%PPO 0%EH 80cm Air Gap		24%PPO 0%EH 60cm Air Gap	
	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?
35							11.2	No (s)					29.3	No (s)
24							11.2	No (s)						
13	29.3	No (nf)	20.8	No (nf)			11.2	No (s)			20.8	No (s)	29.3	No (s)
5.5							4.0 3.0 2.0 1.0 0.5	No (s) No (s) No (s) No (s) No (s)	4.0 3.0 2.0 1.0	No (s) No (s) No (s) No (s)				
3.3							11.2 9.0 8.0 2.0	Yes Yes Yes No (s)	11.2 9.0 2.0	Yes Yes No (s)				
2.5	29.3	No (f)	20.8	No (f)	20.8	No (sc)	13.5 12.4 11.2 10.1 9.0 2.0 1.5	Yes Yes Yes Yes Yes No (s) No (s)	13.5 12.4 11.2 10.1 9.0	Yes Yes Yes Yes Yes	20.8 13.5 11.2 9.0	No (s) No (s) No (s) No (s)	29.3	No (s)
1.5	9.0 2.0	No (nf) No (nf)			9.0 2.0	No (nf) No (nf)	13.5 12.4 11.2 10.1 9.0 4.0 3.0 2.0 1.0 0.5	No (f) Yes Yes Yes Yes Yes Yes Yes Yes No (s)	13.5 12.4 11.2 10.1 9.0 4.0 3.0 2.0 1.0 0.1	No (f) No (f) No (f) Yes Yes Yes Yes No (s) No (nf)	13.5 12.4 11.2 10.1 9.0 0.3	No (f) No (f) No (f) No (f) No (s) No (s)	13.5 12.4 11.2 10.1 9.0 0.3	No (f) No (f) Yes Yes No (s) No (s)
0.75							2.0 1.0 0.3 0.1	Yes Yes Yes No (nf)	2.0 1.0 0.3 0.1	Yes Yes Yes Yes				

Table 3.1 cont. Summary of Hollow Fibres Prepared using 20-24 wt% PPO Solution

Polymer Solution (Flowrate ml/min)	23%PPO 0%EH 74cm Air Gap		23%PPO 0%EH 50cm Air Gap		23%PPO 2%EH 88cm Air Gap		23%PPO 2%EH 74cm Air Gap		23%PPO 2%EH 60cm Air Gap		23%PPO 2%EH 50cm Air Gap		23%PPO 2%EH 29cm Air Gap	
	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?	BLF (ml/min)	Able to test?
5.5					2.0	No (s)			11.2 9.0 2.0	No (s) No (s) No (s)				
3.3					13.5 12.4 11.2 10.1 9.0	No (f) No (f) No (f) Yes Yes	10.1	Yes			10.1	Yes	2.0	No (s)
2.5	11.2	Yes	11.2	No (s)	10.1	Yes								
1.5	10.1	Yes	13.5 10.1	Yes Yes	13.5 12.4 11.2 10.1 9.0 2.0 1.5 1.0 0.8 0.5	No (f) No (f) Yes Yes Yes Yes Yes Yes Yes			13.5 12.4 11.2 10.1 9.0 3.0 2.0 1.5 1.0 0.8 0.7 0.3	No (f) No (f) No (f) No (f) Yes Yes Yes Yes Yes No (s) No (s)	1.0	No (s)	2.0 1.0 0.3	Yes No (s) No (nf)
0.75					2.0 1.5 1.0	Yes Yes Yes			4.0 3.0 2.0 1.5 1.0	No (nf) No (s) Yes Yes Yes				

% PPO concentration of PPO in the polymer solution used for spinning
 % EH concentration of 2- ethyl 1-hexanol in the polymer solution (as a wt % of the solvent)
 AIRGAP length of the airgap used for spinning (cm)
 BLF bore liquid flowrate used in the spinning process (ml/min)
 Yes fibre suitable for gas testing
 No fibre not suitable for testing for the following reasons:
 (nf) no fibre formed
 (s) fibre coils stuck together
 (f) fibre too fragile or brittle
 (sc) fibre formed in a tight coil which could not be straightened

The experiments carried out to prepare hollow fibres from the 20 wt% PPO solution were not successful; only a short length of fibre was produced and it was very fragile. As discussed in section 3.1, fibre breakage during spinning is dependent on the viscosity of the polymer solution and hence is also dependent on polymer solution composition. The 20 wt% PPO in trichloroethylene solution had relatively low viscosity; it did not stabilize quickly enough after exiting the spinneret and tended to form discontinuous strands.

It was possible to produce hollow fibres using the 22 wt % PPO solution at certain conditions, however these fibres were fragile and were produced as a tight coil (of a diameter less than 10 cm). The fibres were also somewhat brittle and could not be straightened for placement into the test module; therefore these fibres would obviously not be suitable candidates for gas permeation testing.

Hollow fibres were successfully prepared using 23 wt% and 24 wt% PPO solutions at many different operating conditions. Hollow fibres were also successfully prepared using 23 wt% PPO solution containing the 2-ethyl 1-hexanol additive. However there were problems when attempting to produce fibres under similar conditions using 24 wt% PPO polymer solution containing the 2-ethyl 1-hexanol additive; the spinneret became blocked as the fibre started to emerge from the spinneret. This was probably due to the high level of PPO concentration which combined with the presence of the nonsolvent had already brought the solution very close to its gelation point. As soon as the polymer solution came into contact with the bore liquid, gelation would take place blocking the spinneret tip. This problem was not encountered for runs carried out using polymer flowrates higher than 10 ml/min. Presumably at the higher flowrate the polymer solution was carried away from the spinneret before any gelation could cause blocking. However as discussed in the next section using high polymer solution flowrates caused the fibres to stick together in the gelation bath.

For these reasons a concentration of 23 wt% PPO was used for the runs in the factorial

design. However, some additional experiments were carried out to study the effect of the concentration of PPO in the polymer solution using a one-factor-at-a-time approach.

3.3 DETERMINING AN APPROPRIATE RANGE FOR POLYMER SOLUTION FLOWRATE

Hollow fibres were produced using a wide range of polymer solution flowrates by using both pressure from a gas cylinder and a water pressure head as driving forces. Many of the fibres produced using an applied pressure of 5-10 psig ($3.4\text{--}6.9 \times 10^4$ Pa) stuck together when the coils made contact in the gelation bath. The polymer solution flowrate, which was 10–35 ml/min was too large to allow sufficient gelation of the fibre before making contact with the next coil entering the gelation bath. Even using the maximum air gap of 88cm (constraint due to the height of the walk-in fume hood) sticking of the fibres was a problem. Using the water pressure head as the driving force it was possible to obtain lower polymer solution flowrates of between 0.75 and 5.5 ml/min. The hollow fibres produced using these polymer solution flowrates had fewer problems with sticking. In particular, polymer solution flowrates of 0.75 and 1.5 ml/min produced the most favourable hollow fibres for a range of bore liquid flowrates. Therefore these two levels were chosen for the polymer solution flowrate factor in the factorial design.

3.4 DETERMINING AN APPROPRIATE RANGE FOR THE LENGTH OF AIR GAP

A range of hollow fibres was produced using air gap lengths of between 29cm and 88cm. Air gaps much shorter than 29cm tended to produce hollow fibres that stuck together or the polymer solution formed a pool at the bottom of the gelation bath. Even at 29 cm, there were

problems with sticking for fibres produced at some conditions. The levels chosen for the air gap factor in the factorial design were 60cm and 88cm. Fibres could be formed using these air gaps for a wide range of spinning conditions.

It was not possible to use a length of air gap greater than 88cm due to the height constraints of the walk-in fume hood. Some researchers have produced hollow fibres using longer air gaps. Lee et al. (1993) found that if very large air gaps (>130cm) were used in the spinning of polysulfone fibres, the fibres produced either fractured or showed leakage during microfiltration tests. They did not give an explanation for this and they did not study the effect of the length of air gap used in spinning on the dimensions and morphology of the fibres. It is possible that the increased length of air gap produced fibres that were prone to breakage due to their thin walls, or the presence of defects caused by stretching of the fibre wall as the fibre elongated in the air gap.

3.5 DETERMINING AN APPROPRIATE RANGE FOR BORE LIQUID FLOWRATE

A bore liquid flowrate range of 9-14 ml/min was used in the preliminary hollow fibre spinning experiments. A pressure head was used to provide the driving force for the bore liquid flow. The hollow fibres produced using the higher bore liquid flowrates were transparent and had fragile thin walls. The smaller flowrates produced the most attractive hollow fibres in terms of strength. However 9 ml/min was the minimum stable flowrate that was possible using a pressure head as the driving force.

Alternative methods for producing the bore flow were investigated. While peristaltic pumps were able to provide very low bore liquid flowrates, their pulsing action caused changes along the length of the fibres. A syringe pump was able to provide a small, very uniform flowrate in the range 0.1 to 10 ml/min. However, during hollow fibre spinning flowrates larger than 4

ml/min could not be used because of the limitation of the capacity of the syringe. At higher flowrates the bore liquid in the syringe would run out before steady state conditions had been reached.

The hollow fibres produced using the bore flowrate range of 0.1- 4 ml/min were, in general, strong and suitable for gas permeation testing. However, some of the fibres produced using the bore liquid flowrate at the extremes of this range had the problem of sticking.

Taking into consideration the levels chosen for the other factors, 1ml/min and 2ml/min were the most suitable levels for the bore liquid flowrate to use for the factorial design.

3.6 DETERMINING AN APPROPRIATE LEVEL FOR THE ADDITIVE 2-ETHYL 1-HEXANOL

The use of various additives has been studied in an attempt to improve the separation performance of PPO membranes. Broens et al. (1978) added the nonsolvent octanol to the polymer solution of PPO in trichloroethylene in an attempt to introduce a grainy texture in the skin layer of PPO membranes, and improve their ultrafiltration performance. In this study, the additive, 2-ethyl-1-hexanol, was chosen based on its favourable performance in flat PPO gas separation membranes (Gagne, 1994). Smid et al. (1991) also used 2-ethyl-1-hexanol as a nonsolvent additive in the spinning of hollow fibres.

Broens et al. (1978) used a polymer solution with a solvent:nonsolvent ratio of 78:22 to spin PPO ultrafiltration hollow fibres. Work carried out by Wijmans et al. (1985) with PPO membranes, using the additive 1-octanol, showed that a lower concentration of additive was favourable for the production of gas separation membranes. For this reason, the level of additive concentration chosen for this study was 2 wt% of the solvent in the polymer solution.

3.7 FACTOR LEVELS FOR THE FACTORIAL DESIGN

A complete factorial experimental design to investigate four factors at two levels requires sixteen runs. From the findings of the preliminary experiments, the following levels were chosen for the factors in the experimental design:

Factors	Levels	
	-	+
A Concentration of Additive*, 2-Ethyl 1- Hexanol in the Polymer Solution	0%	2 wt%*
B Length of Air Gap	60cm	88cm
C Bore Liquid Flowrate	1 ml/min	2 ml/min
D Polymer Solution Flowrate	0.75 ml/min	1.5 ml/min

* As a weight percentage of the solvent

The fibres produced for the factorial design were all prepared using a 23 wt% PPO polymer solution. The sixteen runs were carried out in a random order. Additional fibres were prepared at other experimental conditions in order to illustrate and study the effect of some spinning variables in more detail.

For each of the fibres produced, the outer diameter and wall thickness have been measured. Scanning electron micrographs and atomic force microscope images were taken of some of the fibres to provide information about the morphology of the hollow fibre walls. Many of the hollow fibres have been tested with pure carbon dioxide and methane to determine the permeation rate of these gases through the membrane, and the pure gas separation ratio.

The results from these experiments show how spinning conditions affect membrane dimensions, gas separation performance and morphology of the fibres, and are discussed in the following three chapters.

Chapter 4

RESULTS: HOLLOW FIBRE DIMENSIONS

The dimensions of hollow fibres can be described using just two measurements: the outer diameter of the fibre and the thickness of the walls. Both these dimensions are of practical importance in the use of the hollow fibres for gas separation. The results given in this chapter show how four operating variables associated with the spinning process affect the outer diameter and wall thickness of the hollow fibres.

The results from the factorial design show which of the operating variables had a significant effect on the hollow fibre dimensions. Those variables that were found to be significant were included in linear models, which were developed for the hollow fibre outer diameter and wall thickness.

The graphs given in the subsequent sections illustrate the effect of each of the variables on the hollow fibre dimensions. The error bars in these graphs indicate a 95% confidence interval for the mean value of the dimension. The confidence intervals were calculated using the mean, standard deviation, number of sample measurements taken and a student t factor (Taylor, 1990) as shown in the sample calculation given in Appendix C. The estimate for the dimensions, as calculated using the developed models, is also included in the graphs for the range of operating conditions within the constraints of the factorial design.

The outer diameters of the fibres produced for the factorial design ranged between 0.39 mm – 0.6 mm and the wall thickness of the fibres between 0.018 mm and 0.045 mm. Dimension data had also been obtained for some of the hollow fibres prepared in the preliminary experiments and this data has been included in tables in this chapter. The hollow fibre dimension data is summarized in table D1 given in Appendix D.

4.1 EFFECT OF SPINNING CONDITIONS ON OUTER DIAMETER OF PPO HOLLOW FIBRES

4.1.1 FACTORIAL DESIGN

The statistical analysis of the factorial design was carried out using the spreadsheet program Excel. The sample calculations for the analysis and the subsequent development of the model are shown in Appendix E. The input data for the sixteen runs is shown in Table 4.1.

Table 4.1 Input Data for the Statistical Analysis for the Factorial Design for Outer Diameter of PPO Hollow Fibres using 23 wt% PPO Solution

% Additive in the Polymer Solution*	Length of Air Gap (cm)	Bore Liquid Flowrate (ml/min)	Polymer Solution Flowrate (ml/min)	Outer Diameter of Hollow Fibre (mm)
0	60	1	1.5	0.59
0	60	1	0.75	0.50
0	60	2	1.5	0.60
0	60	2	0.75	0.58
0	88	1	1.5	0.55
0	88	1	0.75	0.39
0	88	2	1.5	0.57
0	88	2	0.75	0.45
2	60	1	1.5	0.55
2	60	1	0.75	0.49
2	60	2	1.5	0.59
2	60	2	0.75	0.58
2	88	1	1.5	0.42
2	88	1	0.75	0.43
2	88	2	1.5	0.52
2	88	2	0.75	0.44

* 2-Ethyl 1- Hexanol as a wt% of the solvent

Dimensionless variables were used in the analysis: the low level of each factor was designated as -1 and the high level was designated by 1. The results from the analysis are shown in Table 4.2.

Table 4.2 Output Data for the Statistical Analysis for the Factorial Design for Outer Diameter of PPO Hollow Fibres using 23 wt% PPO Solution

Factors		Effect	Sum of Squares of Effects	df	Mean Square of Effects	F
Main Effects	A	-0.02625	2.756E-03	1	2.756E-03	2.384
	B	-0.08875	3.151E-02	1	3.151E-02	27.249
	C	0.05125	1.051E-02	1	1.051E-02	9.086
	D	0.06625	1.756E-02	1	1.756E-02	15.184
2-Way Interactions	A*B	-0.01125	5.063E-04	1	5.063E-04	0.438
	A * C	0.00875	3.063E-04	1	3.063E-04	0.265
	A * D	-0.03125	3.906E-03	1	3.906E-03	3.378
	B * C	-0.00375	5.625E-05	1	5.625E-05	0.049
	B * D	0.02125	1.806E-03	1	1.806E-03	1.562
	C * D	-0.00875	3.063E-04	1	3.063E-04	0.265
3-Way Interactions	A * B * C	-0.00125	6.250E-06	1	6.250E-06	
	A * B * D	-0.02125	1.806E-03	1	1.806E-03	
	A * C * D	0.01875	1.406E-03	1	1.406E-03	
	B * C * D	0.02125	1.806E-03	1	1.806E-03	
4-way Interactions	A * B * C * D	0.01375	7.563E-04	1	7.563E-04	
<i>Residual from model not including the 3 and 4 way interactions</i>			5.781E-03	5	1.156E-03	

- A Concentration of 2-ethyl 1- hexanol in the polymer solution (as weight percentage of the solvent)
 B Length of air gap
 C Bore liquid flowrate
 D Polymer solution flowrate

The sum of squares, degrees of freedom and the mean square are shown for each of the main effects and all their interactions. The three-way and four-way interactions were used as an estimate of the error; it was assumed these interactions would be small compared to the main effects and the two-way interactions and could be ignored. The F value shown in the table is the ratio of the mean square to the mean square of the error and is shown for each of the main and two-way interaction effects.

In order to determine which of the main effects or their interactions were significant the F-ratios were compared to the F value in statistical tables of the F distribution for the degrees of freedom for the effect and error estimate.

In this case $F_{1,5} = 6.61$ for a significance level of $\alpha = 0.05$

Therefore the main effects of the length of air gap, polymer solution flowrate and bore liquid flowrate were significant at the $\alpha = 0.05$ level. The effect of the additive and the effect of the interactions between the variables on the outer diameter of the fibre were not significant at this level.

The general model for the expected value of the outer diameter of the hollow fibres as a linear function of the four factors and their interactions is:

$$E(OD) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \beta_6 x_1 x_3 + \beta_7 x_1 x_4 + \beta_8 x_2 x_3 + \beta_9 x_2 x_4 + \beta_{10} x_3 x_4 \\ + \beta_{11} x_1 x_2 x_3 + \beta_{12} x_1 x_2 x_4 + \beta_{13} x_1 x_3 x_4 + \beta_{14} x_2 x_3 x_4 + \beta_{15} x_1 x_2 x_3 x_4$$

where:

$E(OD)$ = expected value of the outer diameter in mm

and the x_i 's are the dimensionless variables:

$$x_1 = A - 1$$

where A = additive concentration in polymer solution
and $0 \text{ wt}\% \leq A \leq 2 \text{ wt}\%$

$$x_2 = (B - 74)/14$$

where B = length of air gap
and $60 \text{ cm} \leq B \leq 88 \text{ cm}$

$$x_3 = (C - 1.5)/0.5$$

where C = bore liquid flowrate
and $1 \text{ ml/min} \leq C \leq 2 \text{ ml/min}$

$$x_4 = (D - 1.125)/0.375$$

where D = polymer solution flowrate
and $0.75 \text{ ml/min} \leq D \leq 1.5 \text{ ml/min}$

The method of least squares was used to determine the parameters in the model and after deleting those terms which were not significant at the $\alpha = 0.05$, the model reduces to:

$$E(\text{OD}) = 0.515625 - 0.044375x_2 + 0.025625x_3 + 0.033125x_4$$

The adequacy of the model was checked by plotting the residuals against the expected value for outer diameter. The graph is shown in Figure 4.1.1 and shows no unusual behavior or changing variance.

Figure 4.1.1 Residual Plot for Hollow Fibre Outer Diameter Model

The graphs in the subsequent sections illustrate the effect of each operating variable on the hollow fibre outer diameter and the model estimated values of the outer diameter are included in these graphs.

4.1.2 EFFECT OF BORE LIQUID FLOWRATE

The factorial design confirmed the significance of the effect of the bore liquid flowrate on the outer diameter of the hollow fibre. Figures 4.1.2 and 4.1.3 illustrate how changing the bore liquid flowrate affected the outer diameter of hollow fibres. Figure 4.1.2 shows the outer diameters of fibres produced using a solution of 23% PPO in trichloroethylene, at a polymer solution flowrate of 1.5 ml/min and an air gap of 88cm, plotted against the bore liquid flowrate. The outer diameters of the fibres increased from 0.55 mm to 0.65 mm as the bore liquid flowrate was increased from 1 to 4 ml/min. The linear model for the outer diameter given in Section 4.1 was used to calculate the hollow fibre outer diameter for the range of bore liquid flowrate within the constraints of the factorial design. The graph shows that the model slightly underestimated the outer diameter for these operating conditions.

Figure 4.1.2 Outer Diameter versus Bore Liquid Flowrate

(Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

Figure 4.1.3 shows the results for fibres produced using a solution of 23% PPO in trichloroethylene containing 2 wt % 2-ethyl 1-hexanol at a polymer solution flowrate of 1.5 ml/min and an air gap of 88cm. The outer diameter of the fibres increased from 0.41 mm to 0.52 mm as the bore liquid flowrate was increased from 0.5 to 2 ml/min. The graph shows the model gives a good estimation of the outer diameter at 2.0 ml/min but slightly overestimated the outer diameter for lower bore liquid flowrates.

Figure 4.1.3 Outer Diameter versus Bore Liquid Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

Table 4.3 shows outer diameter measurements for hollow fibres prepared at the other conditions in the factorial design and also includes data for the hollow fibres prepared in the preliminary experiments.

Table 4.3 Outer Diameter of Hollow Fibres Prepared using 23 wt % PPO

Polymer Solution Flowrate (ml/min)	23%PPO 0%EH 88cm Air Gap		23%PPO 0%EH 60cm Air Gap		23%PPO 2%EH 88cm Air Gap		23%PPO 2%EH 60cm Air Gap	
	BLF (ml/min)	OD (mm)	BLF (ml/min)	OD (mm)	BLF (ml/min)	OD (mm)	BLF (ml/min)	OD (mm)
5.5	4.0	0.69	4.0	0.74				
	3.0	0.67	3.0	0.69				
	2.0	0.65	2.0	0.67			2.0	0.63
	1.0	0.52	1.5	0.64				
	0.5	0.48	1.0	0.49				
3.3					13.5	0.93		
					12.4	0.92		
	11.2	0.88	11.2	0.93	11.2	0.89		
					10.1	0.87		
	9.0	0.84	9.0	0.91	9.0	0.82	2.0	0.59
2.5					10.1	0.79		
	2.0	0.60						
	1.5	0.59						
1.5	13.5	0.87	13.5	0.97	13.5	0.89	13.5	1.00
	12.4	0.86	12.4	1.00	12.4	0.85	12.4	0.95
	11.2	0.85	11.2	0.93	11.2	0.84	11.2	0.91
	10.1	0.85	10.1	0.90	10.1	0.76	10.1	0.91
	9.0	0.83	9.0	0.88	9.0	0.76	9.0	0.89
	4.0	0.65	4.0	0.69				
	3.0	0.61	3.0	0.71				
	2.0	0.57	2.0	0.60	2.0	0.52	2.0	0.59
					1.5	0.44		
	1.0	0.55	1.0	0.59	1.0	0.42	1.0	0.55
					0.8	0.46	0.8	0.52
					0.5	0.41		
							0.3	0.42
0.75							3.0	0.66
	2.0	0.45	2.0	0.58	2.0	0.44	2.0	0.58
					1.5	0.48	1.5	0.54
	1.0	0.39	1.0	0.50	1.0	0.43	1.0	0.49
	0.3	0.36	0.3	0.41				
			0.1	0.28				

% PPO concentration of PPO in the polymer solution used for spinning
 % EH concentration of 2- ethyl 1-hexanol in the polymer solution (as a wt % of the solvent)
 AIRGAP length of the airgap used for spinning (cm)
 BLF bore liquid flowrate used in the spinning process (ml/min)
 OD outer diameter of hollow fibre (mm)
Fibres used in the factorial design are shown in red

An examination of the table shows that the trend of increasing outer diameter with increasing bore liquid flowrate was found for all the hollow fibres produced in this study.

Similar results were obtained in a study by Kim et al. (1995). They prepared polysulfone ultrafiltration hollow fibres using a wet spinning method (0 cm air gap) and found that hollow fibres prepared using lower bore liquid flowrates had smaller outer diameters. However, when using a dry-wet spinning method with an air gap of 65 cm they found the effect of the bore liquid flowrate on the outer diameter was not linear. At low bore flowrates, increasing the bore flowrate produced fibres with larger outer diameters, but at higher bore flowrates ($>12\text{g/min}$) increasing the bore flowrate further caused a reduction in the outer diameter of the resultant fibres. This effect was not observed over the range of variables used in this study, but can be explained by elongation of the fibre as it falls through the air gap as discussed below.

In the hollow fibre spinning process the dimensions of the hollow fibre are mainly determined during the time from when the fibre leaves the spinneret to the time when solidification of the fibre is complete and the whole fibre becomes rigid. The bore liquid and polymer solution come in contact immediately upon emerging from the end of the spinneret, and gelation starts to take place as the non solvent bore liquid enters the fibre wall and solvent in the polymer solution enters the bore liquid. The gelation starts at the interface and a thin solid film is formed between the polymer solution and the bore liquid. Gelation gradually extends towards the centre of the fibre wall. The fibre can be stretched during this gradual gelation. Stretching can occur in a longitudinal direction due to shear between the bore fluid and the polymer solution. Stretching can also occur in a transverse direction due to a differential in pressure between the bore and the outside of the fibre. When the air gap is small, transverse stretching is dominant and increasing the bore liquid flowrate increases the diameter of the resultant fibres. However, at larger air gaps, there is more time for polymer stretching by the shear between bore liquid and polymer solution and an increase in the bore flowrate can cause a reduction in the fibre diameter.

Although the latter effect was not observed in this study, a similar effect may have been seen if hollow fibres were produced at much larger air gaps and bore liquids flowrates than those employed in this experimental design. But, as discussed in chapter 3, it is not always possible to produce fibres at every desired combination of spinning parameters. In particular, large air gaps and very high bore liquid flowrates tend to produce weak fibres which are much more likely to break during the spinning process.

4.1.3. EFFECT OF POLYMER SOLUTION FLOWRATE

The factorial design showed that the polymer solution flowrate had a significant effect on the outer diameter of the hollow fibre. Figures 4.1.4 and 4.1.5 show how changing the polymer solution flowrate affects the outer diameter of hollow fibres. The hollow fibres shown in figure 4.1.4 were prepared from a solution of 23% PPO in trichloroethylene, a bore liquid flowrate of 2 ml/min and an air gap of 88 cm.

Figure 4.1.4 Outer Diameter versus Polymer Solution Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Bore Liquid Flowrate 2.0 ml/min)

The outer diameters of the fibres increased from 0.45 to 0.60 mm as the polymer solution flowrate was increased from 0.75 to 2.5 ml/min. The model gave a good estimate for the outer diameter at the polymer solution flowrates employed for this set of operating conditions.

Figure 4.1.5 shows the outer diameter of hollow fibres prepared from a solution of 23% PPO in trichloroethylene containing 2wt% 2-ethyl-1-hexanol with a bore liquid flowrate of 2 ml/min and an air gap of 60 cm. Under these conditions increasing the polymer solution flowrate from 0.75 to 1.5 ml/min produced only a small increase in outer diameter from 0.58 to 0.59 mm. The model gave a good estimate for the outer diameter but predicted a slightly higher increase in outer diameter as the polymer solution flowrates was increased over this range.

Figure 4.1.5 Outer Diameter versus Polymer Solution Flowrate
 (Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Air Gap 60 cm, Bore Liquid Flowrate 2.0 ml/min)

A comparison of those pairs of fibres shown in Table 4.3 which were prepared under identical conditions except for the polymer solution flowrate shows the same general trend: the outer diameter of the hollow fibres increased with increasing polymer flowrate.

Other researchers have obtained similar results. Nardella et al. (1995) prepared hollow fibres from modified PPO (functionalised with both trimethylsilylation and hydroxyethyl groups) and found that the outer diameter of the hollow fibres increased with increasing polymer solution. McKelvey et al. (1997) observed a similar result for polysulfone hollow fibres produced using a constant take-up velocity.

In the spinneret the polymer solution near the spinneret wall is sheared and polymer molecules tend to become highly oriented. On emerging from the spinneret, the highly oriented molecules tend to curl up to a random kinked state, this results in a shrinking in the extrusion direction and a swell in the radial direction, the latter causes an increase in the outer diameter of the fibre. The post-extrusion spinneret swell is more pronounced for higher polymer solution flowrates because the shearing is higher.

One study has shown a converse effect of polymer solution flowrate on the outer diameter of hollow fibres prepared under certain conditions. Kim et al. (1995) found that when spinning polysulfone ultrafiltration hollow fibres using the dry-wet spinning method with an air gap of 65cm, the outer diameter of the fibres initially increased as the polymer solution flowrate was increased from 1.6 to 2.0 g/min, but the outer diameter started to decrease as the polymer solution flowrate was increased further. They did not observe this latter effect when spinning using smaller air gaps. They concluded that at air gaps above 60cm, the weight of the hollow fibre hanging in the air gap caused increased elongation of the fibre, resulting in a reduction in the diameter.

Although the latter effect was not observed in this study, a similar effect may have been seen if hollow fibres were produced at much larger air gaps and polymer solution flowrates than those employed in this experimental design. But as discussed in Chapter 3, it is not always possible to produce fibres at every desired combination of spinning

parameters. In particular, large air gaps tend to cause breakage of the fibres during spinning. Also, too high a polymer solution flowrate can cause problems with the fibres sticking together, because there is insufficient time for gelation of the fibre before it makes contact with the coil in the gelation bath, and the fibre tends to stick together.

4.1.4. EFFECT OF AIR GAP

Figures 4.1.6 and 4.1.7 show the effect of changing the air gap on the outer diameter of hollow fibres. The fibres shown in Figure 4.1.6 were prepared from a solution of 23% PPO in trichloroethylene with 2% 2-ethyl-1-hexanol at a flowrate of 1.5 ml/min and a bore liquid flowrate of 2.0 ml/min. These fibres show a reduction in the outer diameter from 0.75 to 0.52 mm as the air gap is increased from 29 cm to 88 cm.

Figure 4.1.6 Outer Diameter versus Length of Air Gap
 (Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Polymer Solution Flowrate 1.5 ml/min, Bore Liquid Flowrate 2.0 ml/min)

The graph shows the model gives a good estimation for the outer diameter at the 88 cm air gap under these conditions but slightly overestimated the outer diameter at 60 cm air gap.

Figure 4.1.7 shows the results for fibres prepared using a solution of 23% PPO in trichloroethylene with 2% 2-ethyl-1-hexanol at a flowrate of 1.5 ml/min and a bore liquid flowrate of 1.0 ml/min. As the air gap was increased from 60 to 88 cm the outer diameter of the fibres decreased from 0.55 to 0.42 mm. For these operating conditions the model overestimates the outer diameter at the 88 cm air gap.

Figure 4.1.7 Outer Diameter versus Length of Air Gap

(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Polymer Solution Flowrate 1.5 ml/min, Bore Liquid Flowrate 1.0 ml/min)

A comparison of the columns in Table 4.3 for pairs of fibres prepared under identical conditions except for the length of the air gap show that for almost every case the trend was the outer diameter of the hollow fibres decreased with increasing air gap.

Similar results were obtained by Kim et al. (1995) for polysulfone ultrafiltration hollow fibres produced using the dry-wet spinning method. They carried out a one-variable-at-a-time study and found the outer diameter of the fibres decreased with increasing air gap.

During the passage of the hollow fibre through the air gap, stretching of the fibre takes place in the longitudinal direction due to the action of gravity on the fibre. This stretching causes a reduction in the outer diameter of the hollow fibre. The longer the air gap the more pronounced the stretching because of the additional weight of the longer section of fibre that is in the air gap, and the smaller the diameter of the hollow fibre.

4.1.5. EFFECT OF ADDITIVE 2-ETHYL- 1-HEXANOL

The factorial design showed that the presence of 2 wt% 2-ethyl 1-hexanol in the solvent of the polymer solution did not have a significant effect on the outer diameter of the PPO hollow fibres over the operating region for the design. Figure 4.1.8 shows the outer diameter of the hollow fibres used in the factorial design. The results have been divided into eight cases for comparison. For each case the results shown in grey are for pairs of hollow fibres. Each pair was produced under identical spinning conditions except for the additive 2-ethyl 1-hexanol in the polymer solution which was present for one of the pair and absent for the other. The model estimates for the outer diameter in each case are shown in red. Since the results from the factorial design did not show any significant main effect or two-way interaction effects involving the presence of the additive, the model predicts the same outer diameter for each of the pair of hollow fibres. There was however some difference in outer diameter for the pairs of hollow fibres in each case. The outer diameter was sometimes greater for the fibre produced in the presence of the additive and sometimes for the fibre produced in the absence of the additive. There did not appear to be any consistent pattern to the findings. It is possible that one of the three-

way interaction effects involving the presence of the additive was not insignificant. The significance of all the interaction effects could have been tested if the complete factorial design had been replicated. However this would have required an additional sixteen experimental runs.

Conditions:

- 1: Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min, Length of Air Gap 88cm
- 2: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 1.5 ml/min, Length of Air Gap 88cm
- 3: Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 0.75 ml/min, Length of Air Gap 88cm
- 4: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min, Length of Air Gap 88cm
- 5: Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min, Length of Air Gap 60cm
- 6: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 1.5 ml/min, Length of Air Gap 60cm
- 7: Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 0.75 ml/min, Length of Air Gap 60cm
- 8: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min, Length of Air Gap 60cm

Figure 4.1.8 Effect of Additive 2-Ethyl 1-Hexanol on Outer Diameter
(Hollow fibres prepared using 23% PPO)

The presence of the 2 wt% 2-ethyl 1-hexanol in the polymer solution does not cause any appreciable difference to the density or viscosity of the polymer solution and is therefore unlikely to have a significant effect on the outer diameter of the hollow fibres. It is likely the presence of 2-ethyl 1-hexanol would hasten the gelation of the fibre walls because being a non solvent for PPO it would bring the solution closer to its gelation point, but this would be unlikely to have an effect on the dimension of the walls.

4.2 EFFECT OF SPINNING CONDITIONS ON WALL THICKNESS OF PPO HOLLOW FIBRES

4.2.1 FACTORIAL DESIGN

The statistical analysis of the factorial design was carried out using the spreadsheet program Excel in the same manner as the that in section 4.1.1. The input data for the sixteen runs is shown in Table 4.4. In the analysis dimensionless variables were used: the low level of each factor was designated as -1 and the high level was designated by 1.

Table 4.4 Input Data for the Statistical Analysis for the Factorial Design for Wall Thickness of PPO Hollow Fibres Prepared using 23 wt% PPO Solution

% Additive in the Polymer Solution*	Length of Air Gap (cm)	Bore Liquid Flowrate (ml/min)	Polymer Solution Flowrate (ml/min)	Wall Thickness of Hollow Fibre (mm)
0	60	1	1.5	0.040
0	60	1	0.75	0.025
0	60	2	1.5	0.040
0	60	2	0.75	0.024
0	88	1	1.5	0.041
0	88	1	0.75	0.028
0	88	2	1.5	0.038
0	88	2	0.75	0.028
2	60	1	1.5	0.038
2	60	1	0.75	0.025
2	60	2	1.5	0.033
2	60	2	0.75	0.023
2	88	1	1.5	0.045
2	88	1	0.75	0.030
2	88	2	1.5	0.030
2	88	2	0.75	0.018

* 2-Ethyl 1- Hexanol as a wt% of the solvent

The results from the analysis are shown in Table 4.5.

Table 4.5 Output Data for the Statistical Analysis for the Factorial Design for Wall Thickness of PPO Hollow Fibres Prepared using 23 wt% PPO Solution

	Factors	Effect	Sum of Squares	df	Mean Square	F
Main Effects	A	-0.00275	3.025E-05	1	3.025E-05	4.69
	B	0.00125	6.250E-06	1	6.250E-06	0.97
	C	-0.00475	9.025E-05	1	9.025E-05	13.99
	D	0.01300	6.760E-04	1	6.760E-04	104.81
2-Way Interactions	A * B	-0.00025	2.500E-07	1	2.500E-07	0.04
	A * C	-0.00375	5.625E-05	1	5.625E-05	8.72
	A * D	-0.00050	1.000E-06	1	1.000E-06	0.16
	B * C	-0.00275	3.025E-05	1	3.025E-05	4.69
	B * D	-0.00050	1.000E-06	1	1.000E-06	0.16
	C * D	-0.00100	4.000E-06	1	4.000E-06	0.62
3-Way Interactions	A * B * C	-0.00225	2.025E-05	1	2.025E-05	
	A * B * D	0.00150	9.000E-06	1	9.000E-06	
	A * C * D	-0.00050	1.000E-06	1	1.000E-06	
	B * C * D	-0.00050	1.000E-06	1	1.000E-06	
4-Way Interactions	A * B * C * D	0.00050	1.000E-06	1	1.000E-06	
<i>Residual from model not including the 3 and 4-way interactions</i>			3.225E-05	5	6.450E-06	

- A** Concentration of 2-ethyl 1- hexanol in the polymer solution (as weight percentage of the solvent)
- B** Length of air gap
- C** Bore liquid flowrate
- D** Polymer solution flowrate

The sum of squares, degrees of freedom and the mean square are shown for each of the main effects and all their interactions. The three-way and four-way interactions were

used as an estimate of the error; it was assumed these interactions would be small compared to the main effects and the two-way interactions and could be ignored. The F value shown in the table is the ratio of the mean square to the mean square of the error and is shown for each of the main and two-way interaction effects.

In order to determine which of the main effects or their interactions were significant the F-ratios were compared to the F value in statistical tables of the F distribution for the particular degrees of freedom of the effect and error estimate.

In this case $F_{1,5} = 6.61$ for a significance level of $\alpha = 0.05$

Therefore the main effects of the bore liquid flowrate and polymer solution flowrate on the wall thickness are significant. The interaction between the additive and bore liquid flowrate on the wall thickness is also significant at the $\alpha = 0.05$ level. The main effect of the presence of 2-ethyl 1-hexanol, the length of air gap and the interaction between the other factors are not significant at this level.

The general model for the expected value of the wall thickness of the hollow fibres as a function of the four factors and their interactions is:

$$E(WT) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \beta_6 x_1 x_3 + \beta_7 x_1 x_4 + \beta_8 x_2 x_3 + \beta_9 x_2 x_4 + \beta_{10} x_3 x_4 \\ + \beta_{11} x_1 x_2 x_3 + \beta_{12} x_1 x_2 x_4 + \beta_{13} x_1 x_3 x_4 + \beta_{14} x_2 x_3 x_4 + \beta_{15} x_1 x_2 x_3 x_4$$

where:

$E(WT)$ = expected value of the wall thickness in mm and the x_i 's are the dimensionless variables as defined in section 4.1.1

The method of least squares was used to determine the parameters in the model and after deleting those terms which were not significant at the $\alpha = 0.05$, the model reduced to:

$$E(WT) = 0.031625 - 0.002375x_3 + 0.0065x_4 - 0.001875x_1 x_3$$

The adequacy of the model was checked by plotting the residuals against the expected value for wall thickness. The graph is shown in Figure 4.2.1 and shows no unusual behavior, outliers or changing variance.

Figure 4.2.1 Residual Plot for Hollow Fibre Wall Thickness

The graphs in the subsequent sections illustrate the effect of each operating variable on the hollow fibre wall thickness and the model estimated values of the wall thickness are included in these graphs.

4.2.2 EFFECT OF BORE LIQUID FLOWRATE

The analysis of the factorial design found the effect of the bore liquid flowrate on the wall thickness of the hollow fibre to be significant. Figures 4.2.2 and 4.2.3 illustrate how changing the bore liquid flowrate affected the wall thickness of hollow fibres.

Figure 4.2.2 shows the wall thickness of fibres produced from a solution of 23% PPO in trichloroethylene at a polymer solution flowrate of 1.5 ml/min and using an air gap of 88cm, plotted against the bore liquid flowrate. The wall thickness of the fibres decreased from 0.041mm to 0.025 as the bore liquid flowrate was increased from 1 to 4 ml/min. The linear model for the wall thickness given in Section 4.2 was used to calculate the hollow fibre wall thickness for the range of bore liquid flowrate within the constraints of the factorial design. The graph shows that the model gave a good estimation of the wall thickness for these operating conditions

Figure 4.2.2 Wall Thickness versus Bore Liquid Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

Similar results, shown in Figure 4.2.3, were obtained for hollow fibres prepared from a solution of 23% PPO in trichloroethylene with 2 wt% 2-ethyl 1-hexanol at a flowrate of 1.5 ml/min and an air gap of 88 cm. In this case the wall thickness of the fibres decreased from 0.045mm to 0.03mm as the bore liquid flowrate was increased from 1

ml/min to 2 ml/min. Again the model gave a good estimation for the hollow fibre wall thickness at these operating conditions.

Figure 4.2.3 Wall Thickness versus Bore Liquid Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

Table 4.6 shows wall thickness measurements for hollow fibres prepared at the other conditions in the factorial design and also includes data for the hollow fibres prepared in the preliminary experiments. An examination of the table shows that the trend of decreasing wall thickness with increasing bore liquid flowrate was found for almost all the hollow fibres produced in this study.

Table 4.6 Wall Thickness of Hollow Fibres Prepared using 23 wt % PPO

Polymer Solution Flowrate (ml/min)	23%PPO 0%EH 88cm Air Gap		23%PPO 0%EH 60cm Air Gap		23%PPO 2%EH 88cm Air Gap		23%PPO 2%EH 60cm Air Gap	
	BLF (ml/min)	WT (mm)	BLF (ml/min)	WT (mm)	BLF (ml/min)	WT (mm)	BLF (ml/min)	WT (mm)
5.5	4.0 3.0 2.0 1.0 0.5	0.045 0.050 0.050 0.080 0.105	4.0 3.0 2.0 1.5 1.0	0.040 0.055 0.080 0.080 0.088			2.0	0.070
3.3	11.2 9.0	0.025 0.030	11.2 9.0	0.030 0.028	13.5 11.2 10.1 9.0	0.020 0.023 0.028 0.033	2.0	0.055
2.5	2.0 1.5	0.040 0.045			10.1	0.018		
1.5	13.5 12.4 11.2 10.1 9.0 4.0 3.0 2.0 1.0	0.010 0.018 0.018 0.018 0.023 0.025 0.028 0.038 0.413	13.5 12.4 11.2 10.1 9.0 4.0 3.0 2.0 1.0	0.015 0.018 0.018 0.023 0.025 0.028 0.028 0.040 0.040	13.5 12.4 11.2 10.1 9.0 2.0 1.5 1.0 0.8 0.5	0.013 0.013 0.018 0.018 0.025 0.030 0.045 0.045 0.040 0.053	13.5 12.4 11.2 10.1 9.0 2.0 1.0 0.8 0.3	0.018 0.013 0.020 0.023 0.025 0.033 0.038 0.045 0.075
0.75	2.0 1.0 0.3	0.028 0.028 0.033	2.0 1.0 0.3 0.1	0.024 0.025 0.050 0.045	2.0 1.5 1.0	0.018 0.020 0.030	3.0 2.0 1.5 1.0	0.015 0.023 0.025 0.025

% PPO concentration of PPO in the polymer solution used for spinning
 % EH concentration of 2- ethyl 1-hexanol in the polymer solution (as a wt % of the solvent)
 AIRGAP length of the airgap used for spinning (cm)
 BLF bore liquid flowrate used in the spinning process (ml/min)
 WT wall thickness of hollow fibre (mm)
Fibres used in the factorial design are shown in red

Kim et al. (1995) carried out a study on the spinning of ultrafiltration polysulfone hollow fibres and they also found that the wall thickness of the fibres decreased with increasing bore liquid flowrate. Kneifel et al. (1992) carried out a study on the spinning of polyetherimide hollow fibres for gas separation. While they did not study the effect of changing *only* the bore liquid flowrate, they found that the wall thickness of the fibres decreased as the flow ratio of the bore liquid and polymer solution increased.

In section 4.1.3 it was shown how increasing the bore liquid flowrate in the spinning process produced hollow fibres with larger diameters. It was explained the increased bore liquid flowrate had caused an increase in the diameter of the fibres by stretching of the fibre in a transverse direction, this necessarily causes thinning of the hollow fibre walls. Therefore increasing the bore liquid flowrate produces hollow fibres of decreased wall thickness.

4.2.3. EFFECT OF POLYMER FLOWRATE

The analysis of the factorial design showed that the polymer solution flowrate had a significant effect on the wall thickness of the hollow fibres. Figures 4.2.4 and 4.2.5 illustrate how the polymer solution flowrate affected the wall thickness of hollow fibres. The hollow fibres shown in figure 4.2.4 were prepared from a solution of 23% PPO in trichloroethylene, a bore liquid flowrate of 2 ml/min, and an air gap of 88cm. The wall thickness of the fibres increased from 0.028 to 0.04 mm as the polymer solution flowrate was increased from 0.75 to 2.5 ml/min. The model gave a good estimation for the hollow fibre wall thickness at these operating conditions.

Figure 4.2.4 Wall Thickness versus Polymer Solution Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Bore Liquid Flowrate 2.0 ml/min)

A similar result can be seen in Figure 4.2.5. The graph shows how the wall thickness of hollow fibres prepared from a solution of 23% PPO in trichloroethylene with 2% 2-ethyl-1-hexanol, with a bore liquid flowrate of 2ml/min, and an air gap of 60 cm varies as the polymer solution flowrate is increased from 0.75 to 1.5 ml/min. The fibres are shown to increase in wall thickness from 0.0225mm to 0.0325 mm and the model gives a good estimate for this increase.

A comparison of other pairs of fibres shown in Table 4.3 which were prepared under identical conditions except for the polymer solution flowrate shows the same general trend: the wall thickness of the hollow fibres increases with increasing polymer flowrate.

Figure 4.2.5 Wall Thickness versus Polymer Solution Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Air Gap 60 cm, Bore Liquid Flowrate 2.0 ml/min)

Pesek et al. (1994) studied the spinning of polysulfone gas separation hollow fibres and found a similar result; increasing the polymer solution flowrate produced hollow fibres with increased wall thickness. Kim et al. (1995) also found that when spinning polysulfone ultrafiltration hollow fibres using the wet spinning method (i.e. air gap = 0cm), the wall thickness of fibres increased as the polymer solution flowrate used in the spinning process was increased.

The observed increase of the wall thickness of the hollow fibres with increasing polymer solution flowrate is due to swelling of the polymer solution as it exits the spinneret. In the spinneret the polymer solution near the spinneret wall is sheared and polymer molecules tend to become highly oriented. On emerging from the spinneret, the highly oriented molecules tend to curl up to a random kinked state, this results in a shrinking in

the extrusion direction and a swell in the radial direction, the latter causes an increased thickness of the hollow fibre walls. This swelling of the polymer solution at the spinneret exit is more pronounced for higher polymer solution flowrates because the shearing is higher, and so the walls tend to increase in thickness with increasing polymer solution flowrates.

All the results in this study showed that increasing the polymer solution flowrate produced fibres with increased wall thickness. However, the opposite effect has been observed by some researchers under certain spinning conditions. Kim et al. (1995) found that when spinning polysulfone ultrafiltration hollow fibres using the dry-wet spinning method and an air gap of 65cm, initially the wall thickness of fibres increased as the polymer solution flowrate was increased from 1.6 to 2.0 g/min, but the wall thickness started to decrease as the polymer solution flowrate was increased further. They concluded the latter result was due to the effect of gravity acting on the longer length of fibre suspended in the air gap, causing increased elongation and hence thinning of the walls. Thinning of the fibre walls with increasing polymer solution flowrate was not observed in this research project. Clearly for the range of variables studied in this project, the thickening of walls was more dominant than any thinning due to elongation of the fibre in the air gap.

4.2.4. EFFECT OF AIR GAP

The results from the analysis of the factorial design showed the effect of the air gap on the wall thickness of the hollow fibres was not significant. Figures 4.2.6 and 4.2.7 show graphs of the wall thickness of hollow fibres plotted against the length of the air gap used in their production. The fibres shown in figure 4.2.5 were spun from a solution of 23% PPO in trichloroethylene with 2wt% 2-ethyl-1-hexanol at a flowrate of 1.5 ml/min and a bore liquid flowrate of 2.0 ml/min. While the data showed a reduction in wall thickness from 0.04 to 0.03mm as the air gap was increased from 29 cm to 88 cm, the reduction was within the 95% confidence interval for the means of the wall thickness in each case

and the model gave a good estimation to the data under the operating conditions of the factorial design.

Figure 4.2.6 Wall Thickness versus Length of Air Gap

(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Polymer Solution Flowrate 1.5 ml/min, Bore Liquid Flowrate 2.0 ml/min)

Figure 4.2.7 shows the results for fibres prepared from a solution of 23% PPO in trichloroethylene with 2 wt% 2-ethyl 1-hexanol at a flowrate of 1.5 ml/min and using a bore liquid flowrate of 1 ml/min. Increasing the air gap from 60 to 88 cm caused a slight increase in wall thickness but this was well within the 95 % confidence interval for the means of the wall thickness for each case and the values were well estimated by the model. At operating conditions outside the range of the model however the graph shows the wall thickness of the hollow fibres decreased from 0.065 to 0.0375 mm as the air gap was increased from 29 to 60 cm. It is possible that effect of the air gap was not a linear one. A factorial design carried out at three levels for the factors would confirm if this was the case.

Figure 4.2.7 Wall Thickness versus Length of Air Gap

(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Polymer Solution Flowrate 1.5 ml/min, Bore Liquid Flowrate 1.0 ml/min)

An examination of those pairs of fibres in the columns in Table 4.3 which were prepared under identical conditions except for the length of the air gap showed the latter has a complex effect on the wall thickness. While the factorial design results showed that there were no main effects or two-way effects involving the length of the air gap, it is a possibility that the effects were not linear or that three-way interaction effects may have been significant.

Kim et al. (1995) found that the wall thickness of polysulfone ultrafiltration hollow fibres decreased as the air gap used in the spinning process was increased. But this study was a one variable at a time study carried out at one fixed set of spinning conditions while the length of the air gap was varied from 10 to 90 cm.

4.2.5. EFFECT OF ADDITIVE 2-ETHYL- 1-HEXANOL

The results from the analysis of the factorial design showed that the main effect of presence of 2 wt% 2-ethyl 1-hexanol in the polymer solution on the wall thickness of the hollow fibres was not significant. However the two-way effect of the additive and the bore liquid flowrate was found to be significant.

The results in Figure 4.2.8 show the wall thickness of the hollow fibres prepared for the factorial design.

Conditions:

- 1: Bore Liquid Flowrate 2 ml/min. Polymer Solution Flowrate 1.5 ml/min. Length of Air Gap 88cm
- 2: Bore Liquid Flowrate 1 ml/min. Polymer Solution Flowrate 1.5 ml/min. Length of Air Gap 88cm
- 3: Bore Liquid Flowrate 2 ml/min. Polymer Solution Flowrate 0.75 ml/min. Length of Air Gap 88cm
- 4: Bore Liquid Flowrate 1 ml/min. Polymer Solution Flowrate 0.75 ml/min. Length of Air Gap 88cm
- 5: Bore Liquid Flowrate 2 ml/min. Polymer Solution Flowrate 1.5 ml/min. Length of Air Gap 60cm
- 6: Bore Liquid Flowrate 1 ml/min. Polymer Solution Flowrate 1.5 ml/min. Length of Air Gap 60cm
- 7: Bore Liquid Flowrate 2 ml/min. Polymer Solution Flowrate 0.75 ml/min. Length of Air Gap 60cm
- 8: Bore Liquid Flowrate 1 ml/min. Polymer Solution Flowrate 0.75 ml/min. Length of Air Gap 60cm

**Figure 4.2.8 Effect of Additive 2-Ethyl 1-Hexanol on Wall Thickness
(Hollow fibres prepared using 23% PPO)**

The fibres in each pair were produced under identical spinning conditions, other than the presence of additive 2-ethyl 1-hexanol in the polymer solution which was present in one of the pair and absent in the other. The model estimates for each fibre are also shown on the graph. Since the two-way interaction effect of the bore liquid flowrate and the presence of the additive was found to be significant, the wall thickness would not be expected to be identical for each pair of fibres and the model estimates reflect these differences although in most cases there is some discrepancy between the model estimated and the actual measured values.

Chapter 5

RESULTS: HOLLOW FIBRE GAS SEPARATION PERFORMANCE

The PPO hollow fibres were tested for gas permeation performance using pure carbon dioxide and pure methane gases at a pressure of 100 psig (6.89×10^5 Pa). The hollow fibre modules were used with the feed gas on the bore side of the fibres and permeate was collected from the shell side. Each module contained one to three fibres about 35cm in length. Experiments were usually carried out with six modules: three modules containing fibres prepared under one set of conditions and the other three containing fibres prepared under a different set of conditions.

For each hollow fibre the carbon dioxide permeate flux and the pure methane flux were measured. These have been reported as *pressure normalized* permeate fluxes with units of $\text{mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ in this study. The ideal separation factor was calculated as the ratio of pure carbon dioxide permeate flux to the pure methane flux. Sample calculations are given in Appendix C.

The gas separation performance was found to vary with experimental conditions and the composition of the PPO polymer solution used to produce the fibres. Results for methane permeate flux ranged from 1.5×10^{-11} - 8.4×10^{-11} $\text{mol/m}^2 \cdot \text{s} \cdot \text{Pa}$, while the carbon dioxide permeate flux ranged from 3.5×10^{-10} - 1.7×10^{-9} $\text{mol/m}^2 \cdot \text{s} \cdot \text{Pa}$. Ideal separation factors are in the range of 20-34. The ideal separation factors achieved are higher than those reported by other researchers shown in Section 1.7.

Many experiments were carried out in which the methane permeate flux was measured again after testing with carbon dioxide. The results showed that after being in the presence of carbon dioxide, the fibres became more permeable to methane and an increase in methane permeate flux by 0-10% was observed.

The results given in this chapter show how four variables in the spinning conditions affect the gas separation performance of the PPO hollow fibres. A fractional factorial design was used to determine which of the variables has a significant effect on the hollow fibre gas separation performance. The results are given in section 5.1.1. Those variables that were found to be significant were included in linear models that were developed for the hollow fibre carbon dioxide and methane permeate fluxes and the ideal separation factor.

In the subsequent sections the effect of each of the variables is illustrated in graphs showing the hollow fibres' gas separation performance plotted against the variable. The error bars in the graphs indicate a 95% confidence interval for the mean value of the gas separation variable. The confidence intervals were calculated using the mean, standard deviation, the number of sample measurements taken and a student t factor (Taylor, 1990) as shown in the sample calculation given in Appendix C. The estimate for the permeate fluxes and ideal separation factor as calculated using the developed models are also included in the graphs for the range of operating conditions within the constraints of the factorial design.

Some gas separation performance data had also been obtained for some of the hollow fibres prepared in the preliminary experiments and this data has been included in tables in this chapter. The hollow fibre gas separation data is summarized in Tables F1-3 shown in Appendix F. Some high pressure testing was also carried out on some fibres and these experiments are discussed in Section 5.2.

5.1. EFFECT OF SPINNING CONDITIONS ON HOLLOW FIBRE GAS PERMEATION PERFORMANCE

5.1.1. FACTORIAL DESIGN

A full factorial design investigating four variables at two levels requires 16 runs. Details for the 16 runs are given in Table G1 of Appendix G. For two of the factor combinations gas permeance data could not be obtained because suitable lengths of leak-free fibres were not available. The problem was due to some parts of the fibre length sticking together as the fibre was gelled in the gelation bath during spinning. With data for these two runs missing the *complete* factorial could not be analysed. In some cases where data is missing it is possible to estimate values for the missing data either from a known response curve or interpolating from values at higher and lower factor levels. The latter would not be possible for a two level design, like this one, and since the response curve is not known a better alternative is to use a fractional factorial or a fractional replicate (Dey, 1985).

In this study the half fraction with the defining relation: $I = ABCD$ was chosen; details of this fractional factorial are given in Appendix B. The factorial is designed so that each of the main effects are confounded with the three level interactions effects and each of the two level interaction effects is confounded with another two level interaction effects.

The statistical analysis of the fractional factorial design was carried out using the spreadsheet program Excel in the same manner as that shown in Appendix E. Three analyses were carried out, one for each of the response variables: carbon dioxide permeate flux, methane permeate flux and the ideal separation factor. The input data for the eight runs of the fractional factorial for each of the three response variables are shown in Table 5.1.

Table 5.1 Input Data for the Statistical Analysis for the Fractional Factorial Design for the Gas Permeation Performance of PPO Hollow Fibres prepared using 23 wt% PPO Solution

% Additive in the Polymer Solution*	Length of Air Gap (cm)	Bore Liquid Flowrate (ml/min)	Polymer Solution Flowrate (ml/min)	Average CO₂ Permeate Flux (x10⁻¹⁰ mol /m² s Pa)	Average CH₄ Permeate Flux (x10⁻¹¹ mol /m² s Pa)	Average Ideal Separation Factor
0	60	1	0.75	7.07	2.86	24.7
0	60	2	1.5	6.19	2.32	26.9
0	88	1	1.5	3.52	1.52	23.2
0	88	2	0.75	9.74	3.49	27.9
2	60	1	1.5	5.17	2.12	24.4
2	60	2	0.75	12.5	4.80	26.7
2	88	1	0.75	6.52	2.82	23.3
2	88	2	1.5	8.83	3.28	26.8

* 2-Ethyl 1- Hexanol as a wt% of the solvent

Dimensionless variables were used in the analysis: the low level of each factor was designated as -1 and the high level was designated by 1. The results from the analysis for each of the three response variables are shown in Table 5.2.

The table shows the sum of squares, degrees of freedom and mean square for each of the main effects and the two-way interactions. Since in the fractional factorial design the three-way interactions were confounded with the main effects, they could not be used as an estimate of the error. Therefore in this case the three smallest effects were used as an estimate of the error. The error estimate was used to calculate the F ratio and this is shown in the table for the remaining effects.

Table 5.2 Output Data for the Statistical Analysis for the Factorial Design for the Gas Separation Performance of PPO Hollow Fibres prepared using 23 wt% PPO Solution

CH₄ Permeate Flux		Effect	Sum of Squares of Effects	df	Mean Square of Effects	F
Main Effects	A confounded with B*C*D	0.7075	1.0011	1	1.0011	16.16
	B confounded with A*C*D	-0.2475	0.1225	1	0.1225	
	C confounded with A*B*D	1.1425	2.6106	1	2.6106	42.14
	D confounded with A*B*C	-1.1825	2.7966	1	2.7966	45.15
2-Way Interactions	A*B confounded with C*D	-0.1625	0.0528	1	0.0528	
	A*C confounded with B*D	0.4275	0.3655	1	0.3655	5.90
	A*D confounded with B*C	0.0725	0.0105	1	0.0105	
Residual from model not including the 3 smallest effects			0.1858	3	0.0619	
CO₂ Permeate Flux		Effect	Sum of Squares of Effects	df	Mean Square of Effects	F
Main Effects	A confounded with B*C*D	1.6250	5.2813	1	5.2813	8.40
	B confounded with A*C*D	-0.5800	0.6728	1	0.6728	
	C confounded with A*B*D	3.7450	28.0501	1	28.0501	44.61
	D confounded with A*B*C	-3.0300	18.3618	1	18.3618	29.20
2-Way Interactions	A*B confounded with C*D	-0.5800	0.6728	1	0.6728	
	A*C confounded with B*D	1.0750	2.3113	1	2.3113	3.68
	A*D confounded with B*C	0.5200	0.5408	1	0.5408	
Residual from model not including the 3 smallest effects			1.8864	3	0.6288	
Ideal Separation Factor		Effect	Sum of Squares of Effects	df	Mean Square of Effects	F
Main Effects	A confounded with B*C*D	-0.5250	0.5513	1	0.5513	10.10
	B confounded with A*C*D	-0.2250	0.1013	1	0.1013	
	C confounded with A*B*D	3.0250	18.3013	1	18.3013	335.1
	D confounded with A*B*C	-0.1750	0.0613	1	0.0613	
2-Way Interactions	A*B confounded with C*D	0.0250	0.0013	1	0.0013	
	A*C confounded with B*D	-0.4250	0.3612	1	0.3612	6.62
	A*D confounded with B*C	1.0750	2.3113	1	2.3113	42.33
Residual from model not including the 3 smallest effects			0.1638	3	0.0546	

- A** Concentration of 2-ethyl 1- hexanol in the polymer solution (as weight percentage of the solvent)
B Length of air gap
C Bore liquid flowrate
D Polymer solution flowrate

In order to determine which of the effects were significant the F-ratios were compared to the F value in statistical tables of the F distribution for the degrees of freedom for the effect and error estimate.

In this case $F_{1,3} = 10.13$ for a significance level of $\alpha = 0.05$

Therefore for the methane permeate flux the main effects of the polymer solution flowrate, bore liquid flowrate and the presence of additive 2- ethyl 1- hexanol in the polymer solution were significant at the $\alpha = 0.05$ level. While the main effect of the length of air gap and none of the two-way interactions were found to be significant at this level.

Figure 5.1.1 shows a half normal plot of the effects for the methane permeate flux. All the effects appear to fall on a straight line through the origin except for the three effects found to be significant.

Figure 5.1.1 Half Normal Plot of the Effects for Methane Permeate Flux

For the carbon dioxide permeate flux the main effects of the polymer solution flowrate and bore liquid flowrate were significant at the $\alpha = 0.05$ level. While not significant at the $\alpha = 0.05$ level, the main effect of the presence of additive 2- ethyl 1- hexanol in the polymer solution was found to be significant at the slightly lower level of $\alpha = 0.06$ level. The main effect of the length of air gap on the carbon dioxide permeate flux and none of the two-way interactions were found to be significant at this level. Figure 5.1.2 shows a half normal plot of the effects for the carbon dioxide permeate flux. The main effects of the polymer solution flowrate and bore liquid flowrate are clearly removed from those effects on the straight line though the origin. However the effect of the presence of additive 2- ethyl 1- hexanol in the polymer solution is close to the line. A full factorial or a replicated factorial would have provided a better estimate of error with which to test the significance of this effect.

Figure 5.1.2 Half Normal Plot of the Effects for Carbon Dioxide Permeate Flux

For the ideal separation factor the main effects of the bore liquid flowrate, presence of additive and the two-way interaction between the presence of additive and the polymer solution flowrate were found to be significant at the $\alpha = 0.05$ level. None of the other effects were found to be significant at this level. Figure 5.1.3 shows a half normal plot of the effects for the ideal separation factor. The main effects of the bore liquid flowrate are clearly removed from those effects on the straight line though the origin. However the interaction effect of the presence of additive 2- ethyl 1- hexanol with the polymer solution flowrate and the main effect of the presence of the additive are close to the line. Again a full factorial or a replicated factorial would have provided a better estimate of error with which to test the significance of this effect.

Figure 5.1.3 Half Normal Plot of the Effects for the Ideal Separation factor

In Chapter 4 linear models for the hollow fibre dimensions were developed which included those spinning variables that were found to have a significant effect on the fibre dimensions.

In the same manner the following models have been developed for the three response variables for the hollow fibre gas separation performance:

$$E(\text{CH}_4) = 2.90125 + 0.35375x_1 + 0.57125x_3 - 0.59125x_4$$

$$E(\text{CO}_2) = 7.4425 + 0.8125x_1 + 1.8725x_3 - 1.515x_4$$

$$E(\text{SEP}) = 25.4125 - 0.2625x_1 + 1.5125x_3 + 0.5375x_1x_4$$

where:

$E(\text{CH}_4)$ = expected value of the methane permeate flux in units of $10^{-11} \text{ mol/m}^2 \text{ s Pa}$

$E(\text{CO}_2)$ = expected value of the carbon dioxide permeate flux in units of $10^{-10} \text{ mol/m}^2 \text{ s Pa}$

$E(\text{SEP})$ = expected value of the ideal separation factor

and the x_i 's are the dimensionless variables:

$x_1 = A - 1$ where A = additive concentration in polymer solution
and $0 \text{ wt\%} \leq A \leq 2 \text{ wt\%}$

$x_2 = (B - 74)/14$ where B = length of air gap
and $60 \text{ cm} \leq B \leq 88 \text{ cm}$

$x_3 = (C - 1.5)/0.5$ where C = bore liquid flowrate
and $1 \text{ ml/min} \leq C \leq 2 \text{ ml/min}$

$x_4 = (D - 1.125)/0.375$ where D = polymer solution flowrate
and $0.75 \text{ ml/min} \leq D \leq 1.5 \text{ ml/min}$

Those effects that appeared to be of borderline significance have been included in these models. It is also important to note that because a fractional factorial design was used to develop the model some confounding between the effects will exist. This is unlikely to affect those terms for the main effects; these were confounded with the three-way interactions and the latter are likely quite small. However the model for the separation factor includes a term for the presence of additive and polymer solution flowrate interaction and this was confounded with the length of air gap and bore liquid flowrate interaction term.

The adequacies of the models were checked by plotting the residuals against the expected values for each case. The graphs are shown in Figure 5.1.4, 5.1.5 and 5.1.6 and they show no unusual behavior or changing variance.

Figure 5.1.4 Residual Plot for the Methane Permeate Flux Model for PPO Hollow Fibres prepared using 23 wt% PPO Solution

Figure 5.1.5 Residual Plot for the Carbon Dioxide Permeate Flux Model for PPO Hollow Fibres prepared using 23 wt% PPO Solution

Figure 5.1.6 Residual Plot for the Ideal Separation Factor Model for PPO Hollow Fibres prepared using 23 wt% PPO Solution

The graphs shown in the subsequent sections illustrate the effect of each operating variable on the three response variables for the gas separation performance. The model estimated values are also included in these graphs.

5.1.2. EFFECT OF BORE LIQUID FLOWRATE

The results from the analysis of the fractional factorial design showed that the bore liquid flowrate had a significant effect on the methane and carbon dioxide permeate flux at the $\alpha = 0.05$ level. Figures 5.1.7-5.1.10 show *how* the methane and carbon dioxide permeate flux are effected by the bore liquid flowrate.

Figure 5.1.7 illustrates the effect of changing the bore liquid flowrate on the methane permeate flux of hollow fibres prepared using a 23 wt% PPO polymer solution at a flowrate of 1.5 ml/min and an air gap of 88cm. As the bore liquid flowrate was increased from 1.0 to 4.0 ml/min the methane permeate flux for the resultant fibres increased from 1.52×10^{-11} to $2.96 \times 10^{-11} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$. The model gives a good estimation for the methane permeate flux over the range for the factorial design.

Figure 5.1.7 Methane Permeate Flux versus Bore Liquid Flowrate

(Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

The error bars in the graphs indicate a 95% confidence interval for the mean value of the methane permeate flux. The confidence intervals were calculated using the mean, standard deviation, number of sample measurements taken and the student t factor (Taylor, 1990). Even within the margins of the error bars, the graph clearly shows the methane permeate flux is larger for fibres prepared using higher bore liquid flowrates. At the bore liquid flowrate of 4 ml/min the average methane permeate flux was slightly lower than for those fibres prepared at 3 ml/min. However in general increasing the bore liquid flowrate produced membranes that gave increased methane permeate flux. This can be seen in Table 5.3, which is a summary of the gas separation performance of all the hollow fibres tested including those used in the factorial design and some of those prepared in the preliminary experiments.

Table 5.3 Summary of Gas Separation Performance of PPO Hollow Fibres

Polymer Solution Flowrate (ml/min)	23%PPO 0%EH 88cm Air Gap			23%PPO 0%EH 60cm Air Gap			23%PPO 2%EH 88cm Air Gap			23%PPO 2%EH 60cm Air Gap		
	Bore Liquid Flowrate (ml/min)	CO ₂ Permeate Flux $\times 10^{-10}$ mol / m ² s Pa	CH ₄ Permeate Flux $\times 10^{-11}$ mol / m ² s Pa	Bore Liquid Flowrate (ml/min)	CO ₂ Permeate Flux $\times 10^{-10}$ mol / m ² s Pa	CH ₄ Permeate Flux $\times 10^{-11}$ mol / m ² s Pa	Bore Liquid Flowrate (ml/min)	CO ₂ Permeate Flux $\times 10^{-10}$ mol / m ² s Pa	CH ₄ Permeate Flux $\times 10^{-11}$ mol / m ² s Pa	Bore Liquid Flowrate (ml/min)	CO ₂ Permeate Flux $\times 10^{-10}$ mol / m ² s Pa	CH ₄ Permeate Flux $\times 10^{-11}$ mol / m ² s Pa
3.3	9.0	7.93	3.15	11.2 9.0	7.00 6.93	3.01 2.87	9.0	8.09	3.40			
1.5	11.2 10.1 9.0 4.0 3.0 2.0 1.0	17.00 14.40 12.10 7.50 7.55 6.53 3.52	7.02 5.70 4.70 2.96 3.26 2.67 1.52	10.1 9.0 2.0	fragile fragile 6.19	8.42 3.24 2.32	11.2 9.0 2.0 1.5 1.0	16.00 12.40 8.83 6.45 4.27	7.54 4.11 3.28 2.40 1.78	2.0 2.0 1.0 0.8	7.24 5.17 3.59	2.74 2.12 1.53
0.75	2.0 1.0 0.3	9.74 7.54 5.17	3.49 3.36 2.10	1.0 0.3 0.1	7.07 4.77 4.87	2.86 1.97 1.47	1.0	6.52	2.82	2.0 1.0	12.50 7.26	4.80 3.09

% PPO concentration of PPO in the polymer solution used for spinning
 % EH concentration of 2-ethyl 1-hexanol in the polymer solution (as a wt % of the solvent)
 AIRGAP length of the airgap used for spinning (cm)
Fibres used in the factorial design are shown in red

Figure 5.1.8 shows the effect of changing the bore liquid flowrate on the methane permeate flux of hollow fibres prepared using a 23 wt% PPO polymer solution containing 2 wt% 2-ethyl-1 hexanol in the solvent. The polymer solution flowrate used in the spinning of the fibres was 1.5 ml/min and the air gap was 88cm. As the bore liquid flowrate was increased from 1.0 to 2.0 ml/min the methane permeate flux in the resultant fibres increased from 1.78×10^{-11} to 3.28×10^{-11} mol/m².s.Pa. Again the graph shows the methane permeate flux was larger for fibres prepared using higher bore liquid flowrates and the model gives a good estimation for the methane permeate flux over this range.

Figure 5.1.8 Methane Permeate Flux versus Bore Liquid Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

Figure 5.1.9 illustrates the effect of changing the bore liquid flowrate on the carbon dioxide permeate flux of hollow fibres prepared using a 23 wt% PPO polymer solution at a flowrate of 1.5 ml/min and an air gap of 88cm. As the bore liquid flowrate was increased from 1.0 to 4.0 ml/min the carbon dioxide permeate flux in the resultant fibres increases from 3.52×10^{-10} to 7.5×10^{-10} mol/m².s.Pa. The results clearly show the

carbon dioxide permeate flux is larger for fibres prepared using higher bore liquid flowrates. The model provides a good estimation for the carbon dioxide permeate flux over the range of the factorial design.

Figure 5.1.9 Carbon Dioxide Permeate Flux versus Bore Liquid Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

Figure 5.1.10 illustrates the effect of changing the bore liquid flowrate on the carbon dioxide permeate flux of hollow fibres prepared using a 23 wt% PPO polymer solution containing 2 wt% 2-ethyl-1 hexanol in the solvent. The polymer solution flowrate used in the spinning of the fibres was 1.5 ml/min and the air gap was 88cm. As the bore liquid flowrate was increased from 1.0 to 2.0 ml/min the carbon dioxide permeate flux in the resultant fibres increased from 4.27×10^{-10} to 8.83×10^{-10} mol/m².s.Pa. Again the results show that the carbon dioxide permeate flux is larger for fibres prepared using higher bore liquid flowrates and are well estimated using the model. Similar results are shown in Table 5.3; in general increasing the bore liquid flowrate produced membranes that gave increased carbon dioxide permeate flux.

Figure 5.1.10 Carbon Dioxide Permeate Flux versus Bore Liquid Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

Kneifel et al. (1992) carried out a study on the spinning of polyetherimide hollow fibres for gas separation. While they did not study the effect of changing *only* the bore liquid flowrate, they found that the permeate flux of oxygen through the fibres decreased as the ratio of the flowrates of the bore liquid and polymer solution increased.

The effects observed in this study; i.e. both methane and carbon dioxide permeate fluxes increased with an increase in bore liquid flowrate, can be explained in two ways. The increased flux could be due to the fact that increased bore liquid flowrate produces fibres with thinner walls, this effect was shown in the results in section 4.2.2. The increased permeate flow could also be due to the formation of a more open structured membrane. The latter is discussed in Chapter 6. It is likely the increased permeate flux is due to a combination of the two reasons.

The ideal separation factor for a fibre is the ratio of the permeate flux for pure carbon dioxide to the permeate flux for pure methane. The ideal separation factor for the hollow fibres prepared using a 23 wt% PPO polymer solution at a flowrate of 1.5 ml/min and an air gap of 88cm are shown plotted against bore liquid flowrate in Figure 5.1.11

Figure 5.1.11 Separation Factor versus Bore Liquid Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

From the graph there appears to be little effect of bore liquid flowrate on the separation factor; the data was scattered about a separation factor of 25.

Similar results were observed for the hollow fibres shown in Figure 5.1.12. These fibres were prepared using a 23 wt% PPO polymer solution containing 2 wt% 2-ethyl-1 hexanol in the solvent; the polymer solution flowrate used in the spinning of the fibres was 1.5 ml/min and the air gap was 88 cm. Again there appears to be little effect of bore liquid flowrate on the separation factor; the data were scattered about a separation factor of 26.

Figure 5.1.12 Separation Factor versus Bore Liquid Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% EH, Air Gap 88 cm, Polymer Solution Flowrate 1.5 ml/min)

While the graphs in Figures 5.1.11 and 5.1.12 show little effect of bore liquid flowrate on the separation factor of the resultant fibres, the analysis of the factorial design found there was a significant effect of bore liquid flowrate on the separation factor of the resultant fibres. The probable explanation for this discrepancy is as follows: the fractional factorial design was necessarily carried out at quite low levels of bore liquid flowrate (1 and 2 ml/min) because the fibres at high bore liquid flowrates had poor mechanical strength and for these fibres it was not possible to get gas separation data. At low bore liquid flowrates, Figure 5.1.12 shows a small increase in separation factor with increasing bore liquid flowrate and this was observed for other data pairs used in the factorial design. If it were possible to obtain data for the factorial design over a wider range of bore liquid flowrates, it is possible a significant effect for the bore liquid flowrate on separation may not have been found.

5.1.3. EFFECT OF POLYMER FLOWRATE

The results from the analysis of the fractional factorial design showed that the polymer solution flowrate had a significant effect on the methane and carbon dioxide permeate flux at the $\alpha = 0.05$ level. Figures 5.1.13 and 5.1.14 show how the polymer solution flowrate affected the methane and carbon dioxide permeate flux of hollow fibres prepared using a 23% PPO polymer solution an air gap of 88 cm and a bore liquid flowrate of 2.0 ml/min.

Figure 5.1.13 Methane Permeate Flux versus Polymer Solution Flowrate
(Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Bore Liquid Flowrate 2.0 ml/min)

As the polymer solution flowrate was increased from 0.75 to 1.5 ml/min the methane permeate flux decreased from 3.49 to $2.67 \times 10^{-11} \text{ mol/m}^2 \text{ s Pa}$, and the carbon dioxide permeate flux decreased from 9.74 to $6.53 \times 10^{-10} \text{ mol/m}^2 \text{ s Pa}$. The models gave a good estimation to the results over this range.

Figure 5.1.14 Carbon Dioxide Permeate Flux versus Polymer Solution Flowrate (Hollow fibres prepared using: Polymer Solution containing 23% PPO, Air Gap 88 cm, Bore Liquid Flowrate 2.0 ml/min)

Figures 5.1.15 and 5.1.16 show the methane and carbon dioxide permeate flux results for hollow fibres prepared under eight different conditions. The results have been divided into four pairs for comparison. Each pair was produced under identical spinning conditions except for the polymer solution flowrate, which was 0.75 ml/min for one of the pair and 1.5 ml/min for the other. The actual conditions used in the spinning for the pairs of fibres are listed below the graphs. The model estimates for the permeate flux for each fibre are also shown on the graph.

The results in the graphs shown in Figure 5.16 and 5.1.17 clearly show that decreasing the polymer solution flowrate results in an increase in the permeate flux for both carbon dioxide and methane in the resultant fibres. This general trend was also observed for some other pairs of fibres prepared using higher polymer solution flowrates than those employed in the factorial design. This can be seen by examining those pairs of fibres in Table 5.3 prepared under identical conditions except the polymer solution flowrate used.

- 1: 23 wt% PPO Polymer Solution, Bore Liquid Flowrate 1 ml/min, Air Gap 88 cm
- 2: 23 wt% PPO Polymer Solution with 2 wt% 2-Ethyl 1- Hexanol, Bore Liquid Flowrate 1 ml/min, Air Gap 60 cm
- 3: 23 wt% PPO Polymer Solution with 2 wt% 2-Ethyl 1- Hexanol, Bore Liquid Flowrate 1 ml/min, Air Gap 88cm
- 4: 23 wt% PPO Polymer Solution with 2 wt% 2-Ethyl 1- Hexanol, Bore Liquid Flowrate 2 ml/min, Air Gap 60cm

Figure 5.1.15 Effect of Polymer Solution Flowrate on Methane Permeate Flux

- 1: 23 wt% PPO Polymer Solution, Bore Liquid Flowrate 1 ml/min, Air Gap 88 cm
- 2: 23 wt% PPO Polymer Solution with 2 wt% 2-Ethyl 1- Hexanol, Bore Liquid Flowrate 1 ml/min, Air Gap 60 cm
- 3: 23 wt% PPO Polymer Solution with 2 wt% 2-Ethyl 1- Hexanol, Bore Liquid Flowrate 1 ml/min, Air Gap 88cm
- 4: 23 wt% PPO Polymer Solution with 2 wt% 2-Ethyl 1- Hexanol, Bore Liquid Flowrate 2 ml/min, Air Gap 60cm

Figure 5.1.16 Effect of Polymer Solution Flowrate on Carbon Dioxide Permeate Flux

The effect of polymer solution flowrate on the gas permeate flux through the hollow fibres can partly be explained by the fact that the use of a lower polymer solution flowrate produces fibres with thinner walls (see section 4.2.3). However there can also be changes in fibre morphology with polymer solution flowrate, and this can affect the permeate flux. The effect of spinning conditions on the morphology of hollow fibres will be discussed in more detail in the next chapter.

The effect of polymer solution flowrate on the permeate flux for gas separation hollow fibres has also been studied by Nardella et al. (1995). They prepared hollow fibres from modified PPO (functionalised with both trimethylsilylation and hydroxyethyl groups) and found that the O₂ permeate flow of the hollow fibres was highest for those fibres prepared using the smallest polymer solution flowrates. However, they found it necessary to coat those hollow fibres which showed high permeate flux with silicone rubber to achieve reasonable O₂/N₂ selectivity. Some researchers have found that the rheology of the spinning process can affect the morphology of hollow fibres and this can have a pronounced effect on their gas separation properties. For example, Shilton et al. (1994) found that *increasing* the polymer solution flowrate when spinning polysulfone hollow fibres produced fibres with increased pressure normalized permeate flux. Ismail et al. (1997) studied the spinning of polysulfone hollow fibre membranes and found that increasing the polymer solution flowrate from 1.0 to 2.5 cm³ min⁻¹ caused an increase in the pressure normalized permeate flux of carbon dioxide. They attributed this to enhanced orientation in the skin layer due to the higher shear rate at higher polymer solution flowrates, and were able to detect enhanced molecular orientation in the skin layer using plane-polarized infra red spectroscopy.

Figure 5.1.17 shows the ideal separation factor for the pairs of fibres for which the permeate flux results were shown in Figures 5.1.15 and 5.1.16. The graph shows the separation factor is slightly higher for the fibres prepared using the higher polymer solution flowrate than those prepared at the lower flowrate. While the results from the fractional factorial design indicated the main effect of the polymer solution flowrate was not significant, the two-way interaction between the polymer solution flowrate and the

presence of the 2-ethyl 1-hexanol was found to be significant. The model does provide a good estimate for the separation factor for those fibres prepared using polymer solution containing the 2-ethyl 1-hexanol (cases 2, 3 and 4). But is less accurate for the fibre produced using a polymer solution containing no additive at lower flowrate.

Figure 5.1.17 Effect of Polymer Solution Flowrate on Separation Factor

Nardella et al. (1995) found that changing the polymer solution flowrate during dry-wet spinning had no effect on the O_2/N_2 selectivity of hollow fibres prepared from modified PPO (functionalized with both trimethylsilylation and hydroxyethyl groups). Some researchers however have had different findings. For example, Ismail et al. (1997) studied the effect of polymer solution flowrate on the spinning of polysulfone hollow fibre membranes. They found it necessary to coat the hollow fibres with silicone rubber to achieve reasonable CO_2/CH_4 selectivity, but after coating they found that those fibres produced using the higher solution flowrates showed higher CO_2/CH_4 selectivity, they attributed this to increased molecular orientation in the skin layer that they were able to detect using plane-polarized infra red spectroscopy.

5.1.4. EFFECT OF AIR GAP

The results from the analysis of the fractional factorial design showed that the length of the air gap used in the spinning of the PPO hollow fibres did not have a significant effect on the methane and carbon dioxide permeate flux.

The results from the gas permeation experiments carried out show that in many cases the permeate flux for both methane and carbon dioxide tended to increase with increasing air gap. For example, Figures 5.1.18 and 5.1.19 illustrate the effect of the length of air gap on the methane and carbon dioxide permeate flux of membranes prepared using 23 wt% PPO polymer solution with 2 wt% 2-ethyl 1-hexanol, polymer solution flowrate 1.5 ml/min and bore liquid flowrate 2.0 ml/min. The graphs show an increase in both the methane and carbon dioxide permeate flux with increasing length of air gap.

Figure 5.1.18 Methane Permeate Flux versus Air Gap

(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5 ml/min, Bore Liquid Flowrate 2.0 ml/min)

Figure 5.1.19 Carbon Dioxide Permeate Flux versus Air Gap
(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5 ml/min, Bore Liquid Flowrate 2.0 ml/min)

However in other cases there was either little effect of the air gap on the methane and carbon dioxide permeate flux, or the permeate flux decreased with increasing air gap. Figures 5.1.20 and 5.1.21 show the methane and carbon dioxide permeate flux results for hollow fibres prepared under ten different conditions. The results have been divided into five pairs for comparison. Each pair was produced under identical spinning conditions except for the length of the air gap, which was 60 cm for one of the pair and 88 cm for the other. The actual conditions used in the spinning for the pairs of fibres are listed below the graphs. The model estimates for the permeate flux for each fibre are also shown on the graph. Since the results of the factorial design indicated that neither the main effect of the air gap nor any of the two way interactions involving the air gap were significant; the model predicts the same value for permeate flux for both fibres of each pair.

- 1: 23 wt% PPO Solution, Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min
 2: 23 wt% PPO Solution, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min
 3: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min
 4: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min
 5: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 1.5 ml/min

Figure 5.1.20 Effect of Air Gap on Methane Permeate Flux

- 1: 23 wt% PPO Solution, Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min
 2: 23 wt% PPO Solution, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min
 3: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min
 4: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min
 5: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 1.5 ml/min

Figure 5.1.21 Effect of Air Gap on Carbon Dioxide Permeate Flux

Some of the results show the permeate flux for methane and carbon dioxide increased with increasing air gap, while other results show a decrease in permeate flux as the air gap was increased.

The effect of air gap on the hollow fibres is quite complex. In section 4.2.4 it was shown how the walls of the hollow fibres produced using small air gaps were generally thicker than those produced using larger air gaps (although there was not a simple linear relationship). The hollow fibres with thicker walls would be expected to show lower permeate flux than the fibres with thinner walls. However, the air gap also has an effect on the morphology of the membrane. Small air gaps often produce creamy fibres which are porous in structure (see Chapter 6) and of course this more open structure might lead to higher flux despite any reduction in permeate flux due to the thickness of the walls. The length of air gap can also affect the thickness of the outer skin layer, a longer air gap could be expected to produce a thicker skin layer, and hence reduced permeate flux.

So the effect of the length of air gap on the permeate flux of the PPO hollow fibres is not a simple one. Any effects on the wall and skin layer thicknesses of the fibre and on the morphology of the fibre must be taken into account, and it is possible that the overall effect on the permeate flux is not linear. A three level factorial design would give information about the effect of the air gap if it were non-linear. Indeed Lee et al. (1995) studied the spinning of polysulfone ultrafiltration hollow fibres using an orthogonal array experimental design. They carried out 18 experiments and studied 7 different variables concentrating mainly on the polymer solution composition. They carried out experiments using three different air gap lengths and found that the length of air gap had a significant effect on the ultrafiltration performance of the hollow fibres.

Other researchers have found the length of air gap used in spinning to have a non-linear effect on the permeate flux of hollow fibre membranes. Kim et al. (1995) studied the spinning of polysulfone ultrafiltration hollow fibre membranes; and Lee et al. (1993) studied the spinning of polysulfone microfiltration hollow fibre membranes. Both found the water permeate flux of the hollow fibres to be a maximum when an air gap of 60cm

was used. Lee et al. reasoned that below 60 cm the evaporation of the solvent n-methyl-2-pyrrolidone (NMP) from the polymer solution was not so significant to affect the skin formation, while using longer air gaps increased solvent evaporation produced a thicker skin layer which adversely affected permeate flux. They did not however, study the effect of the air gap on the morphology of the fibres. Kim et al. (1995) found the morphology of the hollow fibres spun using different air gaps was different, and attributed this to changes in the falling time of the fibre through the air gap. They measured the falling time and found that it was a maximum for an air gap of 60cm. As the air gap was increased above 60cm, they found the falling time started to decrease as a result of an increased elongation of the fibre (because of the increased weight of fibre suspended in the air gap), which caused the fibre to fall more quickly through the air gap. The hollow fibre formed using an air gap of 60 cm (falling time 2.5s) had a mono fingered structure and had a very porous outer skin, while the structures formed using both smaller and larger air gaps had a less porous outer skin. They concluded that the longest falling time allowed phase inversion to start from the inner side of the membrane and propagate to the outside before the phase inversion occurred from the outer side.

There are few studies on the effect of the length of air gap on permeate flux for *gas separation* hollow fibre membranes. Ekiner et al. (1990) report a decrease in helium flux with increasing length of air gap used in the spinning of polyaramide hollow fibres. Although, they reported a tenfold increase in selectivity over the same air gap range, they did not give the exact figures for selectivity. They have given only the normalized selectivities (selectivities divided by the highest selectivity they obtained). So it is perhaps likely that the fibres formed at the smallest air gaps had many defects and showed very poor gas separation performance. In this study the fibres produced showed good gas separation performance, so it is likely the skin layer is mostly defect-free for each case, and any thickening of the skin layer due to solvent evaporation would not be likely to improve selectivity to a great extent. This is discussed in the next section.

The results from the analysis of the fractional factorial design showed that the length of the air gap used in the spinning of the PPO hollow fibres did not have a significant effect on the ideal separation factor of the resultant hollow fibres.

Figure 5.22 shows a graph of ideal separation factor plotted against the length of the air gap used in the spinning process to produce the hollow fibres. The hollow fibres were prepared using a 23 wt% PPO polymer solution containing 2 wt% 2-ethyl-1-hexanol using a polymer solution flowrate of 1.5ml/min and a bore liquid flowrate of 2.0 ml/min. The ideal separation factor of the fibres was approximately 25. Although there appears to be a slight increase in ideal separation factor for fibres produced at larger air gaps, the increase is minimal and within the boundaries of the error bars. The model gives a good estimate for the ideal separation factor within the range of the factorial design.

Figure 5.1.22 Separation Factor versus Air Gap

(Hollow fibres prepared using: Polymer Solution containing 23% PPO and 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5 ml/min, Bore Liquid Flowrate 2.0 ml/min)

Figure 5.1.23 shows the ideal separation factor for the five pairs of fibres for which the permeate flux results were given in Figures 5.1.20 and 5.1.21. The separation factors are scattered about 25 and there appears to be no consistent effect of the length of the air gap on the separation factor. The model appears to give a good estimate for the ideal separation factor.

- 1: 23 wt% PPO Solution, Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min
 2: 23 wt% PPO Solution, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min
 3: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min
 4: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min
 5: 23 wt% PPO Solution with 2 wt% 2-Ethyl 1-Hexanol, Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 1.5 ml/min

Figure 5.1.23 Effect of Air Gap on Separation Factor

5.1.5. EFFECT OF ADDITIVE 2-ETHYL- 1-HEXANOL

The results from the analysis of the fractional factorial design showed that the presence of 2 wt% 2-ethyl 1-hexanol in the polymer solution used in the spinning of PPO hollow fibres had a significant effect on the methane and carbon dioxide permeate flux of the resultant fibres.

Figures 5.1.24 and 5.1.25 show the methane and carbon dioxide permeate flux results for hollow fibres prepared under ten different spinning conditions. The results have been divided into five pairs for comparison. Each pair was produced under identical spinning conditions except for the presence of 2-ethyl 1-hexanol, which was absent for one of the pair and present at a concentration of 2 wt% of the solvent for the other. The actual conditions used in the spinning for the pairs of fibres are listed below the graphs. The model estimates for the permeate flux for each fibre are also shown on the graphs.

Figure 5.1.24 Effect of Additive on Methane Permeate Flux

- 1: Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min, Air Gap 60 cm
 2: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min, Air Gap 60 cm
 3: Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min, Air Gap 88cm
 4: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 1.5 ml/min, Air Gap 88cm
 5: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min, Air Gap 88cm

Figure 5.1.25 Effect of Additive on Carbon Dioxide Permeate Flux

Figure 5.1.24 and 5.1.25 show that in most cases the presence of 2-ethyl-1-hexanol in the polymer solution used for spinning the fibres caused an increase in both the methane and carbon dioxide permeate flux of the resultant fibres. However, the fifth pair of fibres actually showed the reverse effect. It should be noted however that the results for the fibre which was prepared with the additive 2-ethyl 1-hexanol in this pair were only based on two measurements of the permeate flux, several other attempts to carry out gas separation experiments had resulted in the breaking of the hollow fibres before steady state had been reached.

The presence of 2-ethyl-1-hexanol in the polymer solution was also found to cause an increase in the methane and carbon dioxide permeate flux for some fibres prepared using conditions outside the range of the factorial design. Examples of this general trend can be seen by examining those pairs of fibres in Table 5.3 prepared under identical conditions except for the presence of additive.

The difference in the permeate flux observed for fibres prepared with and without the presence of 2 wt% 2-ethyl 1-hexanol in the polymer solution cannot be explained by differences in the thickness of the walls causing the effect on the permeate flux. There was no difference observed in the thickness of the walls for fibres prepared from polymer solutions with and without 2-ethyl 1-hexanol (see section 4.2.5). The 2-ethyl 1-hexanol appears to be affecting the hollow fibres in another way. It seems likely the presence of the 2-ethyl 1-hexanol is causing a change in the morphology of the fibre walls and creating a more open structure, this will be discussed in Chapter 6.

Similar results for the effect of the presence of an additive in the polymer solution used for the spinning of gas separation hollow fibres have been noted by several researchers. Smid et al. (1991) also studied the effect of the addition of (0-15 wt%) nonsolvent additive, 2-ethyl-1-hexanol to the polymer solution used for spinning PPO hollow fibres. They found increasing the additive content produced fibres with higher oxygen permeability. Li et al. (1994) studied the effect of the addition of glycerol, a nonsolvent, to the polymer solution for the spinning of polysulfone hollow fibres. They found that as the concentration of additive was increased from 0 to 7 wt% the pressure normalized CO₂ flux of the membranes increased. However they found that the CO₂/CH₄ selectivity of the membrane decreased with increasing additive concentration, and at 7wt % additive, there was almost no selectivity. Kneifel et al. (1992) added gamma-butyrolactone (GBL), a mild non-solvent, to the polymer solution in the spinning of polyetherimide gas separation hollow fibre membranes. They found it increased the viscosity of the polymer solution and reduced the formation of cavities in the hollow fibre, resulting in amore spongy structure. The addition of up to 10% GBL to the polymer solution produced hollow fibres with enhanced oxygen permeability, but at higher GBL concentrations, the permeability started to decrease. The authors concluded that the addition of a certain amount of GBL improved the surface porosity, but at higher concentrations caused a densification of the substrate membrane. When the membranes were coated with silicone rubber the oxygen permeability increased with increasing GBL content, while the O₂/N₂ selectivity decreased at higher GBL concentrations.

The results from the analysis of the fractional factorial design showed that the presence of 2-ethyl 1-hexanol at 2 wt% in the polymer solution used in the spinning of PPO hollow fibres had a significant effect on the ideal separation factor of the resultant fibres and the two-way interaction between the additive and the polymer solution flowrate also had a significant effect.

Figure 5.1.26 shows that the ideal separation factors for the same five pairs shown in Figures 5.1.24 and 5.1.25. The graph shows the presence of the additive does not appear to have a consistent effect on the separation factor of the hollow fibres. However the effect of the presence of 2-ethyl1-hexanol is complex. The results from the fractional factorial design indicated the main effect of the presence of additive was negative, while the two-way effect between the additive and the polymer solution flowrate was positive. The combined effects are integrated in the model and this provides good estimates for the separation factors.

- 1: Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min, Air Gap 60 cm
 2: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min, Air Gap 60 cm
 3: Bore Liquid Flowrate 2 ml/min, Polymer Solution Flowrate 1.5 ml/min, Air Gap 88cm
 4: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 1.5 ml/min, Air Gap 88cm
 5: Bore Liquid Flowrate 1 ml/min, Polymer Solution Flowrate 0.75 ml/min, Air Gap 88cm

Figure 5.1.26 Effect of Additive on Separation Factor

5.2. HIGH PRESSURE TESTING OF PPO HOLLOW FIBRES

Experiments designed to test the ability of the PPO hollow fibres to withstand bore side air pressures of up to 1500 psig (10.3×10^6 Pa) were carried out on several PPO hollow fibres. The pressure applied to the bore side of the fibre in the test module was slowly increased in 100 psig (6.89×10^5 Pa) intervals, waiting for five minutes at each level. The pressure was increased to 1500 psig (10.3×10^6 Pa) or until the hollow fibre was destroyed. The pressure at which the break occurred was recorded. The results are given in Table 5.4.

Table 5.4 High Pressure Testing of Hollow Fibres prepared using 23 wt% PPO

% EH	Length of Air Gap (cm)	Bore Liquid Flowrate (ml/min)	Polymer Solution Flowrate (ml/min)	Pressure Hollow Fibres Broke ($\times 10^6$ Pa)	Wall Thickness (mm)	Outer Diameter (mm)	WT/OD Ratio
0	60	0.3	0.75	8.96	0.0500	0.41	0.12
0	88	0.3	0.75	8.61	0.0325	0.36	0.09
0	88	1.0	0.75	5.86	0.0275	0.39	0.07
2	60	2.0	1.5	5.86	0.0325	0.59	0.06

% EH the concentration of 2-ethyl 1-hexanol in the polymer solution used for spinning (as a wt% of the solvent)

WT/OD the ratio of the wall thickness of the fibre to the outer diameter of the fibre

The four PPO hollow fibres tested at high pressure were all able to withstand an applied bore side pressure of 800 psig (5.52×10^6 Pa). The pressure at which the hollow fibres broke ranged from 850 - 1300 psig ($5.86 - 8.96 \times 10^6$ Pa).

The fibres prepared using a bore liquid flowrate of 0.3 ml/min were able to withstand the highest bore side pressure. A comparison of the second and third cases shows how the fibre prepared at the smaller bore flowrate had the thicker walls and a smaller outer diameter. Both wall thickness and outer diameter are important factors in the ability of a fibre to withstand high applied bore pressures. In general, a fibre with a smaller diameter is able to withstand a higher applied bore pressure than an equivalent fibre having a larger diameter. Also the mechanical strength of a hollow fibre typically increases with the wall thickness.

So the wall thickness to outer diameter ratio is an important factor in the ability of a hollow fibre to withstand high applied bore pressure. The results given in the table show the ability of a hollow fibre to withstand high applied bore pressure seems to correlate with the wall thickness to outer diameter ratio. For example, while the fibre produced at the higher polymer flowrate had relatively thick walls, generally desirable for mechanical strength, its outer diameter was large. The wall thickness to outer diameter ratio was correspondingly lower and the fibre failed at a lower applied pressure.

The results confirm the importance that dimensions of a hollow fibre have on its practical performance in gas separation applications. While thin walls are desirable because in general they tend to maximize permeate flux, the fibre walls should not be so thin as to compromise the strength of a fibre and its ability to withstand the high pressure operating conditions necessary in practical gas separation applications.

The results also illustrate the desirability to minimize the outer diameters of hollow fibres from a point of view of their enhanced ability to withstand the high pressure operating conditions necessary in practical gas separation applications.

Chapter 6

RESULTS: HOLLOW FIBRE MORPHOLOGY

There have been few studies systematically relating the morphology of hollow fibres to the spinning conditions used to produce them. In this chapter, scanning electron micrographs and atomic force microscope images are given for a range of fibres for which the spinning conditions were systematically changed. This allowed the effect of the spinning variables on the morphology of the hollow fibres to be determined.

6.1 SCANNING ELECTRON MICROSCOPE RESULTS

6.1.1 EFFECT OF BORE LIQUID FLOWRATE

Figures 6.1 and 6.2 show scanning electron micrographs (SEM's) of transverse cross sections of the walls of two hollow fibres. The fibres were spun using a 23% PPO solution containing the additive 2-ethyl-1-hexanol (at a concentration of 2wt% of the solvent). The polymer solution flowrate used in the spinning was 1.5 ml/min and the air gap was 88 cm. The bore liquid flowrate used for the fibre shown in Figure 6.1 was 1 ml/min and was 2 ml/min for the fibre shown in Figure 6.2. The fibre formed using the lower bore liquid flowrate has an asymmetric structure, porous in the middle of the wall with a dense skin on either side. The fibre formed using the higher bore liquid flowrate has a dense structure throughout. The cross section shows ridges running parallel with the wall.

Figure 6.1 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
 (Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
 23 wt% PPO with 2 wt% 2-Ethyl 1-Hexanol, Air Gap 88 cm, Polymer Solution
 Flowrate 1.5 ml/min, Bore Liquid Flowrate 1 ml/min)

Figure 6.2 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
 (Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
 23 wt% PPO with 2 wt% 2-Ethyl 1-Hexanol, Air Gap 88 cm, Polymer Solution
 Flowrate 1.5 ml/min, Bore Liquid Flowrate 2 ml/min)

Hollow fibre membranes are formed by the process of phase inversion, in which a homogeneous polymer solution of two or more components is converted into a two-phase gel consisting of a solid (polymer-rich) phase and a liquid (polymer-poor) phase. In order for phase inversion to take place in a polymer solution, it is necessary that there is a miscibility gap over the range of concentrations and temperatures for which the membrane formation is desired. Phase inversion can be initiated by solvent evaporation, a reduction in temperature, or by contact with a nonsolvent and subsequent solvent-nonsolvent exchange.

In dry-wet phase spinning there is a combination of the above. Some solvent is evaporated as the nascent fibre falls through the air gap, this causes an increase in concentration of the polymer near the outer surface of the fibre. Solvent-nonsolvent exchange starts to occur at the inner interface, between the polymer solution and the bore liquid, immediately after the fibre exits the spinneret. There is a mass-transfer of the bore liquid, which is a nonsolvent for the polymer, into the fibre wall and there is a mass-transfer of solvent from the fibre wall into the nonsolvent. When the fibre enters the gelation bath solvent-nonsolvent exchange also starts to occur at the outer interface between the polymer solution and the nonsolvent in the gelation bath. In addition to these mass-transfer processes a reduction in temperature could also play a part in the initiation of phase inversion (e.g. for cases in which the polymer solution is spun at a high temperature into an environment held at a lower temperature). Furthermore, any solvent loss will cause a loss of latent heat at the evaporating surface as a result of the evaporation

The formation of the asymmetric structure of the hollow fibre shown in Figure 6.1 is due to differences in the phase inversion process between the surfaces and the centre of the fibre wall. At the outer surface, solvent is lost by evaporation as the fibre passes through the air gap and this increases the concentration of the polymer in the outer layer of the fibre. In addition, the polymer concentration can be increased when the polymer solution makes contact with the nonsolvent at both the outer and inner surfaces. A relatively large outflow of solvent, compared to the influx of nonsolvent, results in a net loss of liquid and increases

the polymer concentration near the surface. The latter results in a dense skin layer being formed which then acts, somewhat, as a barrier for the diffusion of nonsolvent and solvent in and out of the sublayer. Hence, solvent-nonsolvent exchange is slowed in the interior of the fibre wall and phase separation can take place through a process of liquid–liquid de-mixing. The phase change starts by the formation of a nucleus of a solvent-rich, polymer-poor phase at certain locations in the polymer solution. The nuclei grow into droplets of a solvent-rich-polymer-poor phase in the polymer-rich phase. The droplets grow until their growth is stopped by gelation of the surrounding polymer-rich phase. If the droplets grow large enough to coalesce, a porous structure of interconnected pores will be formed. If the droplets do not coalesce, a structure with independent pores or closed cells is the result. Guo et al. (1995) studied the growth of the droplets of the polymer-poor phase in the formation of polystyrene membranes by thermal inversion. They found that when the polymer solution was subjected to a controlled reduction in temperature; a cellular structure was formed. They concluded that a process of nucleation and growth of the polymer-poor phase produced a structure of closed cells. These gradually increase in size with time, by a coarsening process, in which smaller cells of the solvent-rich phase tend to coalesce and form larger cells. They found that cells formed using a quenching time of 5 minutes were 2.4 μm in diameter and those formed after ten minutes were 37 μm in diameter. The cells were found to evolve through the following shapes: small spherical cells, larger double ellipsoid cells with concave necks, larger ellipsoid cells and larger spherical cells.

The hollow fibre shown in Figure 6.1 clearly shows the presence of closed cells in the centre of the fibre wall, whereas there is a dense skin structure at the outer and inner walls. The outer wall has a relatively thicker skin and a more dense structure, as a result of the loss of solvent from this surface prior to gelation.

The fibre shown in Figure 6.2 was formed under identical conditions to that shown in Figure 6.1, except a higher bore liquid flowrate was used. The structure is different; it is quite dense across the entire cross section. For the case using the higher bore liquid flowrate there was

more nonsolvent available for the solvent to diffuse into, and more nonsolvent available to diffuse into the fibre. Therefore the solvent-nonsolvent exchange took place more quickly and there would have been insufficient time for liquid-liquid de-mixing to produce large droplets of polymer poor phase. In addition, as discussed in section 4.2.2, the wall thickness of hollow fibres decreased as the bore liquid flowrate used for spinning was increased. Therefore the walls were thinner for the hollow fibres produced using the higher bore liquid flowrate and the coagulation fronts forming from the two surfaces of the fibre wall could meet, making the entire cross section dense.

Despite the more dense appearance of the fibres prepared using the bore liquid flowrate of 2 ml/min, they gave a higher carbon dioxide permeate flux than those fibres formed at 1 ml/min. The average carbon dioxide permeate flux was $8.75 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ compared to $4.27 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ for the fibres formed at 1 ml/min. The increased flux was in part due to the walls of the hollow fibres produced at the higher bore liquid flowrate being thinner (0.03mm compared to 0.045mm). However the difference in wall thickness was not sufficient to account for all the variation in flux. Despite the homogeneous appearance of both membranes, there was evidently a difference in their structure at a fine level. This will be discussed in more detail later.

The fibre shown in Figure 6.3 was prepared under identical conditions to the latter fibres, but using an even higher bore liquid flowrate of 9 ml/min. These fibres also appeared to have a dense structure, which was the same across the fibre wall. The fibre wall was much thinner for these fibres, the wall thickness being 0.025mm, and the carbon dioxide permeate flux was correspondingly higher at $1.24 \times 10^{-9} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$.

Figure 6.3 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt% PPO with 2 wt% 2-Ethyl 1-Hexanol, Air Gap 88 cm, Polymer Solution
Flowrate 1.5 ml/min, Bore Liquid flow 9.0 ml/min)

6.1.2 EFFECT OF POLYMER SOLUTION FLOWRATE

Figure 6.4 shows a SEM of a transverse cross section of the wall of a PPO hollow fibre. The fibre was spun using a 23% PPO solution containing 2 wt% 2-ethyl-1-hexanol, an air gap of 88 cm, a bore liquid flowrate of 9 ml/min and a polymer solution flowrate of 3.3 ml/min. The hollow fibre has an asymmetric structure; it is porous in the centre of the fibre wall and more dense near the edges. The fibre shown previously in Figure 6.3 was prepared using similar spinning conditions, but with a polymer solution flowrate of 1.5 ml/min. This fibre had a more dense appearance that was the same across the thickness of the wall.

The differences in the morphology between the two hollow fibres can be attributed to differences in the rate of mass transfer of solvent and non-solvent during the gelation process.

For the case of the higher polymer solution flowrate, the resultant fibre walls were thicker than those produced using the lower polymer solution flowrate (see Section 4.2.3). With the increased distance from the wall to the centre of the fibre, solvent-nonsolvent exchange was slow enough to allow liquid-liquid de-mixing to occur in the centre of the wall and, on gelation, a porous structure was formed. In addition, with the higher polymer solution flowrate there was a higher proportion of polymer solution to non-solvent. With proportionally less available non-solvent to enter the fibre and cause gelation, the gelation process would be slowed down.

Despite the more porous appearance of the fibres formed at the higher polymer solution flowrate of 3.3 ml/min, the fibres had a lower average carbon dioxide permeate flux than those fibres formed at the polymer solution flowrate of 1.5 ml/min (8.09×10^{-10} mol/m².s.Pa compared to 1.24×10^{-9} mol/m².s.Pa). The reason was likely due to the walls being thicker for the former (0.0325 mm compared to 0.025 mm).

Some researchers have studied the rheological conditions during membrane fabrication and their effect on membrane performance and selectivity. Altering the polymer solution flowrate

can affect the degree of shear. Increasing the polymer solution flowrate increases the rate of shear, particularly near the walls of the spinneret. At regions with a high degree of shear the molecules in the forming fibre are expected to become more oriented. Gelation of the fibre can 'freeze' the orientation into the structure, particularly at the inner wall where the fibre contacts the nonsolvent immediately upon exiting the spinneret. At the outer wall the oriented molecules have more time to relax as the fibre falls through the air gap before gelation takes place. Shilton et al. (1997) have used infra-red spectroscopy to confirm this enhanced molecular orientation in the casting of flat polysulfone and polyacrylonitrile flat membranes under conditions of varying levels of shear. Shilton et al. (1994 and 1996) also investigated the spinning of polysulfone hollow fibres and found that increasing the polymer solution flowrate from 0.7 to 2.0 cm³/min produced fibres with enhanced pressure normalized flux and selectivity. They attributed this to increased molecular orientation at the surface of the fibre wall.

In this study, an increase in the pressure normalized flux and selectivity of the hollow fibres was not observed for fibres spun at higher polymer solution flowrates. Indeed for the hollow fibres shown in Figure 6.3 and 6.4, the one produced at the higher polymer solution flowrate showed lower carbon dioxide permeate flux and selectivity (23.6 compared to 30.3).

Figure 6.4 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt% PPO + 2 wt% 2-Ethyl 1-Hexanol, Air Gap 88 cm, Polymer Solution
Flowrate 3.3 ml/min, Bore Liquid Flowrate 9.0 ml/min)

6.1.3 EFFECT OF AIR GAP

Figures 6.5 and 6.6 show scanning electron micrographs (SEM's) of transverse cross sections of the walls of two hollow fibres prepared using a 23% PPO solution containing the additive 2-ethyl-1-hexanol (at a concentration of 2 wt% of the solvent). The polymer solution flowrate used in the spinning of the fibres was 1.5 ml/min and the bore liquid flowrate used was 2 ml/min. The hollow fibre shown in Figure 6.5 was prepared using an air gap of 29 cm and the hollow fibre shown in Figure 6.6 was prepared using an air gap of 60 cm.

The fibre prepared using the smaller air gap has an asymmetric structure; porous in the middle of the wall, with a dense skin on either side, while the fibre formed using the higher air gap has a more dense appearance throughout. The fibre shown previously in Figure 6.2 was prepared under similar spinning conditions, but using a higher air gap of 88cm, this hollow fibre had a dense appearance throughout the wall. Other researchers have had similar findings for the effect of the length of the air gap used in spinning on the morphology of the resultant fibres. Bauer et al. (1991) and Smid et al. (1991) found that for PPO hollow fibre membranes the thickness of the skin layer increased as the length of air gap used in spinning process was increased.

The difference in the structure between fibres produced using different lengths of air gap is partly due to the difference in time available for the evaporation of the solvent as the fibre passes through the air gap. In general, the longer the air gap the greater the time for evaporation of the solvent from the outer fibre wall. The loss of solvent increases the concentration of the polymer near the surface and tends to produce a more dense structure. Hence, a longer air gap tended to produce a thicker dense layer. Many researchers have found that an increase in polymer concentration produces a fibre with a thicker skin layer of lower porosity (Lai et al (1994), Shilton, (1994), Weink, 1994)).

Figure 6.5 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt% PPO with 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5
ml/min, Bore Liquid Flowrate 2.0 ml/min, Air Gap 29 cm)

Figure 6.6 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt% PPO with 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5
ml/min, Bore Liquid Flowrate 2.0 ml/min, Air Gap 60 cm)

Conversely, if a shorter air gap were used for spinning, there would be less time for solvent evaporation before the fibre entered the gelation bath. The dense region formed by solvent evaporation would be thinner and would not extend as far to the centre of the fibre wall before the hollow fibre entered the gelation bath. The thin dense layer would act as a barrier, slowing down the solvent-nonsolvent exchange in the centre of the fibre wall. Similarly, the dense layer formed by the rapid outflow of solvent into the bore fluid at the inner wall would also slow down the solvent-nonsolvent exchange at the centre of the fibre wall. This would allow time for liquid-liquid de-mixing to take place before gelation of the fibre; producing a more porous structure. Figure 6.5 clearly shows the porous structure of the hollow fibre prepared using an air gap of 29 cm. The pores in the centre of the porous region are interconnected. It appears that there has been sufficient time for liquid-liquid de-mixing to reach a stage where the droplets of the polymer-poor phase have started to coalesce, before their growth was stopped by gelation of the surrounding polymer-rich phase.

6.1.4 EFFECT OF ADDITIVE, 2-ETHYL-1-HEXANOL

Figures 6.7 and 6.8 show scanning electron micrographs (SEM's) of transverse cross sections of the walls of two hollow fibres prepared using a 23% PPO solution. The polymer solution used to produce the fibre shown in Figure 6.7 contained the nonsolvent additive 2-ethyl-1-hexanol, while the polymer solution used to produce the fibre in Figure 6.8 contained no additive. The polymer solution flowrate used for the spinning of both fibres was 0.75 ml/min; the bore liquid flowrate used was 2 ml/min and the air gap 88 cm.

The hollow fibre shown in Figure 6.7 was prepared using the polymer solution containing 2-ethyl 1-hexanol, it appears to have pores across the width of its wall. The hollow fibre shown in Figure 6.8 was prepared without the 2-ethyl 1-hexanol and has a dense appearance across the wall. The addition of a nonsolvent additive appears to increase porosity of the hollow fibre. The presence of a nonsolvent additive in a polymer solution shifts the initial

composition of the solution closer to the binodal curve and increases the rate of liquid-liquid de-mixing (Lai et al. (1994)). Wijmans et al. (1985) and Burghardt et al. (1987) have shown that the presence of the nonsolvent 1-octanol in solutions of PPO in trichloroethylene shifts the binodal curve in the phase diagram. This favours the occurrence of liquid-liquid de-mixing, but does not affect crystallization to any great extent. An increase in the rate of liquid-liquid de-mixing rapidly increases the rate of the growth of the droplets of the polymer-poor phase and a porous structure will be formed. The presence of the nonsolvent accelerates the gelation process and because polymer molecules require a finite time to undergo close packing, more free-volume is 'frozen' into fibre structure. Lai et al. (1994) studied the effect of the composition of the polymer solution, used for casting, on the morphology of flat polycarbonate membranes. They found that the addition of the nonsolvent methanol to the polymer solution produced a more asymmetric membrane with increased porosity of the sublayer and a thinner skin layer. The membranes produced with the added nonsolvent had increased gas permeability but reduced O₂/N₂ selectivity.

In addition, the presence of a nonsolvent in the polymer solution can be expected to decrease the solvent power of the solvent for the polymer and hence increase the extent of polymer aggregation in the casting solution. Larger polymer aggregates will create the formation of larger areas of low polymer concentration between them. Broens et al. (1978) have studied the effect of the nonsolvent 1-octanol on solutions of PPO in trichloroethylene and the membranes formed from them. They found that the use of the nonsolvent created a more grainy structure in the membranes. By increasing the amount of nonsolvent they were able to create membranes with large enough spaces between the polymer aggregates to make them suitable for ultrafiltration applications. Other researchers have had similar findings about the effect of nonsolvent additives on hollow fibre morphology. Nguyen et al. (1987) concluded an increase in nonsolvent additive in the casting solution used for the preparation of polyamide membranes caused an increase in the aggregate pore radius (pore originating from the interstitial spaces surrounded by polymer aggregates) near the surface of the membrane.

Figure 6.7 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt% PPO with 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 0.75
ml/min, Bore Liquid Flowrate 2.0 ml/min, Air Gap 88 cm)

Figure 6.8 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt% PPO, Polymer Solution Flowrate 0.75 ml/min, Bore Liquid Flowrate
2.0 ml/min, Air Gap 88 cm)

In this study, the carbon dioxide permeate flux for the fibre (shown in Figure 6.7) prepared without the 2-ethyl 1-hexanol was $9.74 \times 10^{-9} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$. Unfortunately, no carbon dioxide permeation data was available for the hollow fibre (shown in Figure 6.8) prepared using the polymer solution containing 2-ethyl 1-hexanol, because it had poor mechanical strength and all the fibres tested broke before steady state permeation rate was achieved.

Figure 6.9 shows an SEM of a transverse cross section of the wall of a PPO hollow fibre prepared using a 23% PPO polymer solution. The fibre was spun using an air gap of 88cm, a bore liquid flowrate of 2 ml/min and a polymer solution flowrate of 1.5ml/min. The hollow fibre can be compared to the fibre shown in Figure 6.2, which was prepared using similar spinning conditions, except, in this case the 23 wt % PPO polymer solution contained the additive 2-ethyl 1-hexanol. The hollow fibre shown in Figure 6.9 appears dense across the wall and is similar in appearance to the fibre shown in Figure 6.2. But, despite the similar dense appearance of the two hollow fibres, the one prepared using the polymer solution containing the additive, gave a higher carbon dioxide permeate flux than the fibre produced with no additive ($8.75 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ compared to $6.53 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$). So, it is likely the 2-ethyl 1-hexanol causes a more open structure to be formed which is not visible using SEM.

A membrane can appear to be dense and homogeneous, but can have variations in its structure at a fine level; as observed by several researchers. For example, Bauer et al. (1991) found the top layer of the asymmetric PPO hollow fibres they produced were composed of two layers: a compact top layer with a transition layer underneath. Fritzsche et al. (1990) have noticed the skin layer of polysulfone hollow fibre membranes, prepared using Lewis acid-base complexes, was not homogeneous but there was a gradual transition from the outer layer to the sublayer. Khulbe et al. (1995) have used AFM to investigate the upper and lower surfaces of homogeneous membranes of PPO and found there to be structural differences between the two. The fine structure of membranes will be discussed further in the following section.

Figure 6.9 SEM of the Cross Section of the Wall of a PPO Hollow Fibre
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt% PPO, Polymer Solution Flowrate 0.75 ml/min, Bore Liquid Flowrate 2.0
ml/min, Air Gap 88 cm)

6.2 ATOMIC FORCE MICROSCOPE RESULTS

Atomic force microscopy was used to study the fine structure of cross sections of the PPO hollow fibres prepared under various spinning conditions. The spinning conditions used are given in Table 6.2.

Table 6.2 PPO Hollow Fibres* studied using Atomic Force Microscopy

Fibre	Air Gap (cm)	Bore Liquid Flowrate (ml/min)
(a)	60	1
(b)	88	1
(c)	88	2

*All fibres were prepared using a 23 wt% PPO polymer solution containing 2-Ethyl-1-Hexanol (at a concentration of 2 wt% of the solvent) and using a Polymer Solution Flowrate of 1.5 m/min.

Hollow fibre (a) was cream in colour and had an asymmetric porous structure. Figure 6.10 shows an AFM scan taken at the centre of the wall; the porous nature of the fibre is clearly seen. A smaller scan was taken in the centre of the previous scan and is shown in Figure 6.11. A cross section analysis (lines were drawn across the image and the change in height across the section was plotted) showed a pore about 1.8 μm across and above it a 'hill' about 2 μm across. Judging by its size, it is probably an aggregate of nodule aggregates (Kesting, 1993) (they will be referred to as ANA's from now on). A cross section analysis was taken of a scan carried out near the inside wall of the fibre, here the ANA's were very regular in size and about 1.8-2.2 μm .

Figure 6.10 Atomic Force Microscope Scan of PPO Hollow Fibre (14 μ m scan)
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt%PPO with 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5 ml/min,
Bore Liquid Flowrate 1.0 ml/min, Air Gap 60 cm)

Figure 6.11 Atomic Force Microscope Scan of PPO Hollow Fibre
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt%PPO with 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5 ml/min,
Bore Liquid Flowrate 1.0 ml/min, Air Gap 60 cm)

The cross section analysis shows the ANA is made up of smaller entities. It is quite difficult to estimate their size, but they appear to be about 0.1-0.2 μm across. Some other cross section analyses taken from different areas of this ANA show entities about 0.7 μm in size. So, it appears that there is a range of sizes of ANA's. Khulbe et al. (1995) observed a similar size range for nodule aggregates (NA's) in their study of the surfaces of flat PPO membranes. Nodules are the smaller entities that make up the nodule aggregates. Nodules have been observed by Khulbe et al. (1995, 1997) on the surface of flat PPO gas separation membranes using atomic force microscopy. They found the size of the nodules varied according to the solvent used in the polymer solution. Asymmetric membranes produced using trichloroethylene as the solvent were found to have nodules of an average size of 37nm diameter on their top surface, whereas the lower surface was found to be much rougher and was made up of nodules of 113nm diameter. In their study the top surface of homogeneous membranes were found to have nodules of 31nm in size. Other researchers have observed nodules in PPO ultrafiltration membranes, Broens et al. (1978) in flat membranes and Fuji et al. (1992) in hollow fibres. In this study, no nodules were visible on the AFM scans; it would be necessary to scan over a much smaller area to observe nodules. However, roughness is significant when using AFM to investigate surfaces and it is difficult to observe very small nodular structures in cross sections that are very porous because of the resident surface roughness.

Hollow fibre (b) was prepared using the same spinning conditions as those in (a) except a larger air gap was used. The fibre was cream in colour and the SEM, given earlier, shows it has an asymmetric porous structure. Scans taken at the centre of the fibre wall show pores of 1.5-1.8 μm in diameter. The scan shows ANA's, ranging in size from 1.0 - 1.7 μm , and these are clearly smaller than those for hollow fibre (a). It appears that one of the effects of increasing the air gap, used during spinning, is to reduce the size of the ANA's within the fibre wall. This may give an explanation as to why fibres spun at higher air gaps tend to have a more dense structure. Perhaps smaller ANA's allow for tighter and more regular packing, which creates a more dense structure.

Scans closer to the edge of the outer wall of the fibre show ANA's 0.8-1.0 μm across. At the inside wall the ANA's are similar in size, about 1 μm . It appears that the size of the ANA's decrease near the wall edge, this perhaps results in better packing and could be the reason for the dense skin formed there. Other researchers have observed a decrease in the size of nodules from the centre to the edge of the hollow fibre wall. Weink et al. (1994) found the nodules at the surface of polyethersulfone membranes were smaller than those deeper in the film. Fritzsche et al. (1990) studied the skin layer of polysulfone hollow fibre membranes. They found the nodule aggregates in the surface layer were at least an order of magnitude smaller than those below the skin layer, and that the packing of the aggregates increased as the surface layer was approached. Boom et al. (1992) investigated the morphology in polyethersulfone ultrafiltration hollow fibres. They found the size of the nodules increased from 50nm (at 0.5 μm from the surface) to 100nm (at 5 μm below the surface) and that the nodules were more closely packed nearer the surface.

The reduction in size of nodular structures at the skin layer can be explained by *the increased polymer concentration in this area* (the result of solvent loss by evaporation or diffusion of solvent into the nonsolvent of the bore liquid and gelation bath). Several researchers have noted that *the size of the nodules in a membrane decrease as the polymer concentration in the polymer solution increases*. Perez et al. (1993) found that the size of the nodules in flat, polyetherimide gas separation membranes, decreased from 36nm to 18nm as the concentration of the polymer in the casting solution was increased from 16 to 30%. They found a corresponding reduction in flux and an increase in H_2/CH_4 selectivity. Nguyen et al. (1987) found that an increase in polymer concentration in the casting solution for reverse osmosis polyamide membranes caused a decrease in the radius of the polymer aggregates which lead to a reduction in the size of the interstitial spaces surrounding them.

It is expected that an increase in polymer concentration in a solution will cause a reduction in size of polymer aggregates. Linear polymer molecules generally exist as highly entangled random coils in solution rather than as extended chains. As the polymer concentration is

increased; the polymer-polymer interaction increases in relation to the polymer-solvent interaction. Due to their size, diffusion of polymer molecules is slow, but on loss of solvent the random coils tend to collapse and parts of the polymer segments cluster into groups or nodules. Each nodule will contain several tens of macromolecules in a folded state. The polymer clusters are at first highly connected because of the entanglement between adjacent chains. This groups the nodules together as aggregates and there will be regions of lower polymer concentration surrounding these clusters. *Gas separation is thought to occur through pores between the chain segments in the nodule interior, and also between the chain segments in the interstices between nodules Kesting (1993).* If disentanglement is allowed to continue, this will lead to the formation of more independent spheres and there will be a further reduction in the polymer concentration in the regions surrounding them, and these areas will form larger pores.

This mechanism of nodular growth can explain the structure of the dense skin layer in hollow fibre membranes. The nodular aggregates are smallest at the fibre surface where the polymer concentration is highest. Due to extensive entanglement they are more closely packed here, and the regions between them are quite high in polymer concentration. Further away from the surface the local polymer concentration is lower (solvent loss being somewhat hindered by the presence of the dense layer formed above). The nodular aggregates in this region are larger and less entangled. The spaces between them are larger than those in the top layer and the polymer concentration in the areas between them slightly reduced. Deeper in the structure the nodular aggregates become larger and more independent. Khulbe and Matsuura (2000) have used oxygen plasma etching to observe the structure of the skin layer and its underlying structure in homogeneous flat membranes prepared from solutions of PPO in carbon disulfide. They have found an arrangement of nodular aggregates similar to that described above.

Other researchers have not observed this decrease in size of nodular structures from the centre to the edge of the fibre wall. For example, Fuji et al. (1992) measured the size of nodules in the cross section of PPO ultrafiltration hollow fibres. They found the outside layer

consisted of a monolayer of nodules (78nm diameter), the middle layer had a course structure made up of deformed nodules (77nm diameter), and the inside layer was a monolayer supported by randomly packed nodules (93nm diameter). The size of nodular structures will depend on the local coagulation conditions where they are formed, and will depend on both the polymer concentration and the time that passes before the polymer solidifies by gelation. The variables used for spinning were not given in the latter paper, so these could not be related to the nodular size. A study on the relationship between coagulation conditions and nodular size would be an interesting subject for further study.

Hollow fibre (c) was prepared using the same spinning conditions as those used for hollow fibre (b), except a higher bore liquid flowrate was used. The hollow fibre was transparent and the SEM given in Figure 6.2 shows it has a dense structure. There are ridges near the inner wall and a deep gap in the boundary separating this and a second dense region at the outer wall. The deep gap between the two dense regions is clearly visible in the 35 μm AFM scan of the fibre wall, shown in Figure 6.12 . When viewed on the AFM video screen the two dense regions appeared as different shades. The region close to the inner wall was dark and that close to the outer wall was paler. Moving the light source confirmed that this was not just a shadow effect and it may have been due to differences in their structure not visible at this magnification.

Figure 6.13 shows smaller scan taken within the boundary region clearly shows a dense block of membrane material and a porous region containing loosely packed ANA's approximately 1.8 μm across. The dense membrane material appears to be very smooth but it was possible to identify small regular bumps across the surface, which are roughly 0.05-0.1 μm across, these could possibly be nodules. It appears this boundary region is meeting point of the formation of the dense structures being formed near the inner and outer surfaces and extending towards the middle of the fibre.

Figure 6.12 Atomic Force Microscope Scan of PPO Hollow Fibre (35 µm scan size)
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt%PPO with 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5 ml/min,
Bore Liquid Flowrate 2.0 ml/min, Air Gap 88 cm)

Figure 6.13 Atomic Force Microscope Scan of PPO Hollow Fibre (7.0 µm scan size)
(Hollow Fibre prepared using: Polymer Solution of PPO Polymer Concentration:
23 wt% PPO with 2 wt% 2-Ethyl 1-Hexanol, Polymer Solution Flowrate 1.5
ml/min, Bore Liquid Flowrate 2.0 ml/min, Air Gap 88 cm)

As discussed in Section 3.1.1, a fibre formed using a high bore liquid flowrates tends to be more dense across its entire cross section. This is because there is more nonsolvent available for the solvent to diffuse into, and more nonsolvent available to diffuse into the fibre. Hence, the solvent-nonsolvent exchange takes place more quickly and there is insufficient time for liquid-liquid de-mixing to produce large droplets of polymer-poor phase, as seen in the more asymmetric membranes. In addition, as discussed in section 4.2.2, fibre walls are thinner for hollow fibres produced using higher bore liquid flowrate and it is possible for the coagulation fronts forming from the two surfaces of the fibre wall to meet.

AFM scans were taken in each of the two dense regions. In the scan taken from the dense region close to the inner wall of the fibre, one of the ridges seen on the SEM image is clearly visible. The ANA's in this region are closely packed and are 0.3-0.76 μm in size. The dense region close to the outer wall of the fibre has ANA's that are 0.5-0.8 μm in size. The ANA's in the dense regions closer to the wall are clearly smaller than those found in the porous section of the boundary region.

In summary, the AFM work has provided a great deal of detail about the fine structure of the membranes. The size of the aggregates of nodule aggregates (ANA's) varies with the spinning conditions and also across the fibre wall. The ANA's are smaller close to the wall edge and for fibres made using higher air gaps and larger bore liquid flowrates.

Chapter 7

CONCLUSIONS

Hollow fibres were successfully produced using the dry-wet spinning method from polymer solutions of PPO in trichloroethylene using methanol as the gelation medium in the gelation bath and as the bore liquid. A range of experimental conditions that enabled the production of strong hollow fibres suitable for gas permeation testing was determined and the findings are summarized below:

- Polymer solutions of 23 wt% and 24 wt% PPO produced the best hollow fibres in terms of strength and suitability for gas permeation testing. Fibres produced using 22% PPO solutions had poor mechanical strength. Polymer solutions of 20 wt% and 25 wt% PPO were not suitable for hollow fibre spinning because of the low viscosity of the former and because the latter started to gel at room temperature.
- Hollow fibres were produced at several polymer solution flowrates between 0.75 to 5.5 ml/min, those produced using 0.75 and 1.5 ml/min were the most suitable fibres for gas permeation testing. Hollow fibres produced at the higher polymer solution flowrates tended to stick together as the fibre coiled into the gelation bath.
- Hollow fibres were produced using a range of air gap lengths from 29cm to 88cm. Hollow fibres produced using air gaps smaller than 29cm were not suitable for gas permeation testing because they tended to stick together in the gelation bath.

- Hollow fibres were produced using a range of bore liquid flowrates between 0.1 and 13.4 ml/min. The smaller flowrates produced the most attractive hollow fibres in terms of strength, however at the lowest bore liquid flowrates there were some problems of the fibres sticking together in the gelation bath. The highest flowrates produced fibres with poor mechanical strength.
- The use of the 24 wt% PPO polymer solution containing 2-ethyl 1-hexanol caused problems with spinneret blocking during the spinning process. However fibres were successfully prepared using 23wt% PPO polymer solution containing 2-ethyl 1-hexanol.

In order to elucidate relationships between the spinning variables and the hollow fibre dimensions, the effect of four variables on the outer diameter and wall thickness were studied using a one-variable-at-a-time approach. In addition, a two level complete factorial design was used to determine the significance of these effects and their interactions. The four spinning variables studied and the levels used in the factorial design were:

Concentration of 2-Ethyl 1- Hexanol*	0%	2 wt%*
Length of Air Gap	60cm	88cm
Bore Liquid Flowrate	1 ml/min	2 ml/min
Polymer Solution Flowrate	0.75 ml/min	1.5 ml/min

* As a weight percentage of the solvent in the polymer solution

- The outer diameters of hollow fibres produced within the constraints of the factorial design ranged from 0.39–0.6 mm, and the wall thickness from 0.018-0.045 mm.
- Statistical analysis of the factorial design showed that for the hollow fibre outer diameter:
 - the main effects of the length of air gap, polymer solution flowrate and bore liquid flowrate used in the spinning process were significant at the $\alpha = 0.05$ level.

- the main effect of the presence of 2-ethyl 1-hexanol and the effect of the interactions between the variables were not significant at the $\alpha = 0.05$ level.

- The following model was developed for the hollow fibre outer diameter as a function of those spinning variables that were found to be significant

$$E(OD) = 0.515625 - 0.044375x_2 + 0.025625x_3 + 0.033125x_4$$

where the x_i 's are the dimensionless variables:

$$x_1 = A - 1$$

where A = additive concentration in polymer solution and $0\text{wt}\% \leq A \leq 2\text{ wt}\%$

$$x_2 = (B - 74)/14$$

where B = length of air gap and $60\text{cm} \leq B \leq 88\text{cm}$

$$x_3 = (C - 1.5)/0.5$$

where C = bore liquid flowrate and $1\text{ ml/min} \leq C \leq 2\text{ ml/min}$

$$x_4 = (D - 1.125)/0.375$$

where D = polymer solution flowrate and $0.75\text{ml/min} \leq D \leq 1.5\text{ml/min}$

- From the one factor at a time study, the hollow fibre outer diameter was found to decrease with:

- increasing air gap
- decreasing polymer solution flowrate
- decreasing bore liquid flowrate

and was not found to be affected by presence of 2-ethyl-1-hexanol in the polymer solution.

- Statistical analysis of the factorial design showed that for the hollow fibre wall thickness:

- the main effects of the bore liquid flowrate and polymer solution flowrate used in the spinning process were significant at the $\alpha = 0.05$ level.
- the interaction between the presence of 2-ethyl 1-hexanol and the bore

liquid flowrate used in the spinning process was significant at the $\alpha = 0.05$ level

- the main effects of the length of air gap and the presence of 2-ethyl 1-hexanol in the polymer solution and the effect of the interactions between the other variables were not significant at the $\alpha = 0.05$ level

- The following model was developed for the hollow fibre wall thickness as a function of those spinning variables that were found to be significant

$$E \text{ (WT)} = 0.031625 - 0.002375x_3 + 0.0065x_4 - 0.001875x_1x_3$$

- From the one factor at a time study, the hollow fibre wall thickness was found to increase with:
 - increasing polymer solution flowrate
 - decreasing bore liquid flowrate

and was not found to be affected presence of 2-ethyl-1-hexanol in the polymer solution. Decreasing the length of the air gap used in the spinning process caused the wall thickness of the resultant fibre to increase in most cases, but had no effect on the wall thickness for other cases. It is likely the effect of the length of the air gap was not linear, a three level factorial design would confirm if this were the case.

The pure gas permeate flux of the hollow fibres was tested using carbon dioxide and methane gases at a feed gas pressure of 100 psig (6.89×10^5 Pa). The results have been reported as *pressure normalized* permeate fluxes, with the units, $\text{mol/m}^2 \cdot \text{s} \cdot \text{Pa}$. The hollow fibres were observed to give higher permeation for carbon dioxide than for methane; the ideal separation factor has been reported as the ratio of the pure carbon dioxide permeate flux to the pure methane flux. The effect of the four spinning variables on the gas separation performance of the fibres was studied using a one variable at a time approach. A fractional factorial design (using the same factor levels stated earlier) was used to determine the significance of these effects and their interactions.

- The methane permeate flux for the hollow fibres produced within the constraints of the factorial design ranged from 1.52×10^{-11} - 4.8×10^{-11} mol/m².s.Pa, and the carbon dioxide permeate flux from 3.52×10^{-10} - 1.25×10^{-9} mol/m².s.Pa. The ideal separation factor varied between 23.2 and 27.9.
- Statistical analysis of the fractional factorial design showed that for both the carbon dioxide and methane permeate flux:
 - the main effects of the polymer solution flowrate and bore liquid flowrate used in the spinning process were significant at the $\alpha = 0.05$ level
 - the main effect of the presence of 2-ethyl 1-hexanol was significant at a level of $\alpha = 0.05$ for methane and $\alpha = 0.06$ for carbon dioxide
 - the main effect of the length of air gap and none of the two-way interactions were significant at the $\alpha = 0.05$ level
- The following models were developed for the methane and carbon dioxide permeate flux as a function of those spinning variables that were found to be significant

$$E(\text{CH}_4) = 2.90125 + 0.35375x_1 + 0.57125x_3 - 0.59125x_4$$

$$E(\text{CO}_2) = 7.4425 + 0.8125x_1 + 1.8725x_3 - 1.515x_4$$
- From the one factor at a time study, both the carbon dioxide and methane permeate flux were found to increase with:
 - decreasing polymer solution flowrate
 - increasing bore liquid flowrate
 - the presence of 2-ethyl-1-hexanol in the polymer solution

The permeate flux for both methane and carbon dioxide tended to increase with increasing air gap for most cases, but had no effect in other cases. It is possible the effect of the length of the air gap is not a linear one, a three level factorial design would confirm if this were the case.

- Statistical analysis of the fractional factorial design showed that for the ideal separation factor:
 - the main effects of the presence of 2-ethyl 1-hexanol and the bore liquid flowrate were significant at the $\alpha = 0.05$ level
 - the two-way interaction between the presence of 2-ethyl 1-hexanol and the polymer solution flowrate was found to be significant at the $\alpha = 0.05$ level, none of the other interactions were significant at this level.
- The following models were developed for the ideal separation factor as a function of those spinning variables that were found to be significant

$$E(\text{SEP}) = 25.4125 - 0.2625x_1 + 1.5125x_3 + 0.5375x_1x_4$$
- From the one factor at a time study, the ideal separation factor was not found to consistently increase or decrease with an increase in any of the variables. However the model, which integrated all the significant effects, provided a good estimation to the values for the ideal separation factor within the constraints of the factorial design.
- Four PPO hollow fibres were tested at high pressure and were able to withstand an applied bore side pressure of 800 psig (5.52×10^6 Pa). The pressure at which the hollow fibres broke ranged from 850 - 1300 psig ($5.86 - 8.96 \times 10^6$ Pa). The ability of a hollow fibre to withstand high applied bore pressure increased with an increase in the wall thickness to outer diameter ratio.

The relationship between the spinning parameters and the morphology of the PPO hollow fibres was investigated by studying some hollow fibres, produced using various spinning conditions, by scanning electron microscopy. The fine structures of some fibres were also studied using atomic force microscopy.

- The morphology of the PPO hollow fibres was found to vary with the composition of the polymer solution used for spinning and the variables used in the spinning process. Both asymmetric and dense PPO hollow fibres were produced.
- The scanning electron microscope work has shown that spinning conditions leading to the asymmetric structure appear to be low air gaps, low bore liquid flowrate, high polymer solution flowrate, and the presence of 2-ethyl-1-hexanol.
- The atomic force microscope work has shown the size of the aggregates of nodule aggregates (ANA's) vary with the spinning conditions and also across the fibre wall. ANA's are smaller close to the wall edge and for fibres made using higher air gaps and larger bore liquid flowrates.

Several relationships between the dimensions, morphology and the gas separation performance of the PPO hollow fibres were found:

- In general, an asymmetric structure and thinner walls are more desirable for PPO hollow fibres to obtain higher permeate flux. However, asymmetric structure tends to disappear as the walls become thinner. Therefore, an optimization in the spinning conditions is necessary to compromise these mutually contradicting effects.
- In asymmetric hollow fibres, the nodular structure varies across the wall. The ANA's were smaller and more closely packed in the dense skin layer, and larger and more loosely packed in the more porous regions.

From this investigation many relationships between the variables used in the spinning process and the properties of the resultant fibres have been discovered. While other researchers have also observed some of the findings, much of their research has concentrated on only certain

aspects of the hollow fibre fabrication process. It is difficult to draw conclusions from the findings of many different studies, in which quite different experimental conditions have been used. The spinning process is complex, and in order to establish firm cause and effect relationships between the spinning parameters and membrane morphology and performance, it is necessary to consider hollow fibre properties concurrently. However, there are very few examples in the literature of systematic studies on the effects of preparative conditions on the morphology, dimensions *and* gas separation performance of hollow fibre membranes. By encompassing all these aspects of the spinning process in this work has allowed the establishment of relationships between the structure and performance of hollow fibres and increased our understanding of the hollow fibre membrane formation process.

While much research has concentrated on introduction of membranes made from new and modified polymers, an increased understanding of the membrane formation process can lead to the improvement of the performance of these membranes. Information that can be used to fine-tune the spinning process and produce fibres with optimum performance will save a great deal of time and effort in the future.

Chapter 8

RECOMMENDATIONS FOR FUTURE WORK

While this study has produced a great deal of practical information about the production of PPO fibres, some additional work could clarify some of the findings and provide some additional information.

- To carry out a three level factorial design for those variables that might have an effect that is not linear e.g the effect of length of the air gap on the wall thickness of the fibre and on the carbon dioxide and methane permeate flux.
- To determine levels for the five factors studied for which the resultant fibres can be tested for gas separation *all* combinations of factors and levels. This full factorial would allow the interactions between the variables to be investigated.
- To use a response surface methodology to determine the optimum spinning conditions for PPO in terms of gas separation performance.
- To study the relationship between coagulation conditions and the size of the nodular structures in a membrane.

Chapter 9

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Appendix A

Overview of Poly (2,6-dimethyl-1, 4-phenylene oxide)

A.1. Structure of PPO

Poly (2,6-dimethyl-1, 4-phenylene oxide) (PPO) is a member of a class of polymers called polyphenylene oxides, which are made up of substituted phenol groups attached by ether linkages. Poly (2,6-dimethyl-1, 4-phenylene oxide), has methyl substituents at the 2 and 6 carbon positions in the phenol ring; the phenol rings are joined by 1,4 ether linkages. The general structure is shown below.

A.2. Properties of PPO

Thermal Properties and Stability

PPO is a thermoplastic with a glass transition temperature in the range of 205 to 210°C. Its relatively high T_g is attributed to the rigidity of the phenol rings making up the backbone. Strong bonding forces associated with the aromatic backbone also give PPO good thermal stability. In the absence of oxygen it is stable below 250°C; exothermic decomposition starts at 400°C. In the presence of oxygen PPO degrades slowly above 100°C and quite rapidly above 250°C, (Aycock, 1988).

When PPO is isolated by precipitation in methanol it is 5-15% crystalline but has little crystallinity when cooled from the melt. The crystals are square plates and have a melting point of 262-267°C and a heat of fusion 15 J/g, (Aycock, 1988).

Physical Properties

PPO is an opaque polymer with a specific gravity of 1.06. It is a stiff, hard material, extremely tough and with high impact strength: at 23°C it has an Izod impact of 64 J/m. The source of its high impact strength is the ability of PPO to undergo rapid conformational transitions, by the phenol rings rotating freely about the C_{1,4}-O bond, (Feng et al., 1992). Its stiffness is attributed to the rigidity the phenol rings give to the backbone.

Mechanical Properties

PPO has high tensile strength, (80 MPa at 23°C) and modulus (2690 MPa at 23°C); these are retained at elevated temperatures. PPO has good creep resistance; it exhibits only 0.5% creep after 300 hours under a 14 MPa load at 23°C.

Electrical Properties

PPO has excellent electrical properties: its dissipation factor and dielectric strength are low and remain constant over broad temperature ranges (PPO has a dielectric strength of 0.16-0.22 volts/cm and a dissipation factor of 0.0003 at 23°C and 60 Hz). PPO has a poor arc resistance of only 75 seconds; this is quite low compared to other polymers.

Chemical Resistance and Solubility

PPO is resistant to many chemical environments; it is highly resistant to hydrolytic attack and has resistance towards acids, bases, alcohols and detergents. The phenol rings make PPO hydrophobic and subsequently PPO has low water absorption: only 0.06% after 24 hours at 23°C. PPO is also very resistant to repeated exposure to steam (Aycock, 1988).

PPO has poor resistance to strong oxidizing agents and chlorinated, aromatic or ketone solvents. It is soluble in benzene, toluene and halogenated hydrocarbons (Dick, 1987).

A.3. Synthesis of PPO

General Electric first produced poly (2,6-dimethyl-1, 4-phenylene oxide) commercially in 1965, under the trade name PPO (Hay, 1986).

PPO is manufactured by the oxidation coupling of 2,6 dimethyl substituted phenol (DMP). The reaction occurs at room temperature by bubbling oxygen through a solution of DMP in a solvent, usually pyridine. A copper catalyst is required; in general cuprous chloride is used. Diphenoquinone (DPQ) is an undesired side product produced when two phenolic residues are coupled at the C4 positions. Viersen et al. (1992) have shown that by adding DMP slowly throughout, rather than all at the beginning of the reaction, the amount of DPQ formed can be reduced. They were able to reduce the DPQ yield by a factor of 2.5 to only 1.5 %.

PPO can be prepared with a range of molecular weights. Dautenhahn and Lim (1992) have successfully synthesized PPO of molecular weight 50,000 in yields in excess of 80% using a biphasic reaction. The reaction takes place at the interface of chloroform and water phases; triethylphosphite, a surface-active complexing agent, allows the catalyst to be anchored at the interface. Advantages of this new technique are that the catalyst is easily recovered from the reaction mixture, and it avoids the use of toxic, expensive pyridine as the solvent.

A.4. Applications of PPO

PPO is a high molecular weight thermoplastic with good hydrolytic and thermal stability; it can be moulded or cast into tough, rigid products. The high resistance of PPO towards water and detergents make it an ideal polymer for use in hot water plumbing, pipes and fittings, shower heads, parts for washing machines and dryers, and as pump housings. PPO's high

impact strength allows it to be used in protective shields. The excellent electrical properties of PPO allow it to be used in many electrical applications such as: electric connectors, bus bar insulators and switch housings. It is often processed as a blend with high impact polystyrene, which reduces the T_g and enables processing at a lower temperature, while retaining the desirable properties of PPO. PPO modified in this way is sold under the trade name NORYL resin and represents one of the largest volume thermoplastics sold today. Noryl resins have found an expanding market in the car industry; they are used as fascia panels, instrument housings, dashboards, grilles, ventilation controls and wheel covers. Noryl resins are sterilizable and have been used to replace stainless steel in medical and surgical instruments.

With its excellent mechanical properties and good resistance towards many chemicals, PPO is considered to be an attractive material for the preparation of membranes. It has been used in autoclavable membrane filters for decontamination and can be formed into tough, moisture resistant membranes with good permeability towards gases.

Appendix B

Introduction to Factorial Designs

A factorial design is a design of experiments used to evaluate two or more factors simultaneously. The advantages of factorial designs over the one-variable-at-a-time approach are that they are more efficient and they allow interactions to be detected. An excellent source of basic information about the process of factorial design is the book, "Statistics for Experimenters" (Box et al., 1978). This follows the use of statistics and factorial design to study a hypothetical chemical engineering process.

There is some terminology used in factorial designs which is explained below:

Response

This is the variable of interest to be measured in the experiment; it can also be referred to as the dependant variable. The factor may be either quantitative or qualitative.

Factor

This is an independent variable whose effect on the response is of interest to the experimenter. It is a variable that is controlled by the experimenter.

Levels

These are the various values at which a factor is set during the experiment

Treatments

These are the combinations of levels of the factors being studied

Main Effect

This is the simple effect of a factor on a dependent variable. It is the effect of the factor alone averaged across the levels of other factors.

Interaction

This is the variation among the differences between means for different levels of one factor over different levels of the other factor. In other words the variables do not act additively and the effect of one variable depends on the level at which the other variables are set.

In a *complete* factorial design every factor-level combination is utilized. For instance, if there are two factors with **a** levels for factor 1 and **b** levels for factor 2, the experiment will involve collecting data on **ab** treatment combinations.

It is important that after the selection of the factors and the levels for a factorial design the various treatments are carried out in a random order to eliminate the effects of any variation that may occur with time.

The simplest factorial experiments involve factors set at two levels e.g. high/low or presence/absence. The levels are typically denoted by 0 (or -1) for the low level and 1 for the high level. In a two level factorial design with **n** factors being studied there are 2^n different treatment combinations and the design is called a 2^n factorial design. For example, for a two level factorial design with three factors (i.e. a 2^3 factorial design) there are eight treatments.

Factor A	Factor B	Factor C	Response
1	1	1	x_1
1	1	-1	x_2
1	-1	1	x_3
1	-1	-1	x_4
1	-1	-1	x_5
-1	1	1	x_6
-1	-1	1	x_7
-1	-1	-1	x_8

The main effect of a factor in a two level design is the difference between the mean of the response at the high level of the factor and the mean of the response at the low level of that factor. For a 2^3 factorial design, there would be 3 main effects and four interactions, i.e. AB, BC, AC and ABC. The interactions involving two factors are known as two-way interactions and those involving three factors are known as three-way interactions. The interactions AB, for example, is determined by calculating the difference between:

the effect of factor A at the -1 level of B averaged over the levels of C
and

the effect of factor A at the 1 level of B averaged over the levels of C

The determination of the main effects and the interactions is a lengthy process, especially as the number of factors is increased. Instead, these are usually calculated using a statistical software package such as SAS or SPSS.

Once the main effects and interaction terms have been calculated statistics is used to determine whether the main effects and the interactions are large enough to be significant, that is, are they significantly larger than that which might be expected by natural variance alone? To make this determination an estimation of this natural variance or error is needed. In some cases there may be an estimate of this error from many experiments carried out previously, or the whole factorial design can be replicated to give an estimate of the error. Another possibility frequently utilized is to consider the higher-level interactions as being small compared to the main effects and lower level interactions and to use these higher-level interactions as an estimate of the error. For example in a 2^4 factorial design the average of three and four way interactions can be used as an error estimate to determine the significance of the main effects and two level interactions.

This comparison of the effects and interactions to the error is frequently carried out by employing a statistical procedure known as the analysis of variance.

The analysis of variance procedure determines the total variation of a factor known as the Total Sum of Squares (i.e. the sum of the squared deviations of the factor from the mean). The Total Sum of Squares is then partitioned into the treatment and error components. These are known as the sum of squares for the treatment (SST) and the sum of squares for the error (SSE) or the residual sum of squares. The treatment sum of squares is further partitioned into the main effect and interactions sum of squares.

The mean squares are computed by dividing the sums of squares by the number of degrees of freedom for that term, for example, the mean square due to error (MSE) is computed by dividing SSE by its degrees of freedom.

The F value is the ratio of the mean squares to the mean square of the error. By finding the F value in the appropriate table for the F-distribution a level of significance can be found.

For example, a significance level smaller than 0.01 for a main effect would imply that the value calculated for the effect would be observed less than one time in one hundred by chance alone if the true value of the effect were zero.

There are other types of factorial design to consider. Factorial designs can be carried out using higher numbers of levels, e.g. 3^n and 4^n factorial designs use three and four levels respectively. In a two level factorial design, linearity is assumed between the two factor levels. If there is concern over this assumption factorial designs using more levels may be useful.

When many factors are being considered in a design, complete factorials can require large numbers of tests to be carried out, even for two level designs without any replication. For

example a complete factorial design to study six factors requires 64 tests to be carried out, and a factorial design to study seven factors would require 128. In order to reduce the number of tests to be carried out a part of the complete set of treatment combinations can be carried out, the resulting factorial design is known as a fractional factorial design. The use of fractional factorial designs is discussed in many books on experimental design (Dey, 1985, Box et al., 1978). There is a particularly good introductory account in the book “The Design and Analysis of Industrial Experiments”, edited by Davies (1967).

Of course, in the use of fractional factorial designs there is some loss of information that would be available from the complete factorial. The fractional factorial design can be carefully chosen to reduce this loss of information.

For example in a half fraction (a fractional factorial with half the number of combinations of treatments than the complete factorial), there is confounding (confusion) of each effect with another effect. By choosing the fraction so that the main effects and the lower level effects are confounded with higher-level effects (which are probably minimal) a good estimate of the most important effects is achieved. The example shown below illustrates this.

Consider a half fraction of the complete 2^4 factorial. The eight treatments chosen from the possible 16 are shown below. Also shown below are the levels of the factors used to determine the various interactions. The method of setting up a table like this one, which is used to aid in the manual calculation of the effects, is clearly explained in Chapter 12 of the book "Statistics for Experimenters" (Box et al. 1978). For this case the eight treatments were chosen for which the four factor interaction term $ABCD = 1$. In a matrix a column of “1’s” is denoted as I, and therefore the half fraction in this case can be identified by the defining relation:

$$I = ABCD$$

A	B	C	D	AB	AC	AD	BC	BD	CD	ABC	ABD	ACD	BCD	ABCD
-	-	-	-	+	+	+	+	+	+	-	-	-	-	+
-	-	+	+	+	-	-	-	-	+	+	+	-	-	+
-	+	-	+	-	+	-	-	+	-	+	-	+	-	+
-	+	+	-	-	-	+	+	-	-	-	+	+	-	+
+	-	-	+	-	-	+	+	-	-	+	-	-	+	+
+	-	+	-	-	+	-	-	+	-	-	+	-	+	+
+	+	-	-	+	-	-	-	-	+	-	-	+	+	+
+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

On inspection of the columns it can be seen that some are identical. This is the cause of the confounding of the effects. All the main effects are confounded with three way effects: A with BCD, B with ACD, C with ABD and D with ABC, while each two way effect is confounded with another: AB with CD, AC with BD and AD with BC.

So for this half fraction of the 2^4 complete factorial design the main effects can be adequately estimated (assuming the three-way effects are negligible), while the two way interactions are confounded.

Highly fractionated factorial designs are useful in the first stages of a study, where they can be used to estimate the significance of the main effects of many factors using very few tests. Further factorial designs can then be carried out to resolve any ambiguities. This sequential approach using successive factorial designs can be highly efficient.

Appendix C

The sample calculations given below are for the hollow fibre prepared from a solution of 23% PPO in trichloroethylene containing 2 wt% 2-ethyl-1-hexanol using a polymer solution flowrate of 1.5 ml/min, a bore liquid flowrate of 2 ml/min and an air gap of 88 cm.

C.1. SAMPLE CALCULATION OF THE 95% CONFIDENCE INTERVAL FOR THE MEAN OF THE HOLLOW FIBRE OUTER DIAMETER

$$\text{Confidence Interval for Mean Outer Diameter} = m \pm \frac{t s}{\sqrt{n}}$$

where

m = mean value for outer diameter measurements (x_i)

n = number of measurements taken

s = sample standard deviation

t = Student's t value

and

$$\begin{aligned} m &= \sum (x_i) / n \\ &= (0.52 + 0.49 + 0.51 + 0.52 + 0.52 + 0.53 + 0.53 + 0.52 + 0.52 + 0.53 + 0.51 + 0.53) / 12 \\ &= 0.52 \text{ mm} \end{aligned}$$

$$\begin{aligned} s &= \sqrt{\sum (x_i - m) / n - 1} \\ &= 0.01165 \end{aligned}$$

$$t = 2.201 \text{ for a probability level of 95 \% and } (n-1)=12 \text{ degrees of freedom}$$

Therefore,

$$\begin{aligned} \text{Confidence Interval for Mean Outer Diameter} &= 0.52 \pm \frac{2.201 \times 0.01165}{\sqrt{12}} \\ &= 0.52 \pm 0.0074 \text{ mm} \end{aligned}$$

C.2. SAMPLE CALCULATION FOR PRESSURE NORMALIZED PERMEATE FLUX

For each hollow fibre tested for gas separation performance, 3-6 experiments were carried out and the average pressure normalized fluxes were reported. The sample calculation given below is for a single experiment using methane at a pressure of 100 psig (6.89×10^5 Pa).

$$\text{Pressure Normalized Permeate Flux} = V_p / t A \Delta P$$

where

$$V_p / t = \text{Permeate Flowrate}$$

This was measured using a bubble flow meter every 30 minutes until steady state was reached (the average of three readings were taken for each flowrate). For this case, at steady state 50 μL ($50 \times 10^{-9} \text{ m}^3$) of permeate was collected in 82.9 seconds at an ambient temperature of 24.5 $^{\circ}\text{C}$ (297.65K) and pressure of 752.5mmHg (100325 Pa). To enable the flowrates to be compared they were converted to standard temperature and pressure as follows using the ideal gas assumption:

$$\begin{aligned} &= (50 \times 10^{-9} \text{ m}^3 / 82.9 \text{ s}) \times (100325 \text{ Pa} / 101325 \text{ Pa}) \times (273.15 \text{ K} / 297.65 \text{ K}) \\ &= 5.4789 \times 10^{-10} \text{ m}^3/\text{s} \end{aligned}$$

Since 1 mole of ideal gas at standard temperature pressure occupies $22.4 \times 10^{-3} \text{ m}^3$

$$\begin{aligned} \text{Molar permeate flux} &= (5.4789 \times 10^{-10} \text{ m}^3/\text{s}) / (22.4 \times 10^{-3} \text{ m}^3/\text{mole}) \\ &= 2.4459 \times 10^{-8} \text{ mole/s} \end{aligned}$$

and

$$A = \text{Surface area of hollow fibre} = n\pi DL$$

where

n = number of fibre in the module

D = internal diameter of the hollow fibre (since the feed gas was applied to the bore side of the fibres)

L = length of the hollow fibre used (the exact length of the fibre was measured for each case, it varied slightly because of the amount of epoxy injected to seal it in the module)

$$= 2 \times \pi \times 0.46 \times 10^{-3} \text{ m} \times 0.357 \text{ m}$$

$$= 0.00103 \text{ m}^2$$

$$\Delta P = 689473 \text{ Pa}$$

Therefore

$$\text{Pressure Normalized Permeate Flux} = 2.4459 \times 10^{-8} \text{ mole/s} / 0.00103 \text{ m}^2 \times 689473 \text{ Pa}$$

$$= 3.44 \times 10^{-11} \text{ mol/m}^2 \cdot \text{s Pa}$$

C.3. SAMPLE CALCULATION FOR IDEAL SEPARATION FACTOR

The ideal separation factor is reported which is the ratio of the permeate fluxes of pure gases.

$$\text{Ideal Separation Factor} = \text{CO}_2 \text{ Permeate Flux} / \text{CH}_4 \text{ Permeate Flux}$$

For this case:

$$\text{Ideal Separation Factor} = 8.43 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s Pa} / 3.44 \times 10^{-11} \text{ mol/m}^2 \cdot \text{s Pa}$$

$$= 24.5$$

Appendix D

Table D.1 Summary of PPO Hollow Fibre Dimension Data

% PPO	% EH	Air Gap (cm)	Polymer Solution Flowrate (ml/min)	Bore Liquid Flowrate (ml/min)	Mean OD (mm)	95%CI for OD (± mm)	Model OD (mm)	Mean WT (mm)	95%CI for WT (± mm)	Model WT (mm)
23	0	50	1.5	13.5	0.94	0.048		0.0150	0.0000	
23	0	50	1.5	10.1	0.83	0.019		0.0175	0.0025	
23	0	60	5.5	4.0	0.74	0.010		0.0400	0.0100	
23	0	60	5.5	3.0	0.69	0.130		0.0550	0.0250	
23	0	60	5.5	2.0	0.67	0.021		0.0800	0.0400	
23	0	60	5.5	1.5	0.64	0.047		0.0800	0.0300	
23	0	60	5.5	1.0	0.49	0.062		0.0875	0.0325	
23	0	60	3.3	11.2	0.93	0.019		0.0275	0.0075	
23	0	60	3.3	9.0	0.91	0.014		0.0300	0.0050	
23	0	60	1.5	13.5	0.97	0.019		0.0150	0.0050	
23	0	60	1.5	12.4	1.00	0.008		0.0175	0.0025	
23	0	60	1.5	11.2	0.93	0.040		0.0175	0.0025	
23	0	60	1.5	10.1	0.90	0.011		0.0225	0.0025	
23	0	60	1.5	9.0	0.88	0.010		0.0250	0.0050	
23	0	60	1.5	4.0	0.69	0.015		0.0275	0.0025	
23	0	60	1.5	3.0	0.71	0.009		0.0275	0.0025	
23	0	60	1.5	2.0	0.60	0.012	0.62	0.0400	0.0100	0.0376
23	0	60	1.5	1.0	0.59	0.015	0.57	0.0400	0.0100	0.0386
23	0	60	0.75	2.0	0.58	0.012	0.55	0.0240	0.0100	0.0246
23	0	60	0.75	1.0	0.50	0.012	0.50	0.0250	0.0050	0.0256
23	0	60	0.75	0.3	0.41	0.017		0.0500	0.0100	
23	0	60	0.75	0.1	0.28	0.015		0.0450	0.0050	
23	0	74	1.5	10.1	0.88	0.009		0.0175	0.0025	
23	0	88	5.5	4.0	0.69	0.020		0.0450	0.0100	
23	0	88	5.5	3.0	0.67	0.040		0.0500	0.0100	
23	0	88	5.5	2.0	0.65	0.016		0.0500	0.0100	
23	0	88	5.5	1.0	0.52	0.060		0.0800	0.0200	
23	0	88	5.5	0.5	0.48	0.094		0.1050	0.0350	
23	0	88	3.3	11.2	0.88	0.013		0.0250	0.0050	
23	0	88	3.3	9.0	0.84	0.010		0.0300	0.0050	
23	0	88	3.3	8.0	0.79	0.007		0.0275	0.0075	
23	0	88	2.5	2.0	0.60	0.032		0.0400	0.0050	
23	0	88	2.5	1.5	0.59	0.029		0.0450	0.0100	
23	0	88	1.5	13.5	0.87	0.023		0.0100	0.0000	
23	0	88	1.5	12.4	0.86	0.019		0.0175	0.0025	
23	0	88	1.5	11.2	0.85	0.010		0.0175	0.0025	
23	0	88	1.5	10.1	0.85	0.016		0.0175	0.0025	
23	0	88	1.5	9.0	0.83	0.006		0.0225	0.0025	
23	0	88	1.5	4.0	0.65	0.017		0.0250	0.0050	
23	0	88	1.5	3.0	0.61	0.030		0.0275	0.0075	
23	0	88	1.5	2.0	0.57	0.012	0.53	0.0375	0.0025	0.0376

Table D.1 Summary of PPO Hollow Fibre Dimension Data cont.

% PPO	% EH	Air Gap (cm)	Polymer Solution Flowrate (ml/min)	Bore Liquid Flowrate (ml/min)	Mean OD (mm)	95%CI for OD (± mm)	Model OD (mm)	Mean WT (mm)	95%CI for WT (± mm)	Model WT (mm)
23	0	88	1.5	1.0	0.55	0.020	0.48	0.0413	0.0013	0.0386
23	0	88	0.75	2.0	0.45	0.007	0.46	0.0275	0.0025	0.0246
23	0	88	0.75	1.0	0.39	0.027	0.41	0.0275	0.0025	0.0256
23	0	88	0.75	0.3	0.36	0.0041		0.0325	0.0075	
23	2	29	1.5	2.0	0.75	0.100		0.0400	0.0100	
23	2	29	1.5	1.0	0.60	0.087		0.0650	0.0150	
23	2	50	3.3	10.1	0.97	0.015		0.0175	0.0025	
23	2	60	5.5	11.2	0.83	0.008		0.0525	0.0175	
23	2	60	5.5	9.0	0.77	0.036		0.0650	0.0150	
23	2	60	5.5	2.0	0.63	0.030		0.0700	0.0100	
23	2	60	3.3	2.0	0.59	0.011		0.0550	0.0050	
23	2	60	1.5	13.5	1.00	0.037		0.0175	0.0025	
23	2	60	1.5	12.4	0.95	0.027		0.0125	0.0025	
23	2	60	1.5	11.2	0.91	0.021		0.0200	0.0000	
23	2	60	1.5	10.1	0.91	0.015		0.0225	0.0025	
23	2	60	1.5	9.0	0.89	0.013		0.0250	0.0050	
23	2	60	1.5	2.0	0.59	0.011	0.62	0.0325	0.0075	0.0339
23	2	60	1.5	1.0	0.55	0.019	0.57	0.0375	0.0125	0.0424
23	2	60	1.5	0.8	0.52	0.015		0.0450	0.0150	
23	2	60	1.5	0.3	0.42	0.019		0.0750	0.0250	
23	2	60	0.75	3.0	0.66	0.021		0.0150	0.0050	
23	2	60	0.75	2.0	0.58	0.018	0.55	0.0225	0.0025	0.0209
23	2	60	0.75	1.5	0.54	0.017	0.53	0.0250	0.0050	0.0251
23	2	60	0.75	1.0	0.49	0.020	0.50	0.0250	0.0050	0.0294
23	2	74	3.3	10.1	0.81	0.014		0.0175	0.0025	
23	2	88	3.3	13.5	0.93	0.019		0.0200	0.0000	
23	2	88	3.3	12.4	0.92	0.015		0.0225	0.0025	
23	2	88	3.3	11.2	0.89	0.011		0.0225	0.0025	
23	2	88	3.3	10.1	0.87	0.009		0.0275	0.0075	
23	2	88	3.3	9.0	0.82	0.012		0.0325	0.0025	
23	2	88	2.5	10.1	0.79	0.010		0.0175	0.0025	
23	2	88	1.5	13.5	0.89	0.027		0.0125	0.0025	
23	2	88	1.5	12.4	0.85	0.016		0.0125	0.0025	
23	2	88	1.5	11.2	0.84	0.006		0.0175	0.0025	
23	2	88	1.5	10.1	0.76	0.018		0.0175	0.0025	
23	2	88	1.5	9.0	0.76	0.012		0.0250	0.0050	
23	2	88	1.5	2.0	0.52	0.007	0.53	0.0300	0.0050	0.0339
23	2	88	1.5	1.5	0.44	0.012	0.50	0.0450	0.0050	0.0381
23	2	88	1.5	1.0	0.42	0.009	0.48	0.0450	0.0050	0.0424
23	2	88	1.5	0.8	0.46	0.006		0.0400	0.0100	
23	2	88	1.5	0.5	0.41	0.026		0.0525	0.0175	
23	2	88	0.75	2.0	0.44	0.047	0.46	0.0175	0.0025	0.0209
23	2	88	0.75	1.5	0.48	0.016	0.44	0.0200	0.0000	0.0251
23	2	88	0.75	1.0	0.43	0.006	0.41	0.0300	0.0100	0.0294

Table D.1 Summary of PPO Hollow Fibre Dimension Data cont.

% PPO	% EH	Air Gap (cm)	Polymer Solution Flowrate (ml/min)	Bore Liquid Flowrate (ml/min)	Mean OD (mm)	95%CI for OD ($\pm$ mm)	Model OD (mm)	Mean WT (mm)	95%CI for WT ($\pm$ mm)	Model WT (mm)
24	0	60	1.5	13.5	1.00	0.022		0.0100	0.0000	
24	0	60	1.5	12.4	0.92	0.027		0.0125	0.0025	
24	0	60	1.5	11.2	0.90	0.017		0.0175	0.0025	
24	0	60	1.5	10.1	0.89	0.010		0.0175	0.0025	
24	0	60	1.5	9.0	0.86	0.018		0.0175	0.0025	
24	0	88	1.5	13.5	0.86	0.025		0.0100	0.0000	
24	0	88	1.5	12.4	0.83	0.011		0.0125	0.0025	
24	0	88	1.5	11.2	0.81	0.037		0.0125	0.0025	
24	0	88	1.5	10.1	0.80	0.008		0.0150	0.0050	
24	0	88	1.5	9.0	0.75	0.022		0.0225	0.0025	

%PPO = Concentration of PPO in the Polymer Solution

%EH = Concentration of 2-Ethyl 1-Hexanol (as a wt% of solvent)

Mean OD = Mean Outer Diameter of Hollow Fibre (mm)

95% CI for OD = 95% Confidence Interval for the Mean Outer Diameter ($\pm$ mm)

Model OD = Model Estimate for the Outer Diameter (mm) *for those hollow fibres prepared within the constraints of the factorial design*

Mean WT = Mean Wall Thickness of Hollow Fibre (mm)

95%CI for WT = 95% Confidence Interval for the Wall Thickness ($\pm$ mm)

Model WT = Model Estimate of the Wall Thickness (mm) *for those hollow fibres prepared within the constraints of the factorial design*

Appendix E

E.1. SAMPLE CALCULATIONS FOR THE FACTORIAL DESIGN OF THE HOLLOW FIBRE OUTER DIAMETER

The complete factorial design to investigate four factors at two levels required 16 runs.

The levels for the factors were:

x_1 = additive concentration in polymer solution	0 %	2 %
x_2 = length of air gap	60 cm	88 cm
x_3 = bore liquid flowrate	1 ml/min	2 ml/min
x_4 = polymer solution flowrate	0.75ml/min	1.5ml/min

The notation was simplified by using dimensionless coded variables defined as

$x_i = [(value\ of\ variable\ i) - 0.5(its\ upper\ limit + its\ lower\ limit)] / 0.5(its\ upper\ limit - its\ lower\ limit)$

For example for 60 cm air gap

$$x = [60 - 0.5 (88 - 60)] / 0.5 (88 - 60) = -1$$

This way all the variables used were set between -1 and 1 and the

The general model for the outer diameter is:

$$E(OD) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \beta_6 x_1 x_3 + \beta_7 x_1 x_4 + \beta_8 x_2 x_3 + \beta_9 x_2 x_4 + \beta_{10} x_3 x_4 \\ + \beta_{11} x_1 x_2 x_3 + \beta_{12} x_1 x_2 x_4 + \beta_{13} x_1 x_3 x_4 + \beta_{14} x_2 x_3 x_4 + \beta_{15} x_1 x_2 x_3 x_4$$

Where E (OD) is the expected value of the outer diameter

The set of linear equations can be solved by least squares analysis to determine the parameters in the model.

The least squares estimates of the parameters β is given by:

$$\underline{\beta} = (X^T X)^{-1} X^T Y$$

Where

$$\underline{\beta} = \begin{pmatrix} \beta_0 \\ \beta_1 \\ \beta_2 \\ \beta_3 \\ \beta_4 \\ \beta_5 \\ \beta_6 \\ \beta_7 \\ \beta_8 \\ \beta_9 \\ \beta_{10} \\ \beta_{11} \\ \beta_{12} \\ \beta_{13} \\ \beta_{14} \\ \beta_{15} \end{pmatrix}$$

$$\underline{Y} = \begin{pmatrix} 0.50 \\ 0.59 \\ 0.58 \\ 0.60 \\ 0.39 \\ 0.55 \\ 0.45 \\ 0.57 \\ 0.49 \\ 0.55 \\ 0.58 \\ 0.59 \\ 0.43 \\ 0.42 \\ 0.44 \\ 0.52 \end{pmatrix}$$

and

$$\underline{X} = \begin{pmatrix} 1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & 1 \\ 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 \\ 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & 1 & -1 \\ 1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 & -1 & 1 & -1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 \\ 1 & -1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & -1 & 1 \\ 1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 \\ 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 & 1 \\ 1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 & 1 \\ 1 & 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 & -1 & -1 \\ 1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & -1 & -1 & 1 & -1 & -1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & -1 & -1 \\ 1 & 1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & -1 & -1 & -1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix}$$

Solving the equation $\beta = (X^T X)^{-1} X^T Y$ gives the following estimates for the parameters:

$$\underline{\beta} = \begin{pmatrix} 0.515625 \\ -0.013125 \\ -0.044375 \\ 0.025625 \\ 0.033125 \\ -0.005625 \\ 0.004375 \\ -0.015625 \\ -0.001875 \\ 0.010625 \\ -0.004375 \\ -0.000625 \\ -0.010625 \\ 0.009375 \\ 0.010625 \\ 0.006875 \end{pmatrix}$$

The significance of the individual terms in the model can then be tested by comparing the ratio $\Omega = 16\beta^2/\sigma^2$ to the value of F_{v_1, v_2} at a significance level of $\alpha = 0.05$

Since no replicates were carried out and there was no external estimate of the pure error variance, it was assumed the higher terms had no significant effect and these were used as an estimate of the error variance. After deleting the three and four level interaction terms the model reduces to:

$$E(OD) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \beta_6 x_1 x_3 + \beta_7 x_1 x_4 + \beta_8 x_2 x_3 + \beta_9 x_2 x_4 + \beta_{10} x_3 x_4$$

The reduced model was used to calculate $\hat{Y}$ from $\hat{\beta}$ and the following reduced X matrix

$$\begin{pmatrix} 1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 \\ 1 & -1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \\ 1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & -1 & 1 & -1 \\ 1 & 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & -1 & 1 \\ 1 & 1 & 1 & -1 & -1 & 1 & -1 & -1 & -1 & -1 & 1 \\ 1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 & -1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix}$$

This gave

$$\hat{Y} = \begin{pmatrix} 0.501875 \\ 0.586875 \\ 0.556875 \\ 0.624375 \\ 0.406875 \\ 0.534375 \\ 0.454375 \\ 0.564375 \\ 0.509375 \\ 0.531875 \\ 0.581875 \\ 0.586875 \\ 0.391875 \\ 0.456875 \\ 0.456875 \\ 0.504375 \end{pmatrix}$$

The residuals were then calculated, $\underline{e} = \underline{Y} - \underline{\hat{Y}}$

$$\begin{pmatrix} -0.001875 \\ 0.003125 \\ 0.023125 \\ -0.024375 \\ -0.016875 \\ 0.015625 \\ -0.004375 \\ 0.005625 \\ -0.019375 \\ 0.018125 \\ -0.001875 \\ 0.003125 \\ 0.038125 \\ -0.036875 \\ -0.016875 \\ 0.015625 \end{pmatrix}$$

Sum of squares of the residuals = 0.005781

The $\Omega = 16\beta^2/\sigma^2$ ratio was then calculated for the remaining terms in the model.

$$\underline{\beta} = \begin{pmatrix} \beta_0 \\ \beta_1 \\ \beta_2 \\ \beta_3 \\ \beta_4 \\ \beta_5 \\ \beta_6 \\ \beta_7 \\ \beta_8 \\ \beta_9 \\ \beta_{10} \end{pmatrix} \quad \begin{matrix} \Omega \\ 3679 \\ 2.38 \\ 27.2 \\ 9.09 \\ 15.2 \\ 0.44 \\ 0.26 \\ 3.38 \\ 0.05 \\ 1.56 \\ 0.26 \end{matrix}$$

In order to determine which of the main effects or their interactions were significant the ratios were compared to the F value in statistical tables of the F distribution for the degrees of freedom for the effect and error estimate.

In this case $F_{1,5} = 6.61$ for a significance level of $\alpha = 0.05$

Therefore the main effects of the length of air gap, polymer solution flowrate and bore liquid flowrate were significant at the $\alpha = 0.05$ level and the model reduces to:

$$E(OD) = 0.515625 - 0.044375x_2 + 0.025625x_3 + 0.033125x_4$$

Appendix F

Table F.1 Summary of PPO Hollow Fibre Methane Permeate Flux

% PPO	% EH	Air Gap (cm)	Polymer Solution Flowrate (ml/min)	Bore Liquid Flowrate (ml/min)	Mean CH ₄ Permeate Flux ($\times 10^{-11}$ mol /m ² s Pa)	95%CI for CH ₄ Permeate Flux	Model CH ₄ Permeate Flux
23	0	60	3.3	11.2	3.01	0.23	2.53 2.57
23	0	60	3.3	9.0	2.87	0.78	
23	0	60	1.5	2.0	2.32	0.71	
23	0	60	0.75	1.0	2.86	0.08	
23	0	60	0.75	0.3	1.97	0.31	
23	0	60	0.75	0.1	1.47	0.06	
23	0	74	1.5	10.1	1.68	0.00	
23	0	88	3.3	9.0	3.15	1.84	
23	0	88	1.5	11.2	7.02	0.00	
23	0	88	1.5	10.1	5.70	1.08	
23	0	88	1.5	9.0	4.70	1.63	2.53 1.39 3.71 2.57
23	0	88	1.5	4.0	2.96	0.23	
23	0	88	1.5	3.0	3.26	0.29	
23	0	88	1.5	2.0	2.67	0.50	
23	0	88	1.5	1.0	1.52	0.38	
23	0	88	0.75	2.0	3.49	0.88	
23	0	88	0.75	1.0	3.36	0.37	
23	0	88	0.75	0.3	2.10	0.37	
23	2	29	1.5	2.0	2.36	0.20	
23	2	60	1.5	2.0	2.74	0.12	3.24
23	2	60	1.5	1.0	2.12	0.21	2.09
23	2	60	1.5	0.8	1.53	0.32	4.42 3.28
23	2	60	0.75	2.0	4.80	0.00	
23	2	60	0.75	1.0	3.09	0.37	
23	2	88	3.3	9.0	3.40	1.85	
23	2	88	1.5	11.2	7.54	0.00	3.24 2.66 2.09 3.28
23	2	88	1.5	9.0	4.11	0.76	
23	2	88	1.5	2.0	3.28	0.47	
23	2	88	1.5	1.5	2.40	0.00	
23	2	88	1.5	1.0	1.78	0.44	
23	2	88	0.75	1.0	2.82	2.80	
24	0	60	1.5	9.0	3.39	0.25	

% PPO = Concentration of PPO in the Polymer Solution

% EH = Concentration of 2-Ethyl 1-Hexanol (as a wt% of solvent)

95% CI for CH₄ Permeate Flux = 95% Confidence Interval for the CH₄ Permeate Flux
($\pm \times 10^{-11}$ mol/m² s Pa)

Model CH₄ Permeate Flux = Model Estimate for the CH₄ Permeate Flux ($\times 10^{-11}$ mol/m² s Pa)
for those hollow fibres prepared within the constraints of the factorial design

Table F.2 Summary of PPO Hollow Fibre Carbon Dioxide Permeate Flux

% PPO	% EH	Air Gap (cm)	Polymer Solution Flowrate (ml/min)	Bore Liquid Flowrate (ml/min)	Mean CO ₂ Permeate Flux ($\times 10^{-10}$ mol /m ² s Pa)	95%CI for CO ₂ Permeate Flux	Model CO ₂ Permeate Flux
23	0	60	3.3	11.2	7.00	0.57	6.99 6.27
23	0	60	3.3	9.0	6.93	0.38	
23	0	60	1.5	2.0	6.19	1.48	
23	0	60	0.75	1.0	7.07	0.54	
23	0	60	0.75	0.3	4.77	0.51	
23	0	60	0.75	0.1	4.87	0.48	
23	0	74	1.5	10.1	4.68	0.00	
23	0	88	3.3	9.0	7.93	3.43	
23	0	88	1.5	11.2	17.0	0.00	
23	0	88	1.5	10.1	14.4	2.14	
23	0	88	1.5	9.0	12.1	6.49	6.99 3.24 10.02 6.27
23	0	88	1.5	4.0	7.50	1.73	
23	0	88	1.5	3.0	7.55	1.47	
23	0	88	1.5	2.0	6.53	1.35	
23	0	88	1.5	1.0	3.52	1.02	
23	0	88	0.75	2.0	9.74	2.63	
23	0	88	0.75	1.0	7.54	0.14	
23	0	88	0.75	0.3	5.17	0.28	
23	2	29	1.5	2.0	5.57	0.43	
23	2	60	1.5	2.0	7.24	0.62	8.61
23	2	60	1.5	1.0	5.17	0.50	4.87
23	2	60	1.5	0.8	3.59	1.27	11.64 7.90
23	2	60	0.75	2.0	12.5	6.35	
23	2	60	0.75	1.0	7.26	0.82	8.61 6.74 4.87 7.90
23	2	88	3.3	9.0	8.09	6.07	
23	2	88	1.5	11.2	16.0	0.00	
23	2	88	1.5	9.0	12.4	2.00	
23	2	88	1.5	2.0	8.83	0.85	
23	2	88	1.5	1.5	6.45	1.91	
23	2	88	1.5	1.0	4.27	0.67	
23	2	88	0.75	1.0	6.52	1.40	
24	0	60	1.5	9.0	9.35	0.76	

% PPO = Concentration of PPO in the Polymer Solution

% EH = Concentration of 2-Ethyl 1-Hexanol (as a wt% of solvent)

95% CI for CO₂ Permeate Flux = 95% Confidence Interval for the CO₂ Permeate Flux
($\pm \times 10^{-10}$ mol/m² s Pa)

Model CO₂ Permeate Flux = Model Estimate for the CO₂ Permeate Flux ($\times 10^{-10}$ mol/m² s Pa)
for those hollow fibres prepared within the constraints of the factorial design

Table F.3 Summary of PPO Hollow Fibre Ideal Separation Factor

% PPO	% EH	Air Gap (cm)	Polymer Solution Flowrate (ml/min)	Bore Liquid Flowrate (ml/min)	Ideal Separation Factor	95%CI for Ideal Separation Factor	Model Ideal Separation Factor
23	0	60	3.3	11.2	23.3	0.6	26.7 24.7
23	0	60	3.3	9.0	24.2	6.4	
23	0	60	1.5	2.0	26.9	3.9	
23	0	60	0.75	1.0	24.7	1.5	
23	0	60	0.75	0.3	24.2	1.6	
23	0	60	0.75	0.1	33.1	4.6	
23	0	74	1.5	10.1	27.6	0.0	
23	0	88	3.3	9.0	25.5	3.8	
23	0	88	1.5	11.2	24.3	0.0	
23	0	88	1.5	10.1	25.3	7.1	
23	0	88	1.5	9.0	25.6	3.5	26.7 23.6 27.7 24.7
23	0	88	1.5	4.0	25.3	7.9	
23	0	88	1.5	3.0	23.2	3.2	
23	0	88	1.5	2.0	25.0	5.5	
23	0	88	1.5	1.0	23.2	12.7	
23	0	88	0.75	2.0	27.9	0.5	
23	0	88	0.75	1.0	22.4	2.0	
23	0	88	0.75	0.3	24.8	4.9	
23	2	29	1.5	2.0	23.6	2.4	
23	2	60	1.5	2.0	26.4	1.6	27.2
23	2	60	1.5	1.0	24.4	2.5	24.2
23	2	60	1.5	0.8	23.6	13.3	26.1 23.1
23	2	60	0.75	2.0	26.1	12.7	
23	2	60	0.75	1.0	23.5	1.1	
23	2	88	3.3	9.0	23.6	5.5	
23	2	88	1.5	11.2	24.1	0.0	
23	2	88	1.5	9.0	30.3	3.4	
23	2	88	1.5	2.0	26.8	2.3	27.2
23	2	88	1.5	1.5	26.9	7.6	25.7
23	2	88	1.5	1.0	24.5	9.3	24.2
23	2	88	0.75	1.0	23.3	18.4	23.1
24	0	60	1.5	9.0	27.6	4.4	

%PPO = Concentration of PPO in the Polymer Solution

%EH = Concentration of 2-Ethyl 1-Hexanol (as a wt% of solvent)

95% CI for the Ideal Separation Factor = 95% Confidence Interval for the Ideal Separation Factor

Model Ideal Separation Factor = Model Estimate for the Ideal Separation Factor
for those hollow fibres prepared within the constraints of the factorial design

Appendix G

A full factorial design to investigate four variables at two levels had been planned for the gas separation testing of the PPO hollow fibres. Details of the 16 runs that were required are given in Table G1. However, gas permeance data could not be obtained for two of the factor –level combinations because suitable lengths of leak-free fibres were not available. The problem was due to some parts of the fibre length sticking together as the fibre was gelled in the gelation bath during spinning. With data for these two runs missing the *complete* factorial could not be analysed and a half fraction of the full factorial was carried out instead.

Table G.1. Complete Factorial Design Gas Separation Performance Data Available for Hollow Fibres using 23 wt% PPO Solution

% Additive in the Polymer Solution*	Length of Air Gap (cm)	Bore Liquid Flowrate (ml/min)	Polymer Solution Flowrate (ml/min)	Gas Separation Performance Data Available?
0	60	1	1.5	No
0	60	1	0.75	Yes
0	60	2	1.5	Yes
0	60	2	0.75	No
0	88	1	1.5	Yes
0	88	1	0.75	Yes
0	88	2	1.5	Yes
0	88	2	0.75	Yes
2	60	1	1.5	Yes
2	60	1	0.75	Yes
2	60	2	1.5	Yes
2	60	2	0.75	Yes
2	88	1	1.5	Yes
2	88	1	0.75	Yes
2	88	2	1.5	Yes
2	88	2	0.75	Yes

* 2-Ethyl 1- Hexanol as a wt% of the solvent