

DEVELOPMENT OF ASYMMETRIC POLYETHERSULFONE HOLLOW FIBER
ULTRAFILTRATION MEMBRANE FOR CYCLODEXTRIN SEPARATION

MOHD IDHAM BIN MUSTAFFAR

UNIVERSITI TEKNOLOGI MALAYSIA

DEVELOPMENT OF ASYMMETRIC POLYETHERSULFONE HOLLOW FIBER
ULTRAFILTRATION MEMBRANE FOR CYCLODEXTRIN SEPARATION

MOHD IDHAM BIN MUSTAFFAR

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

Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia

AUGUST 2004

Special thanks to my parent (Mustaffar Harun and Habsah Ramli), family (Mohd Izwan Mustaffar and Mohd Ilhamie Mustaffar) and beloved partner (Suhana Jalil) for the encouragement and the support toward the success of this study.

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my sincere appreciation to people and organizations that have directly or indirectly given contributions toward the success of this academic study.

First and foremost, I would like to give special thanks to my supervisor, Professor Dr. Ahmad Fauzi bin Ismail for his keen effort, interest, advice, continuous guidance and insightful comments throughout the course of this research.

It is my great pleasure to give special thanks to my co-supervisor, Associate Professor Dr. Rosli bin Md. Illias for his fruitful discussions, technical assistance, advice and guidance toward the completion of my study.

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

I gratefully express my thanks to my family, friends and all the member of Membrane Research Unit (MRU) especially Miss Suhana Jalil who have given me a substantial moral and technical support to finish the study.

Above all, I thank God the Almighty for His grace, mercy and guidance throughout my life.

ABSTRACT

The main objective of this research is to develop asymmetric polyethersulfone hollow fiber ultrafiltration (UF) membrane for enzyme (cyclodextrin) separation. Manipulation of rheological and phase inversion factors, including polymer concentration, solvent ratio, forced-convective evaporation time and shear rate during fiber spinning provided a potential platform to develop asymmetric hollow fiber membranes with superior separation performance. Therefore, the present research was conducted to investigate the effects of the selected fabrication parameters such as polymer concentration, dope extrusion rate (DER) and type of bore fluid on membrane properties and structures. For the first stage of study, three different types of polymer solution which consists of polyethersulfone, 1-methyl-2-pyrrolidone, polyethylene glycol and distilled water had been developed by using turbidimetric titration method. These polymer solutions were specifically designed to be very close to its cloud point (binodal line) in order to accelerate the coagulation of nascent fibers which reduced the relaxation effect on molecular orientation. At the second stage, the effect of bore fluid on the performance of membrane spun from optimized polymer solution was investigated. Distilled water and a mixture of potassium acetate and distilled water with a different level of water activity were employed. The results showed that the membrane spun using the mixture of potassium acetate and water achieved better performance in terms of flux and rejection as compared to using water as bore fluid. Therefore, the bore fluid of potassium acetate/water (low water activity) was used for the later phase of experiment. In the next stage, the effect of polymer concentration on membrane performance was studied. The three new developed polymer solutions were used in this study. The results revealed that the flux of hollow fiber ultrafiltration membrane decreases while the rejection for particle solute increases with an increase in polymer concentration. At the last stage of the study, the effect of dope extrusion rate on the performance of membrane spun from optimized polymer solution was investigated. The hollow fiber membrane was spun at five different DER. The results suggested that there were optimum conditions at certain DER which yields an optimal performance of cyclodextrin rejection. Once the separation performance reaches maximum (critical point), the rejection decreases with increasing dope extrusion rate. The membrane structure was further characterized by using scanning electron microscopy (SEM) and plane polarized infra-red Fourier transform spectroscopy to investigate the structure and morphology of membranes and to directly measure the molecular orientation on membrane active layer, respectively. As a conclusion, the combination of low water activity bore fluid, polymer concentration of 18.5 wt.% and dope extrusion rate of 3.5 cm³/min has been identified as the most favorable conditions to produce high performance hollow fiber UF membrane for cyclodextrin separation. At this condition, the rejection of ultrafiltration membrane for cyclodextrin separation is about 99.51% with the flux of about 0.47 L/m².h.

ABSTRAK

Objektif utama kajian ini ialah untuk menghasilkan membran ultraturasan gentian geronggang asimetrik untuk pemisahan enzim (cyclodextrin). Manipulasi terhadap faktor reologi dan juga faktor fasa balikan seperti kepekatan polimer, nisbah bahan pelarut, masa pemeruapan perolakan-paksaan dan kadar penyemperitan dapat memberikan panduan untuk menghasilkan membran gentian geronggang asimetrik berprestasi pemisahan tinggi. Oleh itu, penyelidikan ini dijalankan untuk mengkaji kesan beberapa parameter pembuatan membran seperti kepekatan polimer, kadar penyemperitan dan jenis bendalir liang. Pada peringkat pertama kajian, tiga jenis larutan polimer yang berbeza dihasilkan melalui kaedah titratan turbidimetrik. Larutan polimer ini terdiri daripada polietersulfona, 1-metil-2-pirolidon, polietilena glikol and air suling dan dihasilkan sehingga menghampiri takat keruh (pada garisan binodal) supaya proses pembekuan membran gentian geronggang yang baru dapat dipercepatkan di samping dapat mengurangkan kesan rehat ke atas orientasi di antara molekul. Pada peringkat kedua, kesan jenis bendalir liang ke atas prestasi membran dikaji. Dua jenis bendalir liang yang mempunyai tahap aktiviti air yang berbeza digunakan iaitu air suling dan campuran air suling dan potasium asetat. Keputusan menunjukkan bahawa membran yang dihasilkan dengan menggunakan campuran air suling dan potasium asetat mempunyai prestasi yang lebih baik dari segi fluks dan kememilihan dibandingkan dengan membran yang dihasilkan menggunakan air suling sahaja. Oleh itu, campuran air suling dan potasium asetat (aktiviti air rendah) akan digunakan sebagai bendalir liang pada ujikaji seterusnya. Pada peringkat seterusnya, kesan kepekatan polimer ke atas prestasi membran diuji. Tiga jenis larutan polimer yang baru dihasilkan digunakan di dalam kajian ini. Keputusan ujikaji menunjukkan bahawa fluks membran menurun manakala kememilihan membran meningkat apabila kepekatan polimer meningkat. Pada peringkat terakhir kajian, kesan kadar penyemperitan ke atas prestasi membran dikaji. Membran gentian geronggang dihasilkan pada lima tahap kadar penyemperitan dengan menggunakan larutan polimer optimum. Didapati bahawa terdapat keadaan optimum pada kadar penyemperitan tertentu di mana prestasi membran untuk pemisahan cyclodextrin adalah tertinggi. Apabila prestasi membran mencapai tahap maksimum, kememilihan membran akan menurun dengan peningkatan kadar penyemperitan. Pencirian struktur membran kemudian dijalankan menggunakan mikroskopi elektronik imbasan (SEM) untuk mengkaji struktur dan morfologi membran, manakala spektroskopi penukaran Fourier infra-merah berpolar untuk memeriksa penyusunan molekul pada lapisan aktif membran. Sebagai kesimpulannya, didapati bahawa gabungan bendalir liang yang mempunyai aktiviti air yang rendah, kepekatan polimer pada 18.5 % (berdasarkan berat) dan kadar penyemperitan pada 3.5 cm³/min adalah sangat sesuai untuk menghasilkan membran ultraturasan gentian geronggang berprestasi tinggi. Pada keadaan ini, kememilihan membran tertinggi dicapai untuk pemisahan cyclodextrin iaitu 99.51% dengan fluks pada kadar 0.47 L/m².h.

TABLE OF CONTENT

CHAPTER	CONTENT	PAGE
	TITLE PAGE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENT	vii
	LIST OF TABLES	xi
	LIST OF FIGURES	xiii
	NOMENCLATURE	xviii
	LIST OF APPENDICES	xx
CHAPTER I	INTRODUCTION	
	1.1 Historical Background of Membrane Technology	1
	1.2 Problem Statement	5
	1.3 Objectives of the Study	8
	1.4 Research Scopes	8

CHAPTER 2 LITERATURE REVIEW

2.1	Overview of Membrane Technology	10
2.1.1	Type of Membranes	12
2.1.2	Membrane Separation Processes	13
2.1.3	Advantages of Membranes Processes	18
2.2	Ultrafiltration Membranes	19
2.2.1	Fundamental of Ultrafiltration Membranes	19
2.2.2	History of Ultrafiltration Membranes	20
2.2.3	Mechanism of Membrane Transport Through Ultrafiltration Membrane	22
2.2.4	Rejection, Concentration Polarization and Membrane Fouling	23
2.2.4.1	Rejection	23
2.2.4.2	Concentration Polarization and Membrane Fouling	24
2.3	Development of Asymmetric Hollow Fiber Ultrafiltration Membrane for Cyclodextrin Separation	25
2.3.1	Enzyme and other Separation in Biotechnology	25
2.3.2	Membrane Separation in Biotechnology	28
2.3.3	Hollow Fiber Membranes and Its Common Principles	31
2.3.4	Membrane Formation by Phase Inversion Process	36
2.3.4.1	Wet Phase Inversion Process	41
2.3.4.2	Dry/Wet Phase Inversion Process	45
2.3.5	Production of Hollow Fiber Ultrafiltration Membranes	49

2.3.5.1	Hollow Fiber Spinning	50
2.3.5.2	Phase Inversion Effects in Hollow Fiber Membrane Formation	53
2.3.5.3	Rheological Factors in Hollow Fiber Membrane Production	57

CHAPTER 3 METHODOLOGY

3.1	Experimental Design	62
3.2	Dope Formulation	63
3.2.1	Polymer	65
3.2.2	Solvent, Nonsolvent and Polymer Additive	67
3.3	Turbidimetric Titration Method	67
3.4	Preparation of Polymer Solution	69
3.5	Dry/Wet Spinning Process	70
3.5.1	Solvent Exchange Process	73
3.5.2	Practicalities of Fiber Spinning	74
3.6	Preparation of Hollow Fiber Membrane Modules (Potting-up)	75
3.7	Measurement of Membrane Flux and Rejection	77
3.8	Plane Polarized Infrared Fourier Transform Spectroscopy	79
3.9	Scanning Electron Microscopy (SEM)	81

CHAPTER 4 RESULTS AND DISCUSSION

4.1	Hollow Fiber Membrane Performance Testing	82
4.1.1	Effects of Bore Fluid on Membrane Performance and Morphology	82

4.1.2	Effects of Polymer Concentration on Membrane Performance and Morphology	89
4.1.3	Effects of Dope Extrusion Rate on Membrane Performance and Morphology	96

**CHAPTER 5 GENERAL CONCLUSIONS AND
RECOMMENDATIONS FOR FUTURE WORK**

5.1	General Conclusions	108
5.2	Recommendations for Future Work	110

REFERENCES	112
-------------------	-----

PUBLICATIONS	122
---------------------	-----

APPENDIX	123
-----------------	-----

Appendix A-C

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Membrane at a glance	14
2.2	Types and characteristics of widely practiced membrane processes	15
2.3	Factors affecting hollow fiber morphology	54
3.1	Materials used for polymer solution formulation	65
3.2	Physical, mechanical and thermal properties of polyethersulfone (PES)	66
3.3	Water activities of bore fluid solutions	73
3.4	Hollow fiber ultrafiltration membrane spinning dimensions	74
3.5	Infrared bands of functional groups in polyethersulfone (PES)	80
4.1	Effects of bore fluid on membrane performance	84
4.2	Comparison of solution with different polymer concentration	90
4.3	Effect of polymer concentration on membrane performance	92

4.4	Wall thickness, outer and inner diameter of hollow fiber membrane produced with different polymer concentration	95
4.5	Effects of dope extrusion rate on membranes performance	98
4.6	Wall thickness, outer and inner diameter of hollow fiber membrane	102

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Basic of membrane separation process	2
2.1	Asymmetric membrane consists of a very thin skin layer overlaying on a thick and highly porous sublayer	13
2.2	Milestones in the development of ultrafiltration	21
2.3	The sieve mechanism of ultrafiltration membrane	22
2.4	Concentration polarization in ultrafiltration	25
2.5	Types of hollow fiber membrane and its applications	31
2.6	The structure of hollow fiber membrane	32
2.7	Tube-in-orifice spinneret	34
2.8	Spinneret faces: (a) segmented-arc design; (b) plug-in-orifice design; (c) tube-in-orifice; (d) multi-annular design	34
2.9	Schematic depiction of the immersion precipitation process: P, polymer; S, solvent; NS, non-solvent	39
2.10	Schematic ternary phase diagram for ternary system	42
2.11	Ternary phase diagram of polymer/solvent/nonsolvent system	43

2.12	Schematic diagram of an isothermal ternary phase diagram showing the equilibrium tie-lines connecting equilibrium compositions on the binodal curve having polymer rich and polymer poor compositions indicated as PR and PP respectively	45
2.13	Schematic representation of diffusion paths initiating near the binodal boundary and potentially penetrating to the metastable (nucleation and growth) region (A'), the unstable (spinodal decomposition) region (A'') or the 'solidus tie-line' (A''') where the morphology is vitrified immediately upon phase separation and unable to evolve	48
2.14	Hollow fiber spinning technique	51
2.15	Schematic diagram of die swell phenomenon in hollow fiber spinning	59
3.1	Critical issues controlling successful ultrafiltration membranes	62
3.2	Experimental design	64
3.3	The structure of polyethersulfone used for asymmetric hollow fiber preparation	66
3.4	Apparatus for turbidimetric titration	68
3.5	Equipment used for polymer solution preparation	69
3.6	Steps involved in the preparation of asymmetric membrane according to the dry/wet phase separation process	71
3.7	Schematic diagram of hollow fiber spinning system: (1) nitrogen cylinder; (2) dope reservoir; (3) gear pump; (4)	72

	on-line filter, 7 mm; (5) syringe pump; (6) spinneret; (7) forced convective tube; (8) roller; (9) wind-up drum; (10) refrigeration/heating unit; (11) coagulation bath; (12) washing/treatment bath; (13) wind-up bath; (14) schematic spinneret	
3.8	Schematic diagram of a general fiber spinning process	75
3.9	Schematic diagram of hollow fiber membrane module and housing	76
3.10	Testing rig for hollow fiber ultrafiltration membrane module: (1) feed tank; (2) osmotic pump; (3) control valve; (4) flow meter; (5) pressure gauge; (6) hollow fiber membrane module; (7) beaker for collecting permeate	78
4.1	The rejection of the membrane versus molecular weight of tested solutes for membrane spun at dope extrusion rate of $3.5 \text{ cm}^3/\text{min}$ for both type of bore fluid (BF)	85
4.2	The overall cross-section of hollow fiber membranes: (a) and (b) for bore fluid of distilled water and (c) and (d) for a mixture of potassium acetate and distilled water (Magnification: 110x)	86
4.3	Inner and outer edge of cross-section of hollow fiber membranes: (a) and (b) for bore fluid of distilled water and (c) and (d) for a mixture of potassium acetate and distilled water (Magnification: 400x)	87
4.4	The rejection of the membranes versus molecular weight of tested solutes for membrane spun at $3.5 \text{ cm}^3/\text{min}$ of dope extrusion rate	93
4.5	The overall cross-section of hollow fiber membranes:	94

	(a) for solution DS1, (b) for solution DS2 and (c) for solution DS3 (Magnification: 110x)	
4.6	Inner and outer edge cross-section of hollow fiber membranes: (a) for solution DS1, (b) for solution DS2 and (c) for solution DS3 (Magnification: 400x)	95
4.7	Effect of dope extrusion rate on PWP of hollow fiber ultrafiltration membrane	99
4.8	Rejection of membrane at different dope extrusion rate	100
4.9	Flux of membrane at different dope extrusion rate	100
4.10	The rejection of the membranes versus molecular weight of tested solutes for membrane spun at 3.5 cm ³ /min of dope extrusion rate	101
4.11	The overall cross-section of hollow fiber membranes at different dope extrusion rate (Magnification: 110x)	103
4.12	Inner and outer edge cross-section of hollow fiber membranes at different dope extrusion rate (Magnification: 400x)	104
4.13	Scanning electron micrographs of membrane surface at different dope extrusion rate (Magnification: 5000x)	105
4.14	Plane-polarized infrared spectra parallel (darker line) and perpendicular (lighter line) to shear direction for membrane spun at high dope extrusion rate (3.5 cm ³ /min)	106
4.15	Plane-polarized infrared spectra parallel (darker line) and perpendicular (lighter line) to shear direction for membrane spun at low dope extrusion rate (2.5 cm ³ /min)	106

- 4.16 A linear dichroism spectrum (subtraction of parallel spectrum to perpendicular spectrum) for membrane spun at low dope extrusion rate ($2.5 \text{ cm}^3/\text{min}$) (lighter line) and high dope extrusion rate ($3.5 \text{ cm}^3/\text{min}$) (darker line) 107

NOMENCLATURE

A	-	Surface area of hollow fiber membranes (cm^2)
A_{sp}	-	Cross sectional area of the spinneret (cm^2)
DER	-	Dope extrusion rate (cm^3/min)
f	-	Observed/apparent solute rejection (%)
f_o	-	Actual/true solute rejection (%)
g	-	Airgap distance (cm)
J	-	Permeate flux ($\text{L}/\text{m}^2.\text{h}$)
JS	-	Jet stretch ratio or draw ratio
MW	-	Molecular weight (dalton)
MWCO	-	Molecular weight cut-off (dalton)
p	-	Pressure (bar)
p_o	-	Atmospheric pressure (bar)
Δp	-	Transmembrane pressure (bar)
PR	-	Product rate
PWP	-	Pure water permeation rate ($\text{L}/\text{m}^2.\text{h}$)
Q	-	Volumetric flow rate (L/h)
S	-	Standard Deviation
T	-	Temperature (K)
T_g	-	Glass transition temperature ($^{\circ}\text{C}$)
v	-	Permeation velocity of product
V_o	-	Spine line initial velocity (cm/s)
V_f	-	Spine line final velocity (cm/s)
g	-	Shear rate (s^{-1})
i	-	Component i
j	-	Component j
T	-	Total

BF	-	Bore fluid
DS 1	-	Polymer solution 1
DS 2	-	Polymer solution 2
DS 3	-	Polymer solution 3
D	-	Diameter
C_p	-	Solute concentration of permeate (mg/L)
C_f	-	Solute concentration of feed (mg/L)
V	-	Permeate volume (L)
t	-	Time (h)
PVP	-	Polyvinylpyrrolidone
PEG	-	Poly (ethylene) glycol
PES	-	Polyethersulfone
NMP	-	1-methyl-2-pyrrolidone
NSA	-	Nonsolvent additive
TOC	-	Total organic carbon analyzer
SEM	-	Scanning electron microscope
FTIR	-	Fourier transform infra-red spectroscopy
VEP	-	Volume extrusion from pump (cm ³ /rev)
CD	-	Cyclodextrin
CGT	-	Cyclodextrin glycosyltransferase
RO	-	Reverse Osmosis
NF	-	Nanofiltration
UF	-	Ultrafiltration
MF	-	Microfiltration
BFIR	-	Bore fluid injection rate (cm ³ /min)

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Experimental Data	123
B	Feed and Permeate Concentration Measured from Total Organic Carbon Analyzer	149
C	Spinning Conditions	151

CHAPTER 1

INTRODUCTION

1.1 Historical Background of Membrane Technology

The word membrane comes from Latin word ‘membrana’ that means a skin of parchment (Jones, 1997). Besides, it can also be defined basically as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid (Paul and Yampol’Ski, 1994). Today, the word ‘membrane’ has been extended to describe a thin flexible sheet or film, acting as a selective boundary between two phases because of its semi-permeable properties (Lonsdale, 1982). Membrane’s function is as a separation agent that is very selective based on the difference of diffusivity coefficient, electric current or solubility. A typical schematic diagram of simple membrane separation process is shown in Figure 1.1 (Koros, 1995).

Systematic studies of membrane phenomena can be traced to the 18th century philosopher scientists. Abbe Nolet coined the word *osmosis* to describe permeation of water through a diaphragm in 1748. Through the 19th and early 20th centuries, membranes had no industrial or commercial uses but were used as laboratory tools to develop physical and chemical theories. For example, the measurements of solution osmotic pressure made with membranes by Traube and Pfeffer was used by van’t Hoff in 1887 to develop his limit law, which explains the behavior of ideal dilute solution and this work led directly to the van’t Hoff equation. At about the same

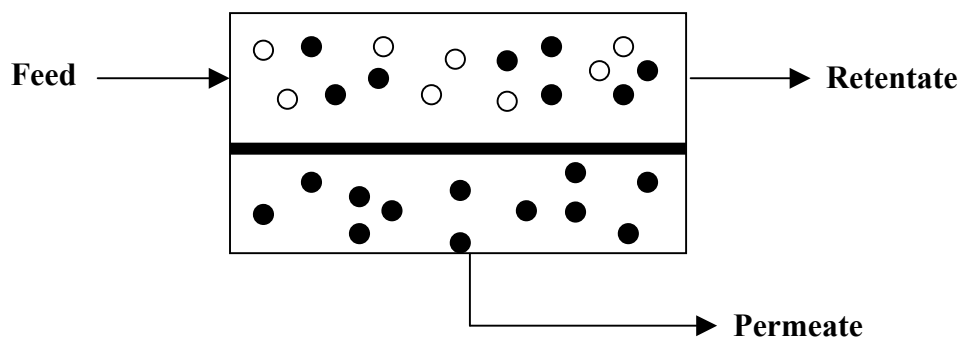


Figure 1.1: Basic of membrane separation process

time, Maxwell and others used the concept of a perfectly selective semi-permeable membrane in developing the kinetic theory of gases.

Early membrane researchers experimented with every type of diaphragm available to them such as bladders of pigs, cattle, fish and sausage casings made of animal gut. Then, collodion (nitrocellulose) membrane was preferred because they could be made reproducibly. In 1907, Bechhold discovered a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble test (Baker, 2000). Then, the other early investigators such as Elford, Zsigmondy and Bachman, and Ferry improved on Bechhold's technique and by the early 1930s microporous collodion membranes were commercially available (Baker, 2000). After 20 years, this early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate. The first significant application of membrane is in the testing of drinking water at the end of World War II. Drinking water supplies serving large communities in Germany and elsewhere in Europe had broken down and filters to test for water safety were needed urgently. Research has been done to develop these filters, sponsored by the U.S Army and was later exploited by Millipore Corporation, the first and still the largest U.S microfiltration membrane producer.

By 1960, the elements of modern membrane science had been developed but membranes were still used in a few laboratories and for small, and specialized industrial applications. No significant membrane industry existed, and total annual

sales of membranes for all industrial applications probably did not exceed \$20 million in 1998 dollars. Membranes suffered from four major problems that prohibited their widespread use as a separation process. They were too unreliable, too slow, too unselective and too expensive. Solutions to each of these problems have been developed during the last 30 years and membrane-based separation processes are now commonplace.

The important discovery and development of membrane that transformed membrane separation from a laboratory technique to an industrial process was found in the early 1960s. Loeb and Sourirajan found the process for making defect-free, high-flux, anisotropic reverse osmosis membrane and this technique was known as Loeb-Sourirajan process (Loeb and Sourirajan, 1962). These membranes consist of an ultra-thin, selective surface film on a much thicker but more permeable microporous support, which provides the mechanical strength. The flux of the first Loeb-Sourirajan reverse osmosis membrane was 10 times higher than that of any membrane then available and made reverse osmosis a potentially practical method of desalting water. The work of Loeb and Sourirajan and the timely infusion of large sums of research and development dollars from U.S Department of Interior, Office of Saline Water (OSW), resulted in the commercialization of reverse osmosis and was a major factor in the development of ultrafiltration and microfiltration. The development of electrodialysis was also aided by OSW funding.

Concurrent with the development of these industrial applications of membranes was the independent development of membranes for medical separation processes, in particular the artificial kidney. In 1945, Kolf and Berk (Baker, 2000) had demonstrated the first successful artificial kidney in The Netherlands. It took almost 20 years to refine the technology for use on a large scale but these developments were completed by the early 1960's. Since then, the use of membranes in artificial organs has become a major lifesaving procedure. More than 800,000 people are now sustained by artificial organs such as by artificial kidneys and further million people undergo open-heart surgery each year, a procedure made possible by the development of the membrane blood oxygenator. The sales of these devices comfortably exceed the total industrial membrane separation market.

Another important medical application of membranes is for controlled drug delivery systems. A key figure in this area was Alex Zaffaroni who founded Alza, a company dedicated to developing these products in 1966. The membrane techniques developed by Alza and its competitors are widely used in the pharmaceutical industry to improve the efficiency and safety of drug delivery.

The period from 1960 to 1980 produced a significant change in the status of membrane technology. Building on the original Loeb-Sourirajan technique, other membrane formation processes including interfacial polymerization and multilayer composite casting and coating were developed for making high performance membranes. Using these processes, membranes with selective layers as thin as 0.1 μm or less are now being produced by a number of companies. Methods of packaging membranes into large membrane area such as spiral wound, hollow fiber, capillary and plate and frame modules were also developed and advanced in order to improve membrane stability. By 1980, microfiltration, ultrafiltration, reverse osmosis and electrodialysis were all established processes with large plants installed worldwide.

The principal milestone in the 1980s was the emergence of industrial membrane gas separation processes. The first major development was due to the Monsanto Prism[®] membrane for hydrogen separation, introduced in 1980 (Henis and Tripodi, 1980). Within a few years, Dow was producing systems to separate carbon dioxide from natural gas. Gas separation technology is evolving and expanding rapidly and further substantial growth will be seen in the coming years. Another advance in the 1980s was the introduction by GFT, a small German engineering company of the first commercial pervaporation systems for dehydration of alcohol. GFT has now sold more than 100 plants. Many of these plants are small but the technology has been demonstrated and other pervaporation applications are now at the pilot plant stage.

Nowadays, membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical

species through the membrane. In controlled drug delivery, the goal is to moderate the permeation rate of a drug from reservoir to the body while in separation applications, the goal is to allow one component of a mixture to permeate the membrane freely and hindering permeation of other components at the same time.

1.2 Problem Statement

One of the important goals in membrane technology is to control membrane structure and thus membrane performance (flux and rejection). Membrane with higher flux leads to higher productivity and lower capital costs whereas membrane with higher rejection leads to higher recovery and lower power costs. This objective is not easy to achieve because membrane structure and performance depend upon different factors like polymer choice, composition and temperature of coagulant and dope solution among others (Torrestiana-Sanchez *et al.*, 1999). Furthermore, by changing one or more of these variables, which are dependent on each other membrane structure can be affected quite significantly. The main task in optimal design of membrane processes is to ensure maximum permeate flow while having maximum solute rejection, with minimum capital and operating cost. Thus, it is desirable to have a membrane lifetime as long as possible. Membrane lifetime and permeate fluxes are primarily affected by the phenomena of concentration polarization (solute build-up) and fouling (microbial adhesion, gel layer formation and solute adhesion) at the membrane surface (Khulbe *et al.*, 2000). Concentration polarization and fouling can reduce the flux and the separation performance of the membrane itself. Therefore, membrane lifetime may be enhanced through the use of spacers between the membranes. Beside that, backflushing technique with high pressure is required to ensure the separation performance back at normal mode. Hence, more energy consumption will be needed.

Most of the early membranes were limited for commercial applications due to a lack of productivity, because membranes had to be relatively thick and dense to avoid irregularities on membrane surface that caused a dramatic loss in selectivity

(Geankoplis, 1995). During the last 30 years, membrane researchers have focused on aspects such as composition and temperature of dope solution, length and humidity of the airgap, dope extrusion rate, composition and temperature of external coagulant and relative exchange rate between the solvent and coagulant at the inner and outer surfaces of nascent fiber during hollow fiber spinning in order to obtain hollow fiber membranes with high performance (Qin *et al.*, 2000). In 1986, East and his co-worker reported that air gap length and spinning temperature had no effect on permeation rate and selectivity whereas increase of draw ratio in the air gap resulted in reduced permeability (East *et al.*, 1986). However, Chung and Hu (1997), Aptel *et al.* (1985) and Ekiner and Vassilatos (1990) reported that the increase in air gap value will result in reduction of permeability but the selectivity was increased. Their view is being shared by Liu *et al.* (1992). They reported that the average pore size on polysulfone/polyethersulfone membrane surface in the bore decreased with an increased in the length of the air gap from 30 to 200 cm. This is because the nascent fiber was stretched and elongated by its own weight and the polymer aggregates moved closer together and rearranged themselves into a state of greater stability. Similarly, Miao *et al.* (1996) demonstrated that PEG separation increased or the average pore size on the bore surface of polyethersulfone hollow fiber ultrafiltration membrane decreased when the air gap length increased from 50 to 120 cm.

In case of shear-induced molecular orientation during hollow fiber formation, Chung *et al.* (2000a; 2000b), and Qin *et al.* (2000) have investigated the effect of shear stress within the spinneret on morphology and properties of hollow fiber membranes for liquid and gas separation. Their results suggested that the hollow fiber membranes spun with enhanced shear had a lower flux but higher separation due to the greater molecular orientation induced in the high-sheared fibers. Later, Qin *et al.* (2001) conducted an experiment in order to study the effect of wet and dry-jet wet spinning on the shear-induced molecular orientation during the formation of ultrafiltration hollow fiber membranes. Experimental results showed that pure water flux of the wet spun fibers is lower than that of the dry-jet spun fibers, but separation performance of the wet spun fibers is higher. The results indicated that the wet spun fiber has smaller pore and/or a denser skin than the dry-jet wet spun fibers.

On the other hand, it is believed that bore fluid has an extraordinary influence on the formation of selective skin layer. The bore fluid must provide a highly open circular lumen on the inside of the hollow fiber without affecting the dry/wet phase separation processes occurring at the outside surface. In order to obtain a circular lumen on the inside of hollow fiber, it is believed that bore fluids having low water activity should be employed. Therefore, Pesek and Koros (1994) investigated the influence of water activity in bore fluid on the separation performance of asymmetric polysulfone hollow fiber membrane. They employed both dimethylacetamide/water and potassium acetate/water mixtures as bore fluids to control mass transfer of solvents and non-solvents at the fiber bore. In case of potassium acetate/water as a bore fluid, they showed that by decreasing water activity, the selectivity of membrane is increased. The same trend was also observed in the case of bore fluid of dimethylacetamide/water mixture. Thus, they concluded that the permeation properties of hollow fiber appear to be dependent only on the water activity of the bore fluid and independent of the type of bore fluid. This view was also agreed by Ismail *et al.* (1999). They suggested that lowering the bore fluid coagulation strength is necessary to preserve a highly engineered super-selective active layer. As a result, the membrane with high selectivity was prepared.

However, not much work has been done to investigate such effect on liquid separation especially on enzyme purification. Although, a study on the purification of lysozyme from chicken egg white using hollow fiber ultrafiltration membrane has been done by Ghosh *et al.* (2000) and Ghosh and Cui (2000), but their study focus more on the effects of the process parameter. The effects of transmembrane pressure (TMP) and cross-flow velocity have been investigated on membrane performance (permeate flux and productivity). Therefore, this present study concentrates more on the development and optimization of membrane formation process in order to produce asymmetric hollow fiber ultrafiltration membrane for cyclodextrin purification.

1.3 Objectives of the Study

Based on the above problem statement, the objectives of this study are as follows:

1. To formulate polyethersulfone polymer solution in order to produce high performance asymmetric hollow fiber ultrafiltration membrane for cyclodextrin separation.
2. To investigate the effects of fabrication conditions on membrane structures and separation performance.
3. To characterize hollow fiber membrane by using scanning electron microscopy (SEM) and plane polarized infrared Fourier transform spectroscopy.

1.4 Research Scopes

In order to achieve the above-mentioned objectives, the following scopes of study were outlined:

1. Developing an optimum polymer solution and spinning condition for asymmetric hollow fiber ultrafiltration membranes.
2. Studying the effects of dope extrusion rate (DER), bore fluid and polymer concentration on membrane performance and morphology.
3. Testing the produced membrane with distilled water, polyvinyl pyrrolidone (PVP) K15, PVP K25, PVP K30 and cyclodextrin solution in order to characterize the membrane in terms of flux and rejection.

4. Characterizing the structure and morphology of asymmetric hollow fiber ultrafiltration membranes by using scanning electron microscopy (SEM).
5. Measuring molecular orientation on the skin layer of asymmetric hollow fiber membranes by using plane polarized infrared Fourier transform spectroscopy.