

DEVELOPMENT OF NANOFILTRATION POLYETHERSULFONE HOLLOW
FIBER MEMBRANE FOR CYCLODEXTRIN GLYCOSYLTRANSFERASE
(CGTase) SEPARATION

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

Faculty of Chemical Engineering and Natural Resources Engineering
Universiti Teknologi Malaysia

AUGUST 2004

Allah the almighty says in the Holy Quran chapter 55: versus 19 – 21:

*He has let free
The two seas
Meeting together:*

*Between them is a barrier
Which they do not transgress:*

*Then which of the favors
Of your lord will ye deny?*

And in Chapter 25: versus 53:

*It is He Who has
Let free the two bodies
Of flowing water
One palatable and sweet
And the other salt
And bitter; yet has He
Made a barrier between them
A partition that is not
To be passed*

(Translation by Abdullah Yusof Ali)

Especially for my beloved parents (Siti Hajar Binti Basirah and Jalil Bin Naim), thank you for all your love and support, this thesis is the symbol of your success in educating me. To my brother (Ismail Bin Jalil), may this thesis be an inspiration and guidance for you in the future. My guardian angel (Kuntik Asmah Binti Abdullah), who gave me inspiration, encouragement and endless support throughout the success of my study. Last but not least, I render my thanks and deep sense of love to Mohd. Idham Bin Mustaffar.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to my beloved parents and my brother. Secondly, I would like to extend my profound sense of gratitude to my both dedicated supervisors, Associate Professor Dr. Shahrir Hashim and Professor Dr. Ahmad Fauzi Ismail (who had really planted the seed of membrane technology in my brain) for their continuous support and steady supervision through out the course of my research. Their strong support and interest in my research project had created a very friendly research environment, which made the research enjoyable.

I also render my thankfulness to School of Graduate Studies, UTM for the generous financial support and providing me scholarship, UTM-PTP as to carry out my study.

Then, I would like to extend my sincere appreciation to all Membrane Research Unit (MRU) UTM members especially to Mr. Sohaimi Abdullah and Mr. Ng Be Cheer for their outstanding help and guidance. To Mr. Mohd. Idham Bin Mustaffar, thank you for all your time and support throughout the study. Thanks also to Miss Suhaina Binti Mohd. Ibrahim for her support and friendship. It is my pleasure to thank Mr. Ayub Bin Abu, from Makmal Sains Bahan (Faculty of Mechanical Engineering) for his outstanding SEM assistance and Dr. Noor Khaidawati Bin Mohd Sayudi for her assistance with Total Organic Carbon (TOC) analyzer equipment.

Finally, I would like to take this opportunity to express my sincere appreciation to all those and organization who contributed to this research as well as to those who have directly or indirectly assisted me in the preparation of this thesis. Above all, I thank Allah the almighty for His grace, love, mercy and guidance through out my life.

ABSTRACT

The main objective of this research is to produce high performance nanofiltration (NF) hollow fiber membranes for Cyclodextrin Glycosyltransferase (CGTase) separation. For the first stage of this study, three types of spinning solution had been formulated by using titration method. These spinning solutions were formulated close to its cloud point (binodal line) in order to speed up the coagulation of nascent fibers so that the relaxation effect of molecular orientation was reduced. The dry/wet spinning process was applied in hollow fiber fabrication with water as bore fluid. At the second stage, hollow fibers were fabricated at four different type of dope extrusion rate (DER) ranging from 2.0 to 3.5 cm³/min. It was found that the optimum condition occurred at DER 2.5 cm³/min, which yields an optimal performance of sodium chloride rejection and better membrane morphology. The results exhibited that as the DER increased, the rejection value increases until critical level is achieved but the flux value gradually reduced. The optimized DER, at 2.5 cm³/min was selected to fabricate the fibers at different air gap length. Thus, by increasing air gap length, the rejection value is significantly increased. The results suggested that it is possible to separate the CGTase enzyme up to 99.11% with the flux of about 0.47 l/m².h and enhance the NF hollow fiber membranes performance in CGTase separation by the approach proposed in this study. Finally, at the last stage, the produced NF membranes were characterized by using Scanning Electron Microscope (SEM) and Attenuated Total Reflection Fourier Transform Infrared (FTIR-ATR). Results revealed that phase inversion and rheological factors significantly influencing the separation performance of Polyethersulfone (PES) NF hollow fiber membranes.

ABSTRAK

Objektif utama kajian ini adalah untuk menghasilkan membran gentian geronggang Nanoturasan (NF) untuk pemisahan Cyclodextrin Glycosyltransferase (CGTase) yang mempunyai prestasi pemisahan yang tinggi. Pada peringkat pertama kajian ini, tiga jenis larutan pemejaman telah dihasilkan menggunakan kaedah titratan. Larutan pemejaman dihasilkan sehingga menghampiri takat awan (garisan binodal) agar dapat mempercepatkan proses pembekuan membran gentian geronggang yang baru dan kesan santaian orientasi molekul dapat dikurangkan. Proses pemejaman kering/basah telah diaplikasikan untuk menghasilkan membran gentian geronggang dan air digunakan sebagai bendalir liang. Pada peringkat kedua, membran gentian geronggang dihasilkan pada empat jenis kadar penyerimpitan dop (DER) berbeza dari lingkungan 2.0 hingga 3.5 cm³/min. Didapati bahawa DER yang optimum berlaku pada 2.5 cm³/min dan menghasilkan prestasi pemisahan larutan garam yang optimum dan morfologi membran yang dikehendaki. Hasil ujikaji menunjukkan apabila DER meningkat, nilai prestasi pemisahan turut meningkat sehingga pada satu takat yang kritikal manakala nilai fluks pula didapati menurun dengan sekata. DER yang optimum pada 2.5 cm³/min telah dipilih untuk menghasilkan membran pada ketinggian sela udara yang berbeza. Oleh itu, dengan peningkatan ketinggian sela udara, nilai prestasi pemisahan turut meningkat. Kajian ini mencadangkan bahawa pemisahan CGTase boleh dilaksanakan dan berkemampuan untuk mencapai sehingga 99.11% dengan nilai fluks 0.47 l/m².h di samping meningkatkan prestasi membran gentian geronggang NF di dalam pemisahan CGTase dengan menggunakan kaedah yang telah dicadangkan. Pada peringkat ketiga, membran NF yang telah dihasilkan akan dicirikan dengan menggunakan Kemikroskopian Elektron Imbasan (SEM) dan Spektroskopi Infra-merah Penukaran Fourier - Pemantulan Jumlah Terkecil (FTIR-ATR). Hasil ujikaji menunjukkan bahawa faktor fasa balikan dan faktor reologi amat mempengaruhi prestasi pemisahan membran gentian geronggang Polietersulfona (PES) NF.

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LIST OF ABBREVIATIONS

DER	-	Dope Extrusion Rate (cm ³ /min)
JS	-	Jet Stretch ratio or draw ratio
MW	-	Molecular Weight (g/mol)
MWCO	-	Molecular Weight Cut-Off (Dalton)
PWP	-	Pure Water Permeability
RO	-	Reverse Osmosis
NF	-	Nanofiltration
UF	-	Ultrafiltration
MF	-	Microfiltration
BF	-	Bore Fluid
R	-	Rejection
TMP	-	Trans Membrane Pressure (bar)
CD	-	Cyclodextrin
CGT	-	Cyclodextrin Glycosyltransferase

NaCl	-	Sodium chloride
PES	-	Polyethersulfone
NMP	-	1-Methyl-2-Pyrrolidone
PVP	-	Polyvinyl pyrrolidone
PEG	-	Poly (ethylene) glycol
NSA	-	Non-solvent additive
TOC	-	Total Organic Carbon Analyser
SEM	-	Scanning Electron Microscope
FTIR-ATR	-	Attenuated Total Reflection Fourier Transform Infrared
VEP	-	Volume Extrusion from Pump
SS1	-	Spinning Solution 1
SS2	-	Spinning Solution 2
SS3	-	Spinning Solution 3
PVP K15	-	Polyvinyl-Pyrrolidone K15
PVP K25	-	Polyvinyl-Pyrrolidone K25
PVP K30	-	Polyvinyl-Pyrrolidone K30
CGTase K67	-	Cyclodextrin Glycosyltransferase K67

LIST OF SYMBOLS

D	-	Diameter
V_o	-	Spine line initial velocity (cm/s)
V_f	-	Spine line final velocity (cm/s)
A_{sp}	-	Cross sectional area of annulus in spinneret (cm ²)
t	-	Time for 1 revolution
C_p	-	Solute concentration of permeate
C_f	-	Solute concentration of feed
V	-	Permeate volume (ml)
t	-	Time (min)
A	-	Surface area of hollow fiber membrane
Δp	-	Pressure gradient
J	-	Flux
K	-	Permeability
u	-	Membrane thickness
M_r	-	Molecular Weight

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CHAPTER I

INTRODUCTION

1.1 Membrane Separation Technology

Membrane processes has become a new demanding separation technique in order to fulfill the requirement in many industrial processes based on separations. Membranes are among the most important engineering component in use today, and each year more effective uses for membrane technologies are found for various applications. This technology have wide industrial applications covering many existing and emerging uses in the chemical, petrochemical, biotechnological, petroleum, environmental, water treatment, pharmaceutical, medical, food, dairy, beverage, paper, textile and electronic industries. The technology has emerge to be the most economical separation technique since it posses low capital investment as well as low energy consumption and operating cost. Therefore, membrane separation technology can be used to satisfy many of the separation requirements in the process industries.

Membrane performance can be defined in terms of two simple factors, flux and retention or selectivity. Flux or permeation rate is the volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time. Selectivity is a measure of the relative permeation rates of different components through the membrane. Retention is the fraction of solute in the feed retained by the membrane (Scott, 1995). Therefore, membrane with the highest selectivity or retention and with a high flux or permeability is required although

typically attempts to maximize one factor are compromised by a reduction in the other.

Membranes and separations have become a multimillion-dollar industry, growing at the rate of 10% to 20% per year. Membrane technology can provide continuous operation and stable separation quality with the potential to remove targeted solutes in one stage. However, recently membrane technology has improved and even widens up its applications in another field which promising very good prospects – biotechnology. The results are tangible and a breathtaking array of basic discoveries having commercial potential in medicine, pharmaceutical, food, beverages, drinking water and waste water treatment. This can be considered new in certain area, and therefore many research and development has been done in order to fulfill the demand and the market growth in this field. To date, enzyme such as Cyclodextrin Glycosyltransferase (CGTase) is one the most important enzyme in industrial since it posses many advantages in pharmaceutical, medical, cosmetics, food processing, toiletry, pesticides and chemical industries.

Recently, membranes have gained wide acceptance and made significant inroads against competing technologies in many areas, because of flexibility and performance reliability of membrane system, cost competitiveness, increasing demand and environmental awareness. In biotechnology, membrane system could be potentially suitable for treating the dilute solutions and finely dispersed solids, especially those which are compressible, have a density close to that of the bulk phase, have high viscosity, or are gelatinous (colloidal suspensions); low molecular weight, non-volatile organics or dissolved salts; pharmaceutical and biological materials which are sensitive to their physical and chemical environment. According to www.bccresearch.com the total market for biotechnology-enabling technologies and selected products (food, medicine and pharmaceutical) is estimated at nearly \$12.5 billion in year 2000. This market is expected to rise at an 'Average Annual Growth Rate' (AAGR) of 19.3% to 22.8% to as much as \$34 billion in year 2005 (Ismail *et al.*, 2002).

The biotechnology industry, which originated in the late 1970s, has become one of the emerging industries that draw the attention of the world, especially with the emerged of producing medically important biological products (i.e protein, enzyme and insulin) by using membrane separation method. Membrane separations have proven to show higher protein yields. Two major interest applications in biotechnology are the separation and purification of the products. Consequently, by using membrane separation technology especially hollow fiber membrane in enzyme separation, it could enhance the enzyme separation up to almost 100 percent. The highest enzyme separation can be only achieved by fabricating the finest hollow fiber membrane especially in its separation performance and the membrane structure.

1.2 Problem Statement

The fast growth in the field of biotechnology along with rapid commercialization of biological products has led to an increased for efficient separation technique. Thus, the new type of separation technique should be developed although the separation efficiency of the conventional method (i.e. High performance liquid chromatography) is high. Membrane materials with high permeability and selectivity, and advanced fabrication technologies to produce membrane with high separation performances are the primary focuses for most membrane scientists in the last two decades. Therefore, membrane processes is believed and probably the most suitable method to replace the old conventional method.

The effect of spinning conditions on the performance of nanofiltration membranes is discussed with strongly emphasis on the rheological effects. Although many works have been done in the past 30 years there was not much research on rheological factors that affecting membrane performance. Since then, this aspect has received great attention by membranologist in developing hollow fiber nanofiltration membrane. Therefore, in this study the effect of both phase inversion and rheological factor in fabricating hollow fiber has been considered. Significant

progresses have been made in membrane materials, dope preparation, and fundamental understanding of membrane formation mechanism. The effect of spinning conditions such as dope extrusion rate (DER) and air gap length on the hollow fiber morphology and separation properties have been much discussed and reported; even though sometimes-contradictory results occurred.

For the past few years, the influences of rheological conditions on the permeation characteristics for gas separation hollow fiber membranes have been extensively studied in order to improve knowledge of membrane manufacture and performance. It was reported by Ismail *et al.* (1997b) and Shilton *et al.* (1997) that increased shear rates during spinning of membranes produced hollow fibers with enhance (or high improvement) selectivity and flux for gas separation application. Recently for liquid separation, Ani Idris *et al.* (2002b) has reported for reverse osmosis hollow fiber membrane that there is a fairly strong correlation between extrusion shear rate and the rejection rate of the membranes, whereby as the shear rate increases, the rejection rate increases, suggesting that there exists an optimum shear rate which yields optimal membrane morphology for reverse osmosis hollow fiber membranes. It was clearly shown that extrusion shear have great effect on the hollow fiber membrane performance for gas or liquid separation.

However, not much research has been done to study the rheological effects in producing nanofiltration hollow fiber membrane for CGTase separation. Therefore, for this research, nanofiltration hollow fiber membranes were fabricated with specially formulated spinning solution at different compositions. Variation in dope compositions provided us with the opportunity to investigate hollow fiber membrane with different morphology and structure. Preparation of Polyethersulfone (PES) nanofiltration hollow fiber membranes and detailed studies regarding the preparation, separation performances and characterizations by coupling the effects of phase inversion and rheological influences are still lacking. Therefore, in order to further advanced the knowledge of nanofiltration hollow fiber membrane fabrication and its influence on separation performance, it is attempts to investigate the possibility of enhancing the nanofiltration separation performance by increasing DER experienced during the fabrication of nanofiltration hollow fiber membranes.

In commercial separation applications, membrane based on liquid separation is broadening up its usage especially in enzyme separation. It is believed that membrane technology is one of the best separation methods because it offers many advantages during its operation. It is economic viability and flexibility since they can be easily scaled down for operation at partial capacity or scale up by adding membrane modules in stages to accommodate higher capacities. However, the ability of nanofiltration membrane to work at lower pressures than reverse osmosis is attracting more interest in the technology. In addition, there is not much research has been done in order to separate enzyme by using membrane technique. For CGTase enzyme separation, it is believed that the nanofiltration separation method can possibly replace the old conventional methods in enzyme separation. If this process is capable, huge amount of energy and money saving can be expected.

1.3 Objectives of Study

The aim of this research is to develop high performance locally produced nanofiltration Polyethersulfone hollow fiber membrane for CGTase enzyme separation. In order to achieve this target, several important matters should be accomplished.

- i) To design and formulate spinning solution composition for the fabrication of nanofiltration hollow fiber membrane.
- ii) To determine the effects of fabrication conditions on the separation performance and membrane structure by using Dry/Wet Spinning Process.
- iii) To evaluate nanofiltration hollow fiber membranes performances for Cyclodextrin Glycosyltransferase (CGTase) separation.
- iv) To characterize the hollow fiber membranes using Scanning Electron Microscope (SEM) and Attenuated Total Reflection Fourier Transform Infrared (FTIR-ATR).

1.4 Research Scopes

To achieve the objectives of this research, some guidelines should be followed. Five main scopes for this study have been recognized to be the guidelines in order to produce high performance nanofiltration hollow fiber membrane that support with high flux and rejection value.

- i) Spinning solutions were formulated from a composition consists of polymer/solvent/polymeric additives/non-solvent. An optimized spinning solution formulation consists of Polyethersulfone (PES) as the polymer, 1-Methyl-2-Pyrrolidone as the solvent, Polyethylene glycol 400 (PEG 400) and Polyvinyl-pyrrolidone K30 (PVP K30) as the polymeric additive and water as the non-solvent.
- ii) Hollow fiber membranes were spun and fabricated at the optimized spinning conditions. During the membrane fabrication, two spinning parameters were studied, there are the dope extrusion rate (DER) and air gap height. The best and optimum level of DER was investigated. Then, fibers were spun at an optimized DER at different level of air gap height.
- iii) Measured the separation performances of developed nanofiltration hollow fiber membranes using sodium chloride (NaCl) solution, different molecular weight of polyvinyl-pyrrolidone (PVK K15, PVP K25 and PVP K30) and CGTase 67 K.
- iv) Morphological studies of the nanofiltration hollow fiber membrane surface and cross-section were determined by Scanning Electron Microscope (SEM). Direct measurement of molecular orientation in nanofiltration hollow fiber membranes were investigated by using (FTIR-ATR).