

**Effect of Organic and Inorganic Additives in
Membrane Composition on the Properties and
Performance of Nanofiltration Membrane for
Xylose and Glucose Separation**

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Membrane Composition on the Properties and
Performance of Nanofiltration Membrane for Xylose
and Glucose Separation**

NUR'AMIRAH BINTI ABDUL GHAFAR

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Hons)

**Faculty of Chemical & Natural Resources Engineering
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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Hons).

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

The Almighty Allah, The most Gracious and The most Merciful

I also want to thank my mum and dad that always inspire, love and stand by me. My beloved friends and also my supervisor that always guide and help me to complete this study.

Thank you for all your love, care and support.

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Bismillah, In the name of Allah S.W.T, The Most Beneficent and the Most Merciful. Alhamdulillah, I have gained my source of strength, protection, guidance, and blessed from Allah and I be able to face all the impediments and the hardships of completing this research.

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ABSTRACT

World production of biomass is estimated at 146 billion tons a year. The biomass resources can be used to meet variety of needs such as energy needs and food industries. Xylose and glucose are among the most abundant component that can be found in the biomass source. The purpose of the separation of xylose from glucose is to fully utilize the sugar component from the biomass source. Recent studies have found that nanofiltration (NF) method is possible for separation of xylose and glucose. Compared to the chromatography process, NF membrane is simple process, cost-effective and easy-maintenance. The objective of this study is to study the effect of organic and inorganic additives in membrane composition on the properties and performance of NF membrane for xylose and glucose separation. PES polymer is used in a casting solution with N-Methyl-2-pyrrolidone (NMP) as a solvent, PEG-200 and zinc chloride ($ZnCl_2$) as an additive to the solution. The membrane performance of the membrane is investigated by varying 2 different types of additives with concentration that is 2 wt. %, for PEG-200 and 2 wt. % for zinc chloride. Membrane performance test was carried out with dead end filtration test by using Amicon Millipore stirred cell (Model 8200) with constant stirring speed at 300 rpm and temperature at ambient. Refractometer was used to analyse the samples concentration from separation process. It is found from the developed membrane, the addition of additives shows decreases in flux and the membrane permeability. The membrane type also changes from NF to RO range as organic additives and inorganic additives are mixed together. The membranes also have 99% rejection for both xylose and glucose and separation factor of xylose from glucose is almost 1. From the separation factor it shows that the membrane cannot separate the xylose from glucose. From the pore radius calculation it is found that the membrane pore size is in average 0.3 nm for all membrane had become one of the reason xylose cannot separated as its radius bigger than the pore size and xylose cannot pass through the membrane.

Key words: Biomass, Nanofiltration membrane, Separation Xylose/Glucose, Organic Additives, Inorganic Additives

ABSTRAK

Di seluruh dunia, bahan biomas dihasilkan dianggarkan berjumlah 146 juta bilion tan setiap tahun. Sumber bahan biomas boleh digunakan untuk menepati pelbagai keperluan seperti sumber tenaga dan di dalam industry makanan. Xylose dan glukosa adalah komponent paling banyak yang boleh dijumpai di dalam sumber biomas. Tujuan memisahkan xylose daripada glukosa adalah untuk menggunakan sepenuhnya komponen gula yang terdapat di dalam sumber biomas. Kajian terbaru telah menemui membran nanofiltrasi mampu untuk memisahkan xylose dan glukosa. Berbanding dengan process kromatografi, membrane nanofiltrasi adalah lebih mudah, kos efektif dan mudah untuk diselenggara. Tujuan kajian ini adalah untuk mengkaji kesan penambahan bahan tambahan organik dan bukan organik di dalam komposisi membrane terhadap sifat and prestasi NF membran untuk pemisahan xylose dan glukosa. PES polimer digunakan di dalam larutan bersama N-Methyl-2-pyrrolidone (NMP) sebagai pelarut, PEG-200 dan zink klorida $ZnCl_2$ sebagai tambahan kepada larutan. Prestasi membrane diuji dengan menggunakan berlainan jenis bahan tambahan dengan kepekatan 2 % berat untuk PEG-200 dan 2 wt. % untuk zink klorida. Untuk ujian prestasi membrane dijalankan menggunakan penapisan ujian buntu menggunakan Amicon Millipore sel dikacau (Model 8200) dengan kelajuan tetap pada 300 putaran per minit dan suhu ambien. Refractometer digunakan untuk menguji kepekatan sampel yang diambil dari ujian buntu. Hasil daripada kajian mendapati penambahan bahan tambah menunjukkan penurunan dalam fluks dan kebolehtelapan membran. Jenis membran juga berubah dari NF kepada RO apabila bahan tambah organik dan bahan tambah bukan organik dicampur sekali. Membran yang dihasilkan juga menunjukkan 99% penolakan terhadap xylose dan glukosa dan faktor pemisahan xylose daripada glukosa hampir 1. Daripada faktor pemisahan itu menunjukkan membran yang dihasilkan tidak dapat memisahkan xylose daripada glukosa. Pengiraan radius liang membrane menunjukkan purata saiz adalah 0.3nm untuk kesemua membrane antara satu sebab xylose tidak dapat dipisahkan kerana radius molekul xylose lebih besar daripada liang membran.

Kata kunci: Biomass, Nanofiltration membran, Pemisahan Xylose/Glukosa, Bahan tambah Organik, Bahan tambah bukan organik

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LIST OF SYMBOLS

R_{xyl}	retention of xylose
R_{glu}	retention of glucose
X_{xyl}	xylose separation factor

Subscripts

f	feed
p	permeate
c	concentrate
r	retentate

LIST OF ABBREVIATIONS

PES	Polyethersulfone
NMP	N,N-dimethylformamide
PEG-200	Polyethylene Glycol (200)
NF	Nanofiltration
UF	Ultrafiltration
MF	Microfiltration
RO	Reverse Osmosis
MWCO	Molecular weight cut off

1 INTRODUCTION

1.1 Background of study

Biomass is organic substances mainly composed of carbon, hydrogen and oxygen. They are living or have recently lived in the world and have solar energy stored in its molecular bonds. The resources included wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing, aquatic plants and algae. Biomass consists of any heterogeneous mixture of organic substances and a small amount of inorganic substances (Demirbas, 2001). Biomass could be the source of lignocellulose feedstock as they have high carbohydrate content and have potential for large-scale bioethanol production. Lignocellulose consists of lignin, carbohydrates such as cellulose and hemicellulose, pectin, proteins, ash, salt and minerals (Van Dyk and Pletschke, 2012). Cellulose is the predominant polymer in lignocellulosic biomass and can be converted to ethanol in a two-step process. First process is through hydrolysis to convert cellulose to glucose sugar and then converted to ethanol by fermentation process (El-Zawawy et al., 2011).

Most of the monosaccharides such as glucose and xylose are very important for the ingredients in food, pharmaceutical industries and as a source of alternative energy. The pure fractions of a specific monosaccharides are thus needed for the production of xylitol and ethanol but the separation of monosaccharides from each other is quite complex for the industrial scale (Sjoman et al., 2007). The separation is important for the commercial purification of xylose for xylitol production. The uses of xylitol in the food industry keep on increasing because of their several advantages such as anticarcinogenic properties, does not cause acid formation, and having low viscosity and negative heat effect when dissolved in a solution.

Currently, the common method used to separate xylose from glucose is by using liquid chromatography. Chromatography is very efficient method to separate chemical compound (Bi et al., 2010) but sometimes it can involve very complex step. A more cost-effective and easy maintenance technique for sugar separation using nanofiltration (NF) membrane was showed by (Sjoman et al., 2007). However, they are using commercial NF membrane.

In the current study, flat sheet NF membrane was developed to separate xylose from glucose. Polyethersulfone (PES) was used as a polymer material with N-Methyl-2-pyrrolidone (NMP) as a solvent. The effect of organic additives, Polyethylene glycol (PEG-200) and inorganic additives, zinc chloride on the membrane performance was studied.

1.2 Motivation

The current method available in the industry to recover xylose is chromatographic separation. While for separation of xylose from glucose by using nanofiltration membrane, currently there is no commercial membrane that is specifically design for sugar separation. During the membrane preparation, some of the crucial factors that need to be controlled are the amount and type of polymer used, type of solvent and additives added into the spinning dope solution (Feng et al., 2013). The blending/additives technique has been considered to be one of the methods for surface improvement of membrane such as hydrophilicity, surface roughness, surface charge, and the pore size (Ahmad et al., 2013). The additives presence in the membrane solution will influence thermodynamic and kinetic properties of membrane solution. It will reduce the strength of polymer-solvent interaction and increase solvent-non solvent exchange rate to enhance the precipitation rate of membrane. By varying the additive concentration and molecular weight, enlarged or suppressed macrovoid can be obtained (Teta et al., 2013). The effect of different PEG molecular weight to PES in the casting solution already being studied on membrane morphologies and permeation properties by Idris et al., (2007). Currently none of the study on the effect of additives focuses on the separation of xylose and glucose.

1.3 Objective of the research

The objective of this research is to study the effect of organic and inorganic additives in membrane composition on the properties and performance of NF membrane for xylose and glucose separation.

1.4 Scopes of this research

The following scopes of research were outline in order to achieve the research objectives:

- i. To cast flat sheet membrane through casting method using 18 wt. % polyethersulfone (PES) in different amount of additives dissolves in N-Methyl-2-pyrrolidone (NMP) solvent
- ii. To study the effect of two different additives composition of PEG 200 (2 wt.%) and ZnCl₂ (2wt.%) in PES dope polymer solution
- iii. To characterize the properties of NF membrane in terms of water flux and pore size.
- iv. To evaluate the performance of NF in terms of retention and separation factor for xylose/glucose under dead end filtration.

1.5 Main contribution of this work

The following are the contributions of this study:

- a) The best type of additives that give better morphology, water flux and membrane pore size to be used for xylose and glucose separation.
- b) The effectiveness of using 2 different additives in the same dope solution for better retention of glucose and separation factor for xylose and glucose separation.
- c) This work will add more research being done to improve the membrane performance for better separation of xylose from glucose.

1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides the literature review for this study. It started with the introduction of biomass where it generally describes the source of biomass and the advantages of utilizing biomass source. This chapter continues to introduce the process involved in biomass processing. Different conversion technologies of biomass are explained briefly. After that, sugar separation technology are being introduces. Currently, there are two methods to separate sugar that is chromatography that already being used commercially and then by using nanofiltration membrane that still in research scale. Membrane technology was discussed next in the literature review which covered

different types of membrane technology such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis. For the separation of xylose from glucose, the best type of membrane process is by using nanofiltration as it has higher selectivity than ultrafiltration and microfiltration membrane and lower pressure needed than reverse osmosis. This chapter continues with the explanation about nanofiltration membrane (NF) and then the effect of additives on the membrane formation.

Chapter 3 describes the material and methodology used in this study. The chapter started with an overview of the whole methods involve follow by brief introduction about the chapter. The following part was covered in Chapter 3 such as, chemicals being used, membrane fabrication method, dead end filtration and analytical method for sugar analysis.

Result and discussion were discussed in the Chapter 4. This followed by the last chapter, which is Chapter 5 that draws the conclusion from current study and lists several recommendation for future study.

2 LITERATURE REVIEW

2.1 Biomass

Biomass is the name given to all the earth's living matter. Its resources come from wood, wood wastes, agricultural crops and their by-products, municipal solid wastes, animal wastes, waste from food processing, aquatic plants and algae. The classification of biomass according to its origin is shown in Figure 2-1 (Roberts et al., 2015). It is an organic substance that is mainly composed of carbon, hydrogen and oxygen (Tekin et al., 2014). World production of biomass is estimated at 146 billion tons a year and most of it is wild plant growth. Biomass resources can be used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles and providing process heat for industrial facilities (Demirbas, 2001). The energy in biomass from plant matter originally comes from solar energy through the photosynthesis process. It will be stored in plants and animals and recovered by burning biomass as fuel (Demirbas, 2001).

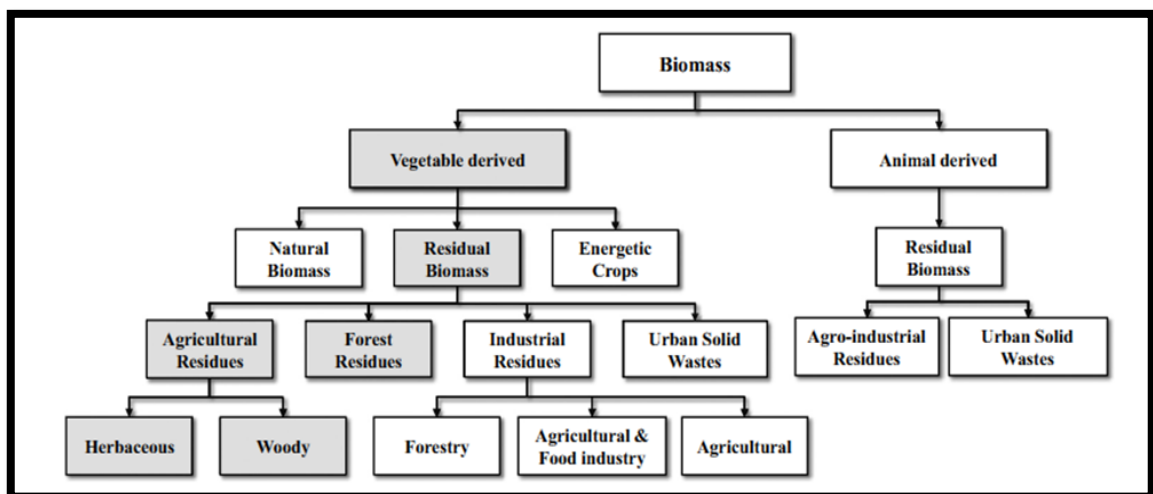


Figure 2-1 Classification of biomass according to its origin (Roberts et al., 2015).

As a result of increasing world population and rapidly evolving industries, energy demand constantly increasing. The consumption of fossil fuels such as oil, coal and natural gas had increased and caused significant environmental pollution. Harmful gases linked to the greenhouse effect and global warming, have been released into the atmosphere. These phenomena had made the search for alternative energy sources have gained great importance because uses of fossil fuels are harmful to the environment and their supply also is limited (Tekin et al., 2014). Besides that, the point where the cost of

producing energy from fossil fuels exceeds the cost of biomass fuels has been reached making the use of biomass as renewable energy keep on increasing (Demirbas, 2001).

Biomass has high utilization potential as an alternative to fossil fuels and one of the most important energy sources of the future. The advantage of biomass is that it is a clean energy source as the usage of this energy does not add carbon dioxide to the environment. The carbon dioxide taken from the atmosphere by plants through photosynthesis is utilized by the plants as a source of energy and returned to the atmosphere without additional carbon dioxide released (Tekin et al., 2014). By using biomass as a source of energy and replacement of non-renewable energy source could result in net reduction in greenhouse gas emissions as it is carbon dioxide neutral. Besides that, biomass fuels have negligible sulphur content which does not contribute to sulphur dioxide emission that cause acid rain.

In addition, biomass is known as the most common forms of renewable energy (Mckendry, 2002). The formation of fossil fuels takes millions of years, while plants used as a source of biomass that grow in periods of months or years. Among the renewable energy resources, biomass has a high utilization potential among renewable energy resources. It can be directly burn or indirectly by converting it into liquid or gaseous fuel.

Besides that, uses of biomass from wastes can give good influence to the economics of plant operations and also helps to solve problem on disposal of wastes in the developed country. One analysis provided by the United Nations Conference on Environment and Development estimates that biomass could supply about half of the present world primary energy consumption by the year 2050.

Biomass source is a potentially sustainable and relatively environmentally benign source of energy. Using of biomass resources also could reduce the problems towards waste disposal. As for the benefits of using biomass energy it will provide clean, renewable energy source that could dramatically improves our environment, economy and energy security. Other than that, biomass energy will generate far less air emissions than fossil fuels, reduces the amount of waste sent to landfills and decreases our reliance on foreign oil.

In addition, production and utilization of bioethanol had attracted a worldwide attention as a strategy for reducing global warming and to improve global energy security. Since 2007, most of the bioethanol produced from sugar or a starch that is obtained from fruits and grains. Ethanol also could be produced from a number of renewable resources other than starches or sugar such as lignocellulosic materials. Currently, lignocellulosic materials continue to be investigated as a source of fermentable sugars for biofuels production because of its high availability (Tekin et al., 2014).

2.2 Biomass processing

A biomass is any heterogeneous mixture of organic substance and a small amount of inorganic substance. Cellulose, hemicellulose, lignin, and extractives are the main components of lignocellulosic materials. Lignocellulose feed stock, such as agricultural and forest residues, industrial and municipal wastes, and dedicated energy crops, by virtue of their high carbohydrate content, hold tremendous potential for large-scale bioethanol production. Lignocellulosic waste materials contain cellulose that is the predominant polymer in combination with lignin and hemicellulose in smaller amount. The cellulose compound can be converted into glucose sugar by hydrolysis and the resulting sugars can be converted to ethanol by fermentation. There also has been significant progress in the conversion of vegetable oil and animal fat into biodiesel as an alternative to petroleum-based diesel fuels. Biodiesel can be produced by the transesterification of oils. Oils obtained from plants, such as soybean, canola, corn, and rapeseed, are the most widely used raw materials for biodiesel production (Tekin et al., 2014).

Technologies used to convert biomass into either bio-fuel with high energy content or valuable chemicals can be classified under two groups as shown in the Figure 2-2.

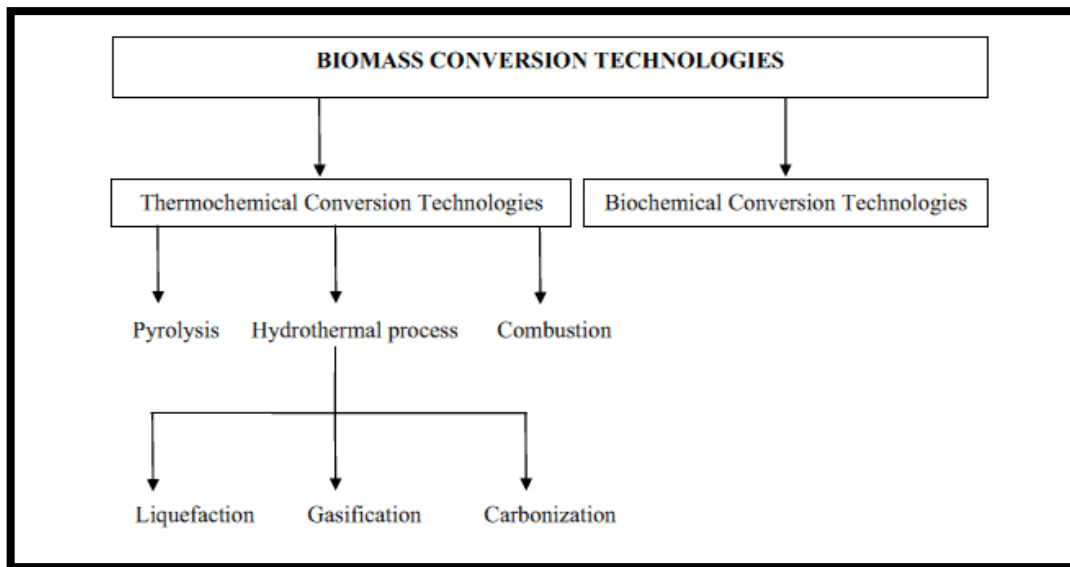


Figure 2-2 Biomass conversion technologies(Tekin et al., 2014)

The first group, biochemical conversion technologies, degrades biomass with enzymes and microorganisms. While, second group will convert biomass with thermochemical conversion technologies that degrade biomass with heat. The degradation of biomass by biochemical processes occurs naturally. These processes, which include aerobic and anaerobic degradation, fermentation, and enzymatic hydrolysis, are performed by bacterial enzymes and micro-organisms. The process in which yeast converts biomass into sugar and subsequently ethanol and other chemicals is called fermentation. It is used for commercial purposes and usually, a hydrolysis pre-treatment is used to convert cellulose and hemicellulose into sugar. Biomass can be directly used in combustion processes in order to obtain heat or to generate electricity. Products obtained from biomass gasification processes are generally used to generate heat or electricity in an engine or turbine. Solid and liquid products resulting from pyrolysis and liquefaction processes can be used as fuel after various improvements(Tekin et al., 2014).

The thermochemical conversion technologies can be subdivided into combustion, pyrolysis, liquefaction and gasification. The direct combustion is widely used on various scales to convert biomass energy to heat or electricity with the help of a steam cycle such as stoves, boilers and power plants. It is the main process that is being adopted to utilize biomass energy. The energy produced through the combustion process can be used to provide heat or steam for cooking, space heating and industrial processes. Large biomass power generation systems can have comparable efficiencies to those of

fossil fuel system, but the conversion process has a higher cost due to the moisture content of biomass. However, the economics can be significantly improved by using the biomass in combined heat and electricity production systems (Demirbas, 2001).

In the meantime, pyrolysis conversion process will convert biomass into liquid (bio-oil or bio-crude), charcoal and non-condensable gases, acetic acid, acetone and methanol by heating the biomass to about 750 K in the absence of air. It will produce energy fuels with high fuel-to-feed ratios, making it the most efficient process for biomass conversion and the method is the most capable of competing with and eventually replacing non-renewable fossil fuel resources. Through this process, the biomass will be heated in the absence of oxygen, or partially combusted in a limited oxygen supply. This will produce a hydrocarbon rich gas mixture, an oil-like liquid and a carbon rich solid residue.

For gasification conversion technology it is a form of pyrolysis, which is performed at high temperatures in order to optimize gas production. It is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency and to reduce the investment cost of biomass electricity generation through the use of gas turbine technology. Conversion efficiency up to 50% can be achieved using combined cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine.

The ethanol could be produced from certain biomass materials which contain sugars, starch or cellulose with alcoholic fermentation conversion method. The best known source of ethanol is sugar cane, but other materials also can be used such as wheat and other cereals, sugar beet, Jerusalem artichoke and wood. Before undergoing the fermentation process the biomass needs to be converted into monomer sugars by using enzymatic hydrolysis process. Throughout this process, the biological degradation of the carbohydrates within the biomass is achieved using multiple enzymes in defined ratios to convert the carbohydrates to their monomer sugars (Van Dyk and Pletschke, 2012). Based on the study by Chu et al. (2012) they explored an integrated process of enzymatic hydrolysis and fermentation to enhance ethanol production from corn stover. Enzymatic hydrolysis at low substrate loading was carried out to obtain high hydrolysis yield, which avoids high viscosity and end product inhibition.

Pre-treatment of lignocellulose biomass is crucial for achieving effective hydrolysis of substrates as enzymatic hydrolysis of native lignocellulose produces less than 20% glucose from the cellulose fraction. Although pre-treatment is costly, the cost of hydrolysis will even larger without pre-treating removal or disruption of lignin has been established as essential for efficient bioconversion of lignocellulose to sugars. The removal can be achieved in several ways either through physical, chemical or enzymatic means. Removal of lignin by chemical means is achieved through pre-treatment of biomass by methods such as acid hydrolysis, steam treatment or alkaline treatment (Van Dyk and Pletschke, 2012).

2.3 Sugar separation technology

2.3.1 High performance liquid chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) systems are commonly used technology to separate sugar such as monosaccharides, oligosaccharides, polysaccharides and neutral sugars in the industrial scale. There are different modes being used to separate sugars such as based on size exclusion, ligand conversion, partition, anion exchange and borate complex anion exchange.

Based on the previous study, one of the stationary phases used in liquid chromatography to separate sugar solution of xylose and glucose is silica-confined ionic liquid (IL) stationary phases (Bi et al., 2010). It is an efficient method for separation and determination of chemical compound. The stationary phases in liquid chromatography are used for separation of xylose and glucose includes those based on octadecylsilane and amino group as well as ion exchange resins. A typical separation media for ion-exchanged chromatography is sulfonated cross-linked styrene divinylbenzene cation exchange resin and it is the most applied in industrial separation. Silica-based columns still widely applied in small scale industries to separate sugar mixture with elution generally in order to increase the molecular weight. The disadvantage of the silica-based column is that it will gradually damage with the increase in water proportion. To overcome the weaknesses of the silica-based ionic liquid (IL) stationary phases were employed. It has been applied in many fields of analytical chemistry due to excellent chemical properties. It also had been synthesized and used as the stationary phases in high-performance liquid chromatography (HPLC) for separation of inorganic and organic compound (Bi et al., 2010).

2.3.2 Nanofiltration membrane (NF)

A cost-effective and easy maintenance method for the separation pentose sugar from hexose is by using nanofiltration (NF) membrane (Sjoman et al., 2007). The separation of uncharged substances is mostly based on the difference in molecular size and diffusivities. There is possibility for a partial separation of disaccharides (~300-360 g/mol) from monosaccharides (pentose and hexose, ~150-180 g/mol). Factors affecting the NF separation of saccharides, together with the membranes selectivity, are filtration pressure and temperature and total solution composition and concentration. An increase in pressure will lead to increased solvent flux and membrane compaction and these effects together will lead to an overall increase in retentions. While, for an increase in temperature from 25 to 60 °C was reported to decrease the retention due to reduced viscosity and increased diffusion. The size of a monosaccharide is equal or smaller than the cut-off sizes of NF membranes. The calculated diameters of the monosaccharide molecule approx. 0.6-0.8 nm and popular commercial NF are from 0.6-2.0 nm. Based on this study, NF has the possibilities to enhance the yield and partially replace chromatographic methods in xylose production. Sieving is the main separation mechanism with these small, uncharged and organic molecules. The retention of monosaccharides depend strongly on the permeate flux and higher retention were measured as permeate fluxes increased (Sjoman et al., 2007).

In addition, after researcher had found that it is possible to separate xylose and glucose with nanofiltration membrane, more advanced research had been made in order to improve the performance of membrane. Current research by (Mah et al., 2014) had study the ability membrane developed using interfacial polymerization reaction to separate xylose from glucose. Based on the characterization of the membrane developed, the average pore size of the membrane radius is 0.34 nm. Theoretically, xylose (Stoke radius = 0.325 nm and equivalent molar radius = 0.36 nm) can pass through the membrane and glucose (Stoke radius = 0.34 nm and equivalent molar radius = 0.36 nm) will be retained. Based on this study, increase in pressure will lead to decrease of separation performance which not in agreement with past studies and theory. The pressure difference used in this study was most likely too low for significant effect of pressure on NF to be seen. Decrease in xylose separation factor was observed at high xylose concentration in feed. This is probably caused by the concentration of polarization occurred that hindering the permeation of xylose.

2.4 Membrane technology

Membrane is a selective barrier between two phases. The membrane technology market is witnessing an era of rapid growth due to continuous research and development in both academia and private industry. Membrane technology has been applied for large variety of advance separation and purification processes, including biofuel production and purification. The advantages of membrane technology are it can minimize the capital cost, very flexible, provide compactness of the plant, have an optimal ratio between productivity and efficiency and also could save energy. Overall membrane separation basically depends on three basic principles: adsorption, sieving and electrostatic phenomenon. Figure 2-3 shows the schematic representation of the basic principle behind the membrane separation.

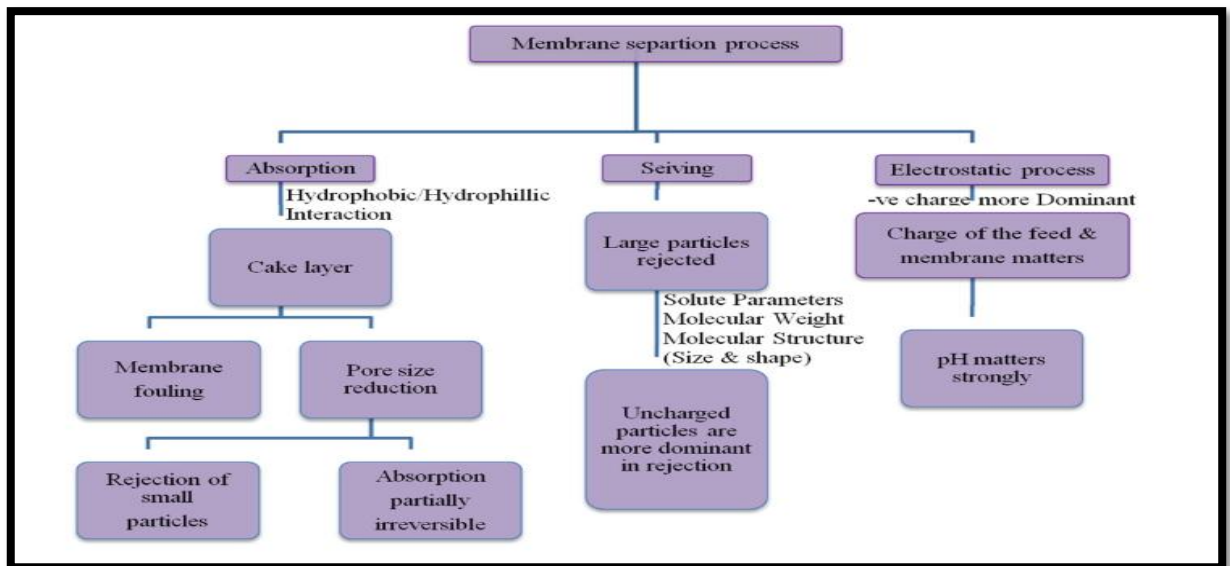


Figure 2-3 Schematic representing basic principles involved in membrane separation(Padaki et al., 2015).

2.4.1 Type of membrane

Figure 2-4 shows different type of membrane separation process together with the substance that can be separated by each process and also the membrane pore size.

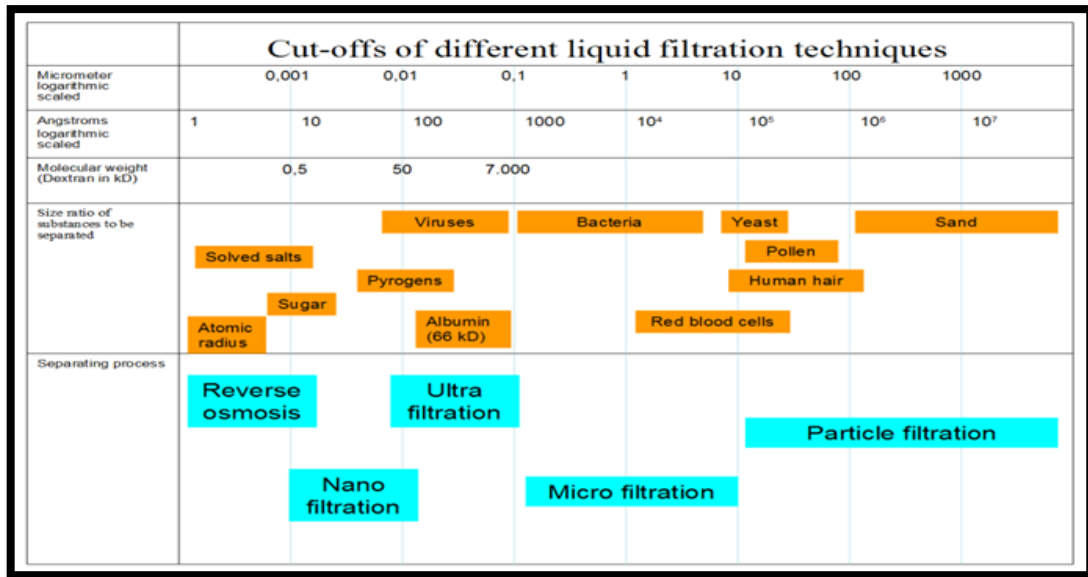


Figure 2-4 Cut-offs of different liquid filtration techniques

Ultrafiltration (UF) process is applied for the particles removal, microorganism and certain amount of dissolved organic matter. UF has been increasing used in the water treatment, separation and purification of different proteins. It has properties such as hydrophilicity, porous structure and antifouling nature that have a great influence on membrane performance (Nair et al., 2013) but to achieve high permeability, high surface porosity and good pore structure of membranes is very crucial (Yan et al., 2006). The weaknesses of UF process is, it is not being able to discriminate efficiently between the low molecular weight molecules

Whereas, for nanofiltration (NF) process it has gained their popularity once it was first introduced in the early 1980s because of their high selectivity for mono and multivalent ions, low operating pressures, and low operating cost compared to reverse osmosis (Liu et al., 2014). As an intermediate process between the UF and reverse osmosis (RO), the NF process offers a better rejection than UF. It had been widely used in various applications ranging from water treatment, pharmaceutical, oil and food industries.

RO is a high-efficient technique for dewatering process streams, concentrating or separating low-molecular-weight substance in solution, or cleaning wastewater. RO has the ability to concentrate all dissolved and suspended solids. The permeate will contain a very low concentration of dissolved solids. RO is commonly used for the desalination of seawater. RO is a pressure-driven process so no energy-intensive phase changes or

potentially expensive solvents or adsorbents are needed for RO separations (Williams, 2003).

Membranes are typically made of polymeric materials and inorganic (ceramic) materials. Polymer materials that were commonly used to prepare membrane are polysulfone (PSF), polyethersulfone (PES) and cellulose acetate (CA). Polymeric membranes offer some advantages including high efficiency to remove particles, low energy requirement and inexpensive compared with ceramic-based membranes. Polymeric blending approach has been extensively utilized for polymeric membrane fabrication due to its facile preparation procedure, versatility to incorporate desirable properties on the membrane, and also its profound ability to simultaneously modify the membrane properties during the phase inversion process. In order to enhance flux and antifouling property, hydrophilic additives such as hydrophilic polymers, amphiphilic copolymers and inorganic nanoparticles have been introduced (Padaki et al., 2015).

2.4.2 Membrane configuration

Membranes come in four basic configurations such as tubular, spiral, hollow fiber and flat sheet. Each configuration has their own unique characteristics to suit a wide range of process requirements. Flat sheet membrane has planar configuration and are mainly rectangular. They are used almost exclusively for membrane bioreactors for industrial and municipal application. Flat sheet usually being cast on solid backing materials and it has high surface area.

2.5 Nanofiltration membrane

Nanofiltration membrane process is a pressure-driven membrane separation technology in between reverse osmosis process and ultrafiltration membrane process. NF is termed as “Loose” reverse osmosis membrane. It operates at low pressure while reverse osmosis process need pressure >600 psi (Razdan and Shah, 2001). Organics >300 g/mol will be retained based on the cut-off solute with rejection above 92% because it is based on size and involves sieving effect. While ions rejection will be based on the size and valency. The average pore size diameter of NF is ~2nm and it is more porous compared to RO membrane and could cause concentration polarization and fouling but it can be overcome by having a better design and selecting material processing desirable properties (Razdan and Shah, 2001).

The nominal molecular weight cut off of a NF membrane is in the range 100-1000 Da. For mono and bivalent ions as well as organic compounds NF membrane will have good separation and high rejection for molecular weight from 100 to 500 Da (Han et al., 2014). Separation of solutes in the NF range is also dependent upon the microhydrodynamic and interfacial events occurring at the membrane surface and inside the membrane pore (Liu et al., 2014).

NF also has the ability of rejection low salt and high water flux at low pressure, separating low molecular weight organics from high molecular weight organics and passing solutions with high osmotic pressure at low pressure. With that ability, NF is an ideal membrane for water softening, desalting, food processing, waste-water treatment and for various separation processes in industry (Razdan and Shah, 2001).

NF is mainly fabricated via interfacial polymerization technique as it is a facile and fast method. The active layer can be attached onto various substrates. However, the substrate can be easily detached from the skin layer in harsh environment containing organic solvents such as ethanol because the compatibility between the support layer and the skin layer is so poor. Great effort had been made such as creating covalent linkage and constructive adhesive transition layer to enhance the strength between skin layer and the substrate surface (Lv et al., 2015).

Currently, most of commercially available membranes for NF are composite in nature; with a selective skin layer on the top of the porous substrate. There are several ways to construct the selective layer for NF membrane. Firstly, an active layer can be fabricated by integrally connecting it to the support layer. This method requires a delicate polymer dope formula and a precise control of casting conditions to avoid defect formation. Next, the selective layer can also be made based on the composite membrane concept that is the active layer and porous substrates are fabricated separately using different materials (Setiawan et al., 2011).

2.6 Effect of additives in nanofiltration

Flat sheet membrane will be prepared by the phase inversion technique. The crucial factor that need to be controlled during the membrane preparation are amount and type of polymers, types of solvent, type of additives mixed into the casting dope solution, coagulated bath temperature and type of coagulant bath (Feng et al., 2013). The effect of

additives concentration and molecular weight on the membrane structure and morphology has been reported by several researches. The presence of additives in membrane solution will influence thermodynamic and kinetic properties of membrane solution. Thus the membrane morphology can be controlled by adding a small amount of additives. Membrane performance such as contactors, porosity and suitable pore sizes and pore size distribution are a must to increase membrane hydrophobicity. Pore formation can be promoted by reducing the polymer concentration but membrane mechanical strength might reduce. This is the reason most common approach to increase pore formation by using additives or pore formers to balance or improve the permeation performance of membrane (Wongchitphimon et al., 2011). Presence of additives in the dope solution normally changed rheological property and viscosity of the solution. They are an important parameter that could affect the kinetics of the phase inversion in membrane formation process (Wongchitphimon et al., 2011).

2.6.1 Effect of addition Zinc chloride (ZnCl₂)

The addition of inorganic salts in the polymeric solution can be an effective method to enhance the membrane performance. These solutes changed the solvent properties as well as interaction between the macromolecular chains. Previous study had shown that the membrane pores were reduced when using zinc chloride as additives in the absence of any organic additives. Addition of ZnCl₂ will result in dense and homogenous morphology of membrane. By increasing the ZnCl₂ concentration the viscosity of casting solution also increase. At high ZnCl₂ concentration, the polymer will become closely packed that result to a denser morphology (Panda and De, 2014).

2.6.2 Effect of addition PEG-200

The existence of PEG as additives leads to higher polymer concentration and increases the viscosity of polymer. The viscosity will increase with an increase in PEG molecular weight for PEGs with different molecular weight. PEG with longer molecular chains may result in stronger macromolecule chain entanglement, which may be responsible for the viscosity increase. Low viscosity reported for PEG-200 may be due to the relatively poor interaction between PEG-200 and solvent (Wongchitphimon et al., 2011). Increased in viscosity will cause the polymeric solution become less stable, resulting to rapid demixing.

Besides that, due to hydrophilic properties of PEG, the increase in PEG concentration increases the inflow rate of water diffusion in the polymer solution. By increasing the PEG concentration the porosity and water permeability of membrane also increases (Teta et al., 2013). It is also well known as a pore former due to their strong hydration and large excluded volume in the gelation bath but Kim and Lee (2004) have found that smaller molecular weight of polyethylene glycol (PEG 200 and PEG 400) can be used as pore reducing hydrophilic additive rather than as a pore forming.

Difference molecular weight of PEG will not cause obvious effect for the outer surface morphologies of the membrane but it will cause different dimension formation of finger-like macrovoid. The dimension will increase together with increased of PEG molecular weight (Wongchitphimon et al., 2011).

3 MATERIALS AND METHODS

3.1 Introduction

In this study, the membrane was fabricated using different additive in dope solution through phase inversion method. The flux and rejection of the membrane was tested under dead end filtration for single xylose, glucose and acetic acid solution. Based on the permeation data, the separation factor and pore size were calculated. Refractometer was used to determine the concentration of xylose and glucose in the sample.

3.2 Chemicals

Radel Polyethersulfone (PES) was used as base polymer. N-Methyl-2-pyrrolidone (NMP), Zinc Chloride, and PEG-20 used to make a dope solution were purchased from Sigma –Aldrich Malaysia. Xylose and glucose used in filtration experiment were also purchased from Sigma.

3.3 Dope solution preparation

The PEG is added to a premixed PES in NMP dissolved at 60°C. The solution was continuously stirred about 12 hours as shown in Figure 3-1 until homogenous dope solution was formed (Panda and De, 2014). During the whole process of stirring, the lid container was kept closed to prevent the loss of solvent due to evaporation. The prepared solution was put into an ultrasonic bath for about 3 hours to remove bubbles and kept for at least 24 hour without stirring at room. Detail composition of dope solution prepared using different additives amount is shown in Table 3-1.



Figure 3-1: Stirring process

Table 3-1 : Composition of PES, NMP, PEG-200 and ZnCl₂

Components	A (wt.%)	B (wt.%)	C (wt.%)	D (wt.%)
Polyethersulfone (PES)	18	18	18	18
N-Methyl-2-pyrrolidone (NMP)	82	80	80	78
PEG-200	-	-	2.0	2.0
ZnCl ₂	-	2.0	-	2.0

3.4 Casting process of NF Membrane

A multi-component dope solution was cast by a simple dry/wet casting technique using pneumatically controlled casting machines as shown in Figure 2-1. The membranes were cast on a glass plate at ambient temperature with casting knife notch of 250 μ m. The glass plate was immediately immersed in water bath at room temperature. Then the membranes were immersed into another water bath and remained there for a day. This was done to ensure complete removal or evaporation of residual solvent from the membranes (Jung et al., 2004).

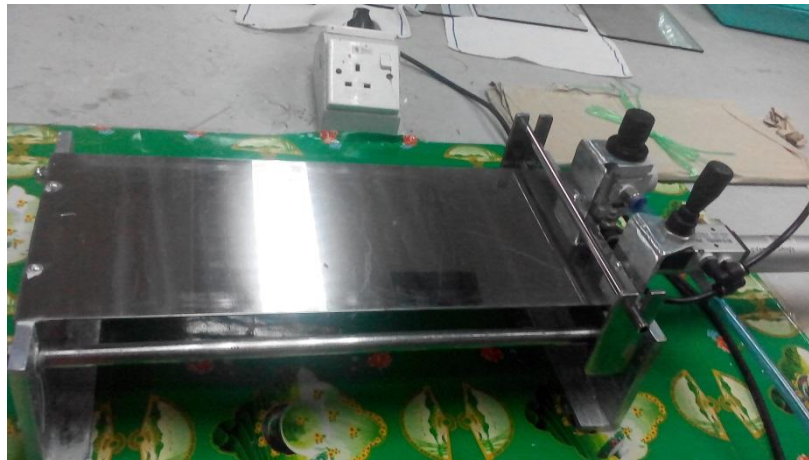


Figure 3-2 Casting machine

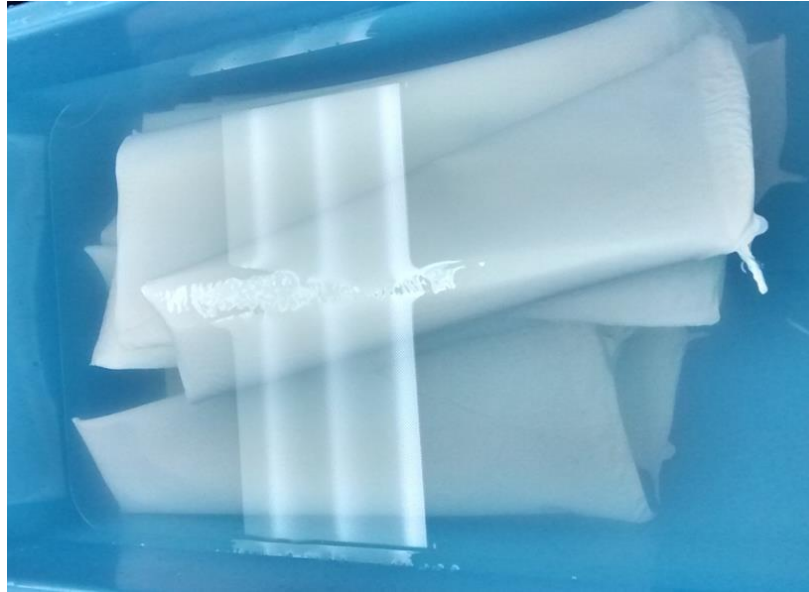


Figure 3-3 : Membrane immersed in water after casting

3.5 Dead end filtration

Before proceed with testing the xylose and glucose separation, the pure water flux was measured to ensure that the membranes used were stable. Freshly prepared membranes were first flushed with pure water at ambient temperature and pressure of 4 bar for 2 hours. Next, the water flux was measured at two different pressures of 3 bar and 4 bar. 1 mL of permeates were collected and the total time taken was also noted. Water flux was measured using $PWP = \frac{Q}{A\Delta P}$ Equation 3.1. The permeate side was opened to the atmosphere. The pure water permeability value can be obtained from the slope of graph flux versus feed pressure. This test was done to predict the characterization of the prepared membranes.

$$PWP = \frac{Q}{A\Delta P} \text{Equation 3.1}$$

Where:

Q is the water volumetric flow rate at the permeate side (L/h)

A is the effective filtration area (m²)

ΔP is the transmembrane pressure (bar)

Circular membrane discs were cut and secured in a cylindrical filtration cell by a porous support and tightened by a rubber O-ring as shown in Figure 3-4. Effective permeation area of each membrane was about 25.52 cm². Other parts were then assembled together and place on top of magnetic stirrer. A pressure gauge and flow control valve were used

to control the pressure on the feed. Pressure of 4 bar was provided by the attached nitrogen cylinder and 1 mL of permeates were collected and the total time taken was recorded. The concentration of xylose and glucose were quantified by refractometer.



Figure 3-4 Dead end test set-up

The rejection (%), R , permeability (flux) of the membranes and separation factor were calculated using **Retention or Rejection, R (%) = $(1 - \frac{C_p}{C_f}) \times 100$**

Equation 3.2 and **Permeability = $\frac{V}{t \times A \times \Delta p}$**

Equation 3.3, respectively with the following formula (Suhana et al., 2014):-

Retention or Rejection, R (%) = $(1 - \frac{C_p}{C_f}) \times 100$ Equation 3.2

Permeability = $\frac{V}{t \times A \times \Delta p}$ Equation 3.3

Where:

C_f solute mass for feed (g/L)

C_p solute mass for permeate (g/L)

V permeate volume

t time

A surface area membranes

Δp Pressure gradient

$$\textit{Separation factor} = \frac{\frac{C_p(xyl)}{C_p(glu)}}{\frac{C_f(xyl)}{C_f(glu)}} = \frac{1-R_{xyl}}{1-R_{glu}} \quad \text{Equation 3.4}$$

Where :

$C_p(xyl)$ xylose concentration in permeate

$C_p(glu)$ glucose concentration in permeate

$C_f(xyl)$ xylose concentration in feed

$C_f(glu)$ glucose concentration in feed

3.6 Refractometer

A refractometer is a piece of test equipment used to determine the sugar content in a liquid. It will instantly read gravity, in Brix, of sample by measuring the degree that light passing through the sample is bent. Samples of xylose and glucose from the dead end filtration were tested with digital refractometer to determine Brix %. Then the concentration of sample determined from the calibration curve constructed. To use the refractometer, it must be calibrated first by cleaning the prism face and placing a few drops of distilled or RO water on the glass. Cover the glass and make sure the glass has no dry spots or air bubbles. Push the zero button then the refractometer was already calibrated. Next, all the sample can be tested by placing a few drops of sample into the glass prism.

3.7 Approximation of membrane pore size

Previous study by Ahmad and Ooi, (2005) had determined membrane properties of charged and uncharged solute permeation test and the hypothetical mechanistic structure such as pore size by using Donnan steric pore flow model (DSPM). They also can be determined using Hagen-Poiseuille equation as studied by Bowen and Mohammad, (1998).

$$R_{real} = 1 - \frac{C_{i,p}}{C_{i,m}} = 1 - \frac{K_{i,c}\phi}{1 - \exp(-Pe_m)[1 - \phi K_{i,c}]} \quad \text{Equation 3.5}$$

Where:-

R_{real} real rejection of solute,

$C_{i,p}$ concentration of solute in the permeate,

$C_{i,m}$ concentration of solute on the membrane.

Determination of Peclet Number, Pe_m is defined as

$$Pe_m = \frac{K_{i,c} J_v \Delta x}{K_{i,d} D_{i,\infty} A_k} \quad \text{Equation 3.6}$$

Where:-

$D_{i,\infty}$ bulk diffusivity of solute ($m^2 s^{-1}$)

J_v volume flux (based on membrane area) ($m s^{-1}$)

$\Delta x/A_k$ ratio of effective membrane thickness over porosity

$K_{i,d}$ and $K_{i,c}$ come from $K_{i,d} = K^{-1}(\lambda, 0) = 1.0 - 2.30\lambda + 1.154\lambda^2 + 0.224\lambda^3$

Equation 3.7 and $K_{i,c} = G(\lambda, 0) = (2 - \phi)(1.0 + 0.054\lambda - 0.988\lambda^2 + 0.441\lambda^3)$

Equation 3.8,

$$K_{i,d} = K^{-1}(\lambda, 0) = 1.0 - 2.30\lambda + 1.154\lambda^2 + 0.224\lambda^3 \quad \text{Equation 3.7}$$

$$K_{i,c} = G(\lambda, 0) = (2 - \phi)(1.0 + 0.054\lambda - 0.988\lambda^2 + 0.441\lambda^3) \quad \text{Equation 3.8}$$

Where;-

ϕ steric partition term

λ ratio of solute radius/ pore radius (limitation $0 < \lambda < 0.95$)

The Hagen-Poiseuille equation relates the pure water flux and the applied pressure across the membrane,

$$J_w = \frac{r_p^2 \Delta P}{8\mu \left(\frac{\Delta x}{A_k}\right)} \quad \text{Equation 3.9}$$

Where:-

J_w water flux (based on membrane are) ($m^3 m^{-2} s^{-1}$)

μ viscosity of solution (kPa.s)

For a stirred cell configuration, the observed rejection was related to the real rejection by volume flux, J_v and mass transfer coefficient, k as in

$$\ln\left(\frac{1-R_{obs}}{R_{obs}}\right) = \ln\left(\frac{1-R_{real}}{R_{real}}\right) + \frac{Jv}{k}$$

Equation 310

$$k = k' \omega^{0.567}$$

Equation 3.11

$$k' = 0.23 \left(\frac{r_r^2}{v}\right)^{0.567} \left(\frac{v}{D_\infty}\right)^{0.33} \frac{D_\infty}{r_r}$$

Equation 3.12

Where:-

- r_r radius of stirrer
- ω stirring speed (rad/s)
- v velocity of solute

4 RESULT AND DISCUSSION

4.1 Pure water permeability

Pure water permeability (PWP) is one of the indicators to know whether the membrane produced was within the NF range or not. The value of PWP could also be used to determine the membrane stability and cleanliness after each filtration experiment. Figure 4-1 Water permeability test shows the water flux of all membranes at 3 and 4 bar measurement. The slope of the line represents the PWP for each membrane in unit $L.m^{-2}.h^{-1}.bar^{-1}$ and summarized in **Error! Reference source not found.**

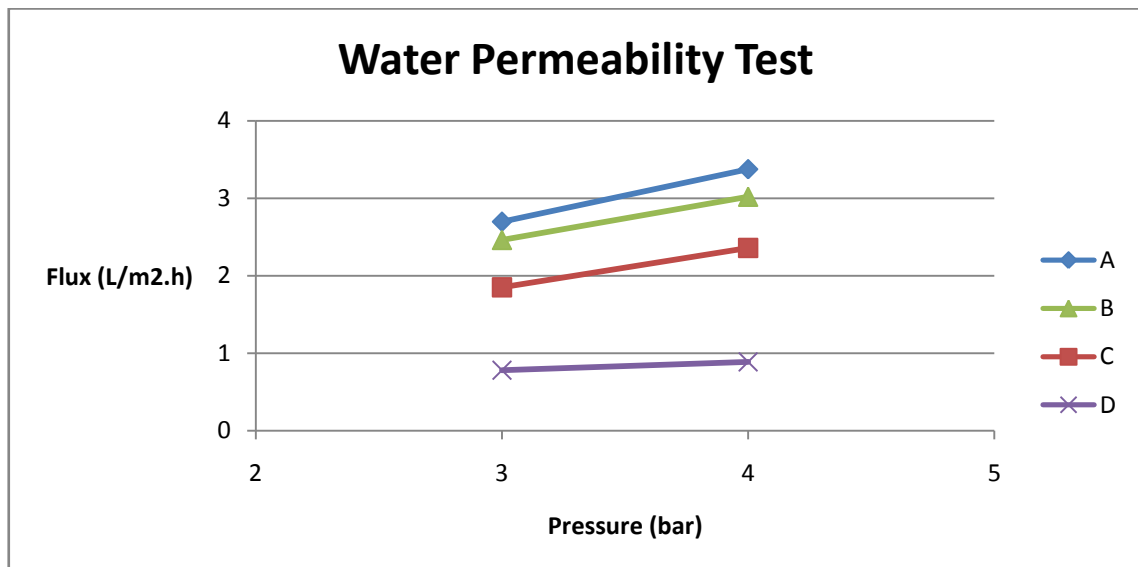


Figure 4-1 Water permeability test

Table 4-1 Membrane permeability

Type of Membrane	Composition	PWP (L/m ² .h.bar)
A	18% PES, 82% NMP	2.0658
B	18% PES, 80% NMP, 2% ZnCl ₂	1.8202
C	18% PES, 80% NMP, 2% PEG-200	1.4286
D	18% PES, 78% NMP, 2% PEG-200, 2% ZnCl ₂	0.1066

From Figure 4-1 effect of addition of PEG-200 and Zinc Chloride can be seen. As zinc chloride was added into the dope solution, the permeability decreases from 2.0658 $L.m^{-2}.h^{-1}.bar^{-1}$ to 1.8202 $L.m^{-2}.h^{-1}.bar^{-1}$ about 11.9% lesser compared to membrane permeability without additives. This is because addition of ZnCl₂ will result to dense and

homogenous morphology of the membrane. This phenomenon is explained by increase in viscosity of dope solution when $ZnCl_2$ is added as studied by Panda and De (2014).

Furthermore, addition of PEG-200 also shows in decrease of permeability. About 30.85% lower than membrane without additives. PEG-200 does affect more membrane permeability compared to zinc chloride. Based on Panda and De (2014) study, low molecular weight of PEG can be used as pore reducing hydrophilic additive rather than a pore forming. This is because molecular weight of the additives has a fine control over the morphology and permeability of the membranes. Besides that, based on their study membrane formed at this composition is expected to show the lowest permeability and higher retention characteristics compared to higher composition of PEG-200. When lower PEG concentration is used less amount of PEG is leached out of the membranes giving rise to small pores below the skin layer with a thicker and denser spongy bottom layer. This is due to the fact that, at lower PEG concentration, slower demixing occurs. If 4% concentration of PEG is being used, more macrovoids will appear and the membrane matrix become more porous thus permeability will increased.

As pure water permeation is strongly dependent on the top layer and sublayer of the membranes (Idris et al., 2007). Finally, the last membrane shows the effect of addition organic and inorganic additives in the same dope solution. The permeability of membrane decrease about 94.83% compared to membrane permeability without additives. Addition of PEG-200 and $ZnCl_2$ together, made the membrane become very thick and dense. The skin layer has an active role in determining the transport properties of the asymmetric membrane by solution diffusion mechanism. A relatively dense skin shows lowest permeability with a good selectivity. Thus this membrane theoretically will shows the lowest permeability and higher retention of solutes.

The PWP values obtained from this experiment is within the range based on previous study for commercial NF membrane which is between $1.33 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$ to $50.50 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$ except for membrane with combination 2 types of additives (Bowen and Mohammad, 1998).

4.2 Effect of addition organic additives and inorganic additives for sugar separation

The separation of xylose and glucose with fabricated flat sheet NF membrane succeed or not for this research depends on the dead end filtration result. Figure 4-2 shows the flux for pure xylose and pure glucose solution resulted from the dead end filtration with developed membrane. From the result, it shows that xylose flux is bigger than glucose. This is because xylose has smaller molecular size $150.13 \text{ g.mol}^{-1}$ compared to glucose 180 g.mol^{-1} .

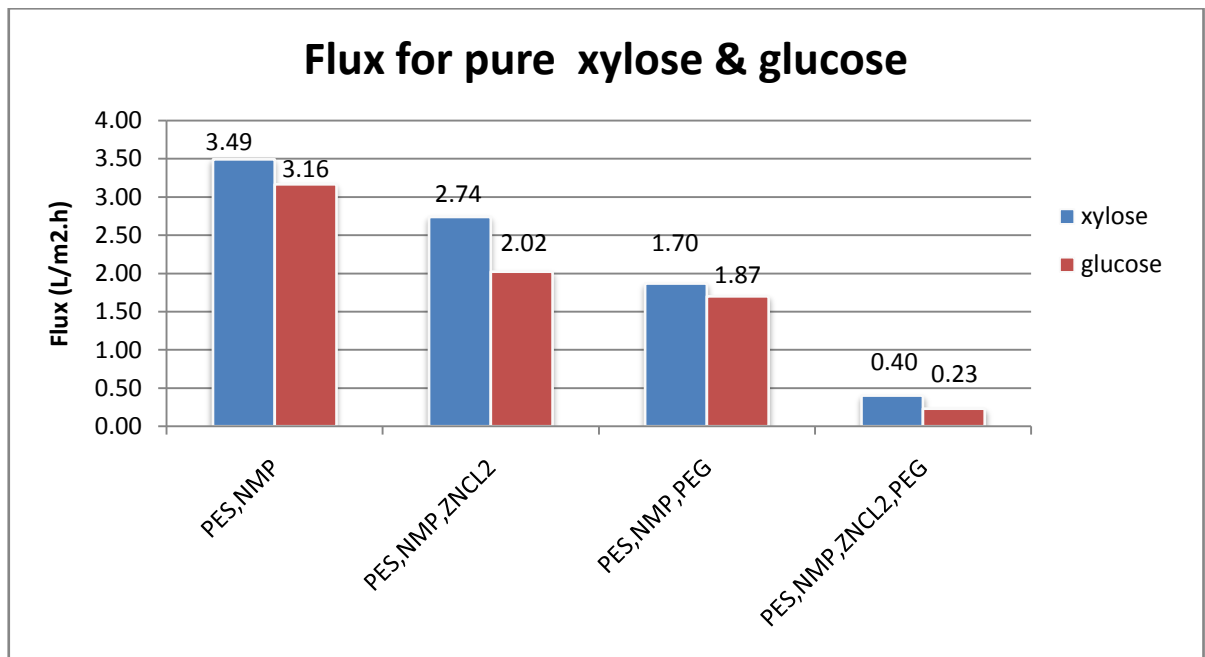


Figure 4-2 Flux of pure xylose and glucose for different membrane at 4 bar

From the Figure 4-2, the flux for pure glucose shows the same trend as pure xylose. Addition of PEG-200 or ZnCl_2 will decrease the flux of xylose and glucose. The membrane with combination PEG-200 and ZnCl_2 shows greater decline of the flux. It is matched with the pure water permeability test as the permeability of membrane decreases with the addition of additives.

Furthermore, Figure 4-3 and Figure 4-4 illustrate the standard calibration curve for pure xylose and pure glucose. These calibrations were obtained from the solution with different concentration and tested with refractometer to get the brick (%). Then a graph was constructed and the slope equation obtained from the standard calibration curve acts as references for the sample tested with refractometer and the sample concentration can be calculated.

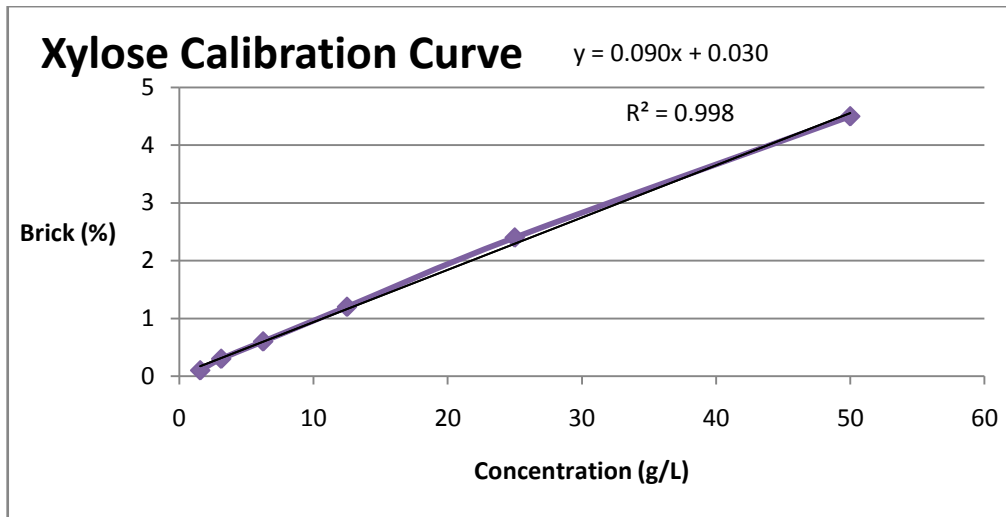


Figure 4-3 Pure xylose standard calibration curve

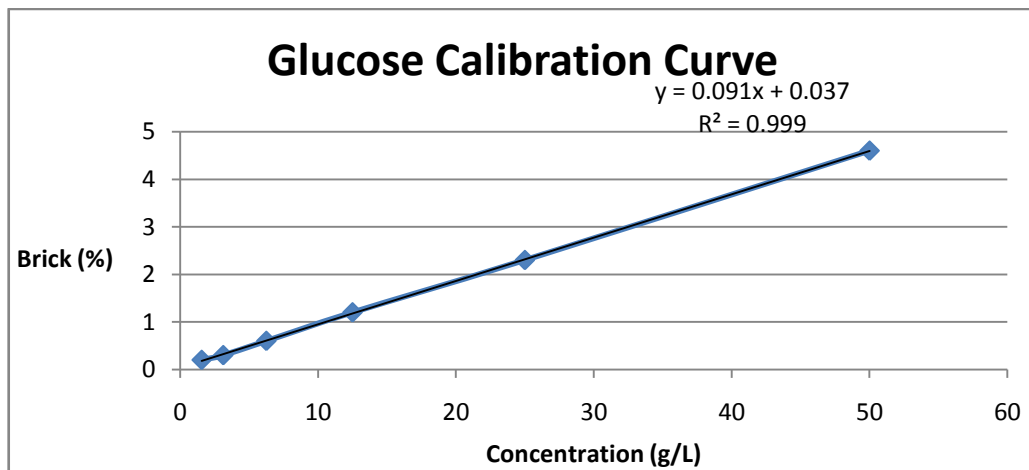


Figure 4-4 Pure glucose standard calibration curve

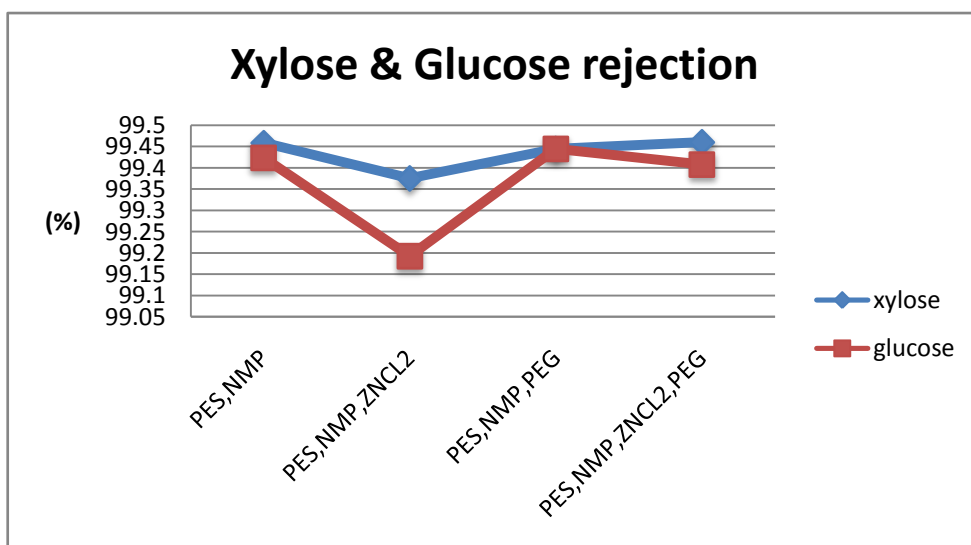


Figure 4-5 Xylose and glucose rejection

As shown in Figure 4-5, the rejection of xylose and glucose for all membrane is about 99%. The lowest rejection can be seen when $ZnCl_2$ additives is used. The rejection increases when PEG-200 is an additives and a mixture of PEG-200 and $ZnCl_2$ due to the pores inside the membrane are much smaller and decrease in number of pores resulted in lower flux and higher rejection. In Figure 4-5, the result shows that glucose rejection is lower than xylose rejection is opposite from the literature which stated the size of glucose is bigger thus the rejection of glucose should be higher compared to xylose. This could due to the cleanliness of the membrane as the flux of virgin membrane compared with used membrane after xylose in average for all membrane about 25% lower. Nevertheless, result from the pure water flux measurement suggested that membrane fouling was minimal under the present experimental conditions.

Besides that, the lower glucose rejection compared to xylose might due to the rate of diffusion coefficient of membrane towards specific component. In addition, the difference of rejection between xylose and glucose did not differ much and still in the range of 99%. Thus it rejection can be said similar for both xylose and glucose.

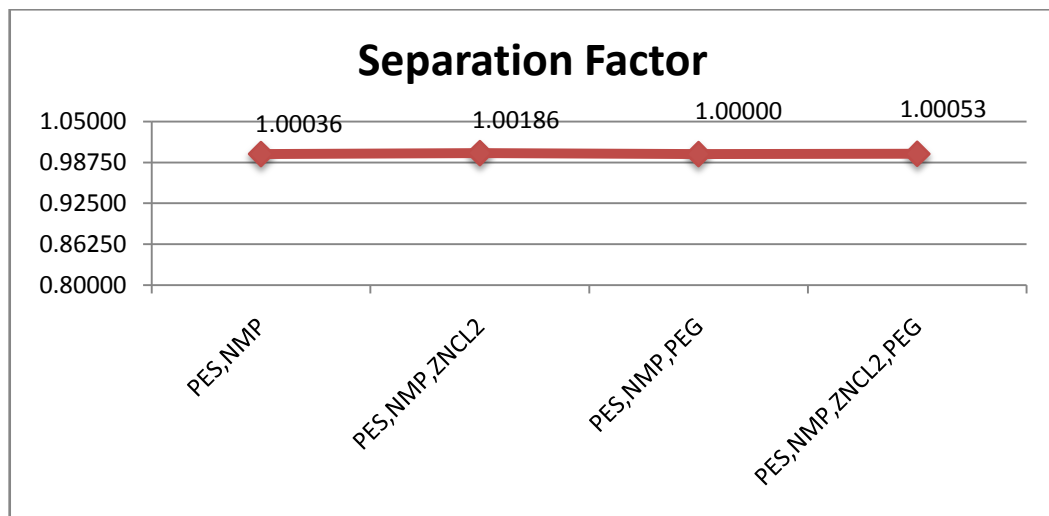


Figure 4-6 Membrane separation factor

Lastly, result that is going to be discussed is the separation factor between xylose and glucose. As shown in the Figure 4-6, the separation is about the same for all membrane that is 1. The highest separation is 1.00186 for membrane with only zinc chloride as additives. This separation factor indicates the difference in permeated between xylose compositions with glucose composition. As the xylose separation factor all in range of 1, it indicates that xylose cannot be separated from glucose.

4.3 Membrane pore size

The pore radius of the commercial NF membranes studied by Bowen and Mohammad, (1998) is from 0.3 to 1 nm. The average estimated pore radius in this study is 0.3088 nm is in agreement with previous studies. Based on the pore size membrane calculated compared with stroke radius of xylose and glucose, xylose and glucose in Table 4-2 will be retained by the membrane. As they have bigger stroke radius compared to membrane effective pore radius. This is strongly support for the 99% rejection of xylose and glucose in previous discussion.

Table 4-2 Physical properties xylose and glucose

Properties	Xylose	Glucose
Molar mass (g/mol)	150.3	180.6
Stroke radius (nm)	0.325	0.365

Table 4-3 Effective pore radius for different membrane

Type of membrane	Average effective pore radius
A	0.3088
B	0.3088
C	0.3088
D	0.3089

5 CONCLUSION

5.1 Conclusion

In this present study, membrane is prepared by simple dry/wet casting method of PES membrane with additional organic additives (PEG-200) and inorganic additives (ZnCl_2). The membrane characterization was performed by using water permeability test. The average pore size radius of membrane used in this study was estimates at 0.3 nm. Thus xylose and glucose cannot pass through the membrane and shows 99% rejection.

In this study, the effect of organic and inorganic additives with separation of Xylose and Glucose is demonstrated as addition of additives led to high rejection for both solution and no separation of xylose and glucose occurred. The finding from this experiment is not in agreement with past studies and theory. Only trend of flux and permeability is showing similar trend with previous study. The pressure used in this study was most likely too low for pressure driven to push the xylose and acetic acid to pass through the membrane pores. Addition of both PEG-200 and ZnCl_2 into the solution does reduce the pore size as membrane permeability decreases as well as flux of solution but the pore size is too small for xylose to pass through.

The scope of this study to fabricate NF PES membrane, characterized and evaluate the performance was successfully conducted. Membrane pores does play an important role in studying the membrane characteristic and performances. Decrease in membrane permeability as additives are added mostly caused by the membrane become denser and the only small pores present that increase the membrane selectivity. This is because an additive does affect the membrane structure and membrane separation performances. The porosity of membrane became lower and membrane become more dense with combination of two types of additives as it shows the lower permeability, lowest permeate flux and high retention.

5.2 Recommendation

In order to ensure more correct result in the future for sugar separation technology it is important to ensure dope solution are prepared accurately in terms of measurement and other factor that could affect the dope solution. Inaccurate measurements could lead to

membrane formation is not according to membrane concentration planned earlier. Next, high pressure should be used for feed pressure in order ensure high separation of xylose can be obtained. As separation xylose and glucose based on sieving method, driving force is important to push the xylose molecule out of membrane pore. Furthermore, chemical used must be same with reference study in terms of type, molecular weight and manufacturer to ensure the result obtained in study will become similar with reference study and not differ much.

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