FABRICATION OF NANOFILTRATION HOLLOW-FIBER MEMBRANE FOR THE SEPARATION OF XYLOSE-GLUCOSE

SITI NORMUNIRA BINTI RAMLI

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

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JUNE 2014

ABSTRACT

Biomass is a biological material derived from living things, or recently living organism. Abundant plant biomass has the potential to become a renewable energy source of fuels and chemicals. Monosaccharide produced from the fermentation of biomass could produce various types of biofuels such as ethanol, butanol, methane, biodiesel, and hydrogen which greatly useful as sustainable energy. By the hydrolysis process of biomass, glucose and xylose were the most hemicelluloses sugar found in biomass. Nanofiltration membranes could offer a relatively cost-competitive separation steps, less complex and easier to maintain compared to chromatographic methods. The objective of this study is to produce PES hollow fiber nanofiltration membrane for the separation of xylose and glucose. Polyethersulfone (PES) polymer was used in a spinning solution with polyvinylpyrrolidone (PVP) as an additive to the solution. The performances of the membrane were investigated by varying the concentration of PVP from 1 wt. %, 3 wt. %, 7 wt. % and 9 wt. %. The surface morphological structure of the NF membrane were clarifying using SEM test. The performances test of membrane was carried out by separated a xylose and glucose. HPLC separation test was used to analyse the samples from the separation process. The result from this experiment is the composition of xylose in permeate is larger than glucose since xylose has lower molecular size than glucose. The results showed that, as the concentration of additive increase, the fluxes also increase and the sugar rejection will lower. As the concentration of PVP increase, the separation of xylose and glucose increase based on the xylose separation factor and solute rejection of xylose and glucose in the mixture solution.

Keywords: Biomass, Nanofiltration, Hollow fiber membrane, Xylose/glucose separation

ABSTRAK

Biomas adalah bahan biologi yang diperolehi daripada benda-benda hidup, atau organisma hidup pada baru-baru ini. Banyak biomas tumbuhan mempunyai potensi untuk menjadi sumber tenaga yang boleh diperbaharui untuk menjadi bahan api dan bahan kimia. Monosakarida yang dihasilkan daripada penapaian biomas boleh menghasilkan pelbagai jenis bahan api bio seperti etanol, butanol, metana, biodiesel, dan hidrogen yang sangat berguna sebagai tenaga mampan. Dengan proses hidrolisis daripada biomass, glukosa dan xylose adalah hemiselulose gula paling banyak terdapat dalam biojisim. Membran Nanofiltration boleh menawarkan langkah-langkah pemisahan dengan kos yang kompetitif, kurang kompleks dan lebih mudah untuk dikekalkan berbanding dengan kaedah kromatografi. Objektif kajian ini adalah untuk menghasilkan membran gentian geronggang nanofiltration untuk pemisahan gula (xylose dari glukosa) dari hidrolisis biomass buatan tempatan. Polimer Polietersulfon (PES) telah digunakan di dalam larutan untuk membuat putaran gentian dengan penggunaan polyvinylpyrrolidone (PVP) sebagai tambahan kepada larutan. Prestasi membran telah disiasat dengan mengubah kepekatan PVP dari 1 % berat, 3% berat, 7% berat dan 9% berat. Permukaan struktur morfologi membran NF telah dijelaskan dengan menggunakan ujian SEM. Ujian prestasi membran telah dijalankan dengan memisahkan xylose dari glukosa. Ujian HPLC telah digunakan untuk menganalisis sampel daripada proses pemisahan. Hasil daripada eksperimen ini adalah komposisi xylose yang meresap lebih besar daripada glukosa kerana xylose mempunyai saiz molekul yang lebih kecil berbanding glukosa. Hasil kajian menunjukkan bahawa, bila tambahan kepekatan yang meningkat, fluks juga meningkat dan penolakan gula membran yang terhasil akan berkurangan. Apabila kepekatan PVP bertambah, pemisahan xylose dan glucosa juga bertambah berdasarkan faktor pemisahan xylose dan penolakan gula xylose dan glukosa di dalam larutan campuran.

Keywords: Biomass, Nanofiltration, membran gentian Hollow, perpisahan xylose / glukosa

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

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
PVP	Polyvinyl pyrrolidone
NMP	N-methyl-2-pyrrolidone
HPLC	High performances liquid chromatography
LC	Liquid chromatography
SEM	Scanning Electron Microscopic
NF	Nanofiltration
UF	Ultrafiltration
MF	Microfiltration
RO	Reverse Osmosis
HF	Hollow Fiber
MWCO	Molecular weight cut off

1 INTRODUCTION

1.1 Background of study

Biomass is a biological material derived from living things, or recently living organism. In the recent context of biomass, it is often refer to plant derived-materials called lignocelluloses materials. The biomass can be derived from numerous types of sources such as from plant (sugarcane, corn, bamboo, willow, switch grass, miscanthus, poplar, hemp and etc.), forest residues, palm oil, yard clippings, wood chips and even municipal solid waste. Abundant plant biomass has the potential to become a renewable energy source of fuels and chemicals. Based on the sources of biomass, the estimated production of biomass per year is 146 billion tons per year (Balat & Ayar, 2005).

Many studied have been done to produce economical conversion of lignocelluloses into useful intermediates such as sugar. By the hydrolysis process of biomass, glucose and xylose were the most hemicelluloses sugar found in biomass. Monosaccharide produced from biomass fermented to produce various types of biofuels such as ethanol, butanol, methane, biodiesel, and hydrogen which greatly useful as sustainable energy. Ethanol is one of the alternative energy resources that could partially replace gasoline and eliminate air pollution (Weng et al., 2009). However, to produce these alternatives energy many steps of process should be done such as pre-treatments, enzymatic hydrolysis, separation of monosaccharide, microbial fermentation, etc.

The main focus in this study is the monosaccharide separation. Common method for sugar separation of xylose and glucose was based on chromatographic method. Membrane based process especially nanofiltration and reverse osmosis had a potential for separating these two sugars. However the used of them still very limited and not thoroughly study. Nanofiltration membranes could offer a relatively cost-competitive separation steps, less complex and easier to maintain compared to chromatographic methods (Sjoman et al., 2007). Instead of using the commercial nanofiltration membrane, hollow fiber NF membrane was fabricated in the current study of the NF hollow fiber membrane characteristic and a performance on separation of xylose and glucose was investigated. Polyethersulfone (PES) was used in the preparation of dope solution with addition of polyvinylpyrrolidone (PVP) as an additive and N-methyl-2-Pyrrolidone (NMP) as a solvent.

Polyvinylpyrrolidone (PVP) is a water-soluble polymer (hydrophilic) and soluble in other polar solvent. (PVP) typically used to control the membrane structure in the preparation of NF hollow fiber membrane. PVP is known as a hydrophilic polymer and non-toxic that can increase the porosity of membrane and reduce the formation of macrovoids (Ismail & Hassan, 2006). Polyvinylpyrrolidone widely used in membrane preparation and fibres to regulate pore size and pore size distributions, increase membrane permeability, produce hydrophilic membrane. In the current study, the effect of PVP on the performance and of the NF hollow fiber membrane for xylose-glucose separation was investigated.

1.2 Objective of the research

The objective of this research is to produce PES nanofiltration hollow fiber membrane for the separation of xylose and glucose.

1.3 Scope of the research

The scopes of the research was outlined as below:

i. To study the effect of PVP concentration in PES spinning solution in the range of 1-9 wt. %.
ii. To produce, characterize and evaluate the performance of NF hollow fiber membrane for xylose-glucose separation.

2 LITERATURE REVIEW

2.1 Biomass processing

The term of 'biomass' refers to forestry, purposely grown agricultural crops, trees and plants, organic wastes, agricultural, agro industrial and domestic wastes (Garg and Datta, 1998). Biomass is the biological material from living organisms such as wood, waste materials, gases and alcohol fuels that mostly come from plant, which used to produce electricity and heat. Biomass consists of three chemical elements which carbon, hydrogen and oxygen. However, the other compound besides than these three elements such as nitrogen and small quantities of other atoms, including alkali, alkaline earth and heavy metals can also be found. Biomass is part of the carbon cycle whereas was taken in by plants during photosynthesis. Then, by decomposition or combustion it goes back into the air. This ensures that there is always a stable level of carbon in the atmosphere. Table 2-1 shows various source of the biomass.

Table 2-1: Biomass resources (Imperial Centre for Energy Policy and Technology & E4Tech UK Ltd., 2003)

Biomass Resource Categories	**Examples**
Residues from primary biomass production	Wood from forestry thinning and felling residues; straw from a variety of cereal crops; other residues from food and industrial crops such as sugarcane, tea, coffee, rubber trees and oil and coconut palms
By-products and wastes from a variety of processes	Sawmill waste, manure, sewage sludge and organic fractions on municipal solid waste, used vegetable cooking oil
Dedicated plantations	Short rotation forestry crops such as eucalyptus and willow; perennial annual crops such as miscanthus; arable crops such as rapeseed and sugarcane

Lignocelluloses materials obtained from crop or food industrial wastes contain a large amount of cellulose (40-50%), hemicelluloses (25-30%), and lignin (10-20%) (Hniman et al., 2010). The lignocelluloses biomass was convert to fuels and chemicals by saccharification process, which is followed by catalytic processing of sugar (hemicelluloses) and lignin. The main saccharification method used is enzymatic hydrolysis of biomass polysaccharides after a pre-treatment stage, followed by chemical or biochemical conversion of the sugar intermediates (Størker et al., 2012). Acid and enzymatic hydrolysis has been proposed as methods to produce sugars from cellulose components (Mishima et al., 2005). Between these two methods of hydrolysis, acid hydrolysis was completely optimizing technology.

In the hydrolysis of lignocelluloses biomass, physical, chemical or biological pre treatment need to be applied to remove lignin, reduce the degree of cellulose crystallinity and increase the surface area of biomass resulting in an enhancement of lignocellulose substrate digestibility. Chemical pre-treatments are considered as especially promising approaches because of their high reactivity under adequate condition such as room temperature and normal pressure (Mishima et al., 2005). The use of simple monosaccharide as process intermediates may enable the production of a diverse range of compounds, either by fermentation or by catalytic hydro de-oxygenation. However, successful and operational production of monosaccharide in high yields is still a challenge. Figure 2-1 shows the converting of lignocellulosic biomass to fuels and chemicals by saccharification process.

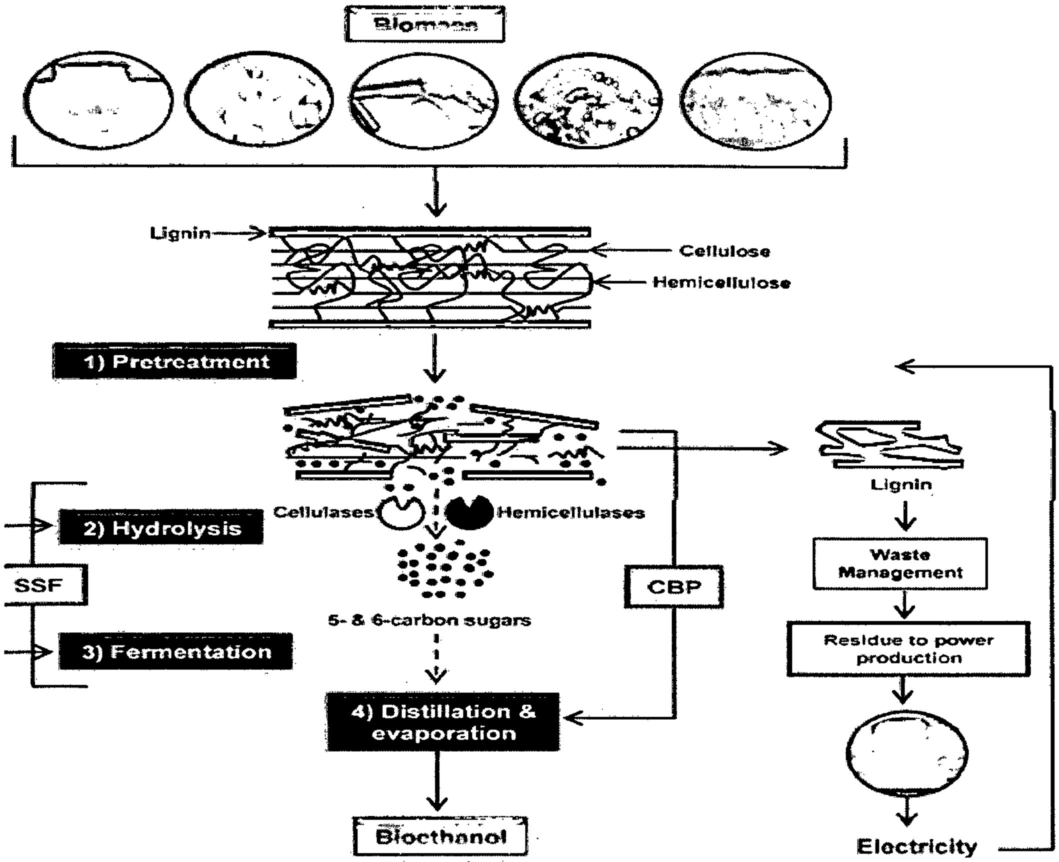

Figure 2-1: Saccharification process of lignocellulosic biomass

A fermentation process produced ethanol, in which sugar that extracted from the biomass was mixed with water and yeast to break down the sugar into ethanol is warmed in a large tanks called fermenters (Balat and Ayar, 2005). 13 million barrels of oil will be displaced by 500 million gallons of biomass ethanol by the year 2000 and after 20 year, 14 billion gallons of ethanol is expected will displace 348 million barrels of oil (Balat and Ayar, 2005). Bio-ethanol is a promising renewable alternative to petroleum or liquid bio-fuels in the transportation sector. Bio-ethanol is already been generate on a large scale from sugars and starchy grains, while lignocellulose ethanol is in the later stages of commercial development (Erdei et al., 2012). Inhibitor tolerance is a serious problem when fermenting sugars from pre-treated lignocelluloses material using yeast. Pre-treatment of lignocellulose residues, furans, weak acids and phenolic are released to affect the rate and yield of ethanol fermentation.

Fermentation can be performed in two different methods: batch fermentation and fed-batch fermentation. Batch fermentation was performed using only the liquid pressed from steam-pre-treated wheat straw (SPWS), while fed-batch fermentation was performed by feeding the liquid obtained from enzymatic hydrolysis of the solid residue from pre-treated wheat straw (Erdei et al., 2012). Ethanol recovered by distillation column when the concentration is high. The ethanol concentration in the feed has a major effect on the energy demand, increasing the ethanol concentration reduces the production costs (Ohgrenet al., 2006). This concentration serves as standard when different process alternatives are calculated. The industrial fermentation of lignocelluloses hydrolyses to ethanol involves microorganisms, which have a extensive substrate range, and which produce ethanol with high yield and productivity. Glucose can be fermented to ethanol with high yield using baker's yeast *Saccharomyces cerevisiae* (Ohgrenet al., 2006).

Sugar fermentation had been studied as a critical step for production of biofuels and other bio-based product (Zheng et al., 2013). Due to the insolubility of cellulose, cellulase has to bind to the solid-state substrate to initiate sugar release; rate of cellulase binding to cellulose plays a limiting role in determining hydrolysis of cellulose (Fox et al., 2012). The pre-treated biomass may contain certain amount of lignin residues, yet they offer much more open structures for cellulase to access cellulose. The lignin residues imitate the effectiveness of cellulase in several ways such as by limiting the accessibility of cellulase in substrate, by unproductively adsorbing cellulase and by inhibiting or deactivating cellulose (Zheng et al., 2013). The pure cellulose is desired to obtain the best enzyme activity, yet that requires substantial energy and material inputs for pre-treatment, and is often connected with substantial lost of valuable cellulosic sugars. Thus, most enzymatic sugar releasing processes must be accompanied with the presence of certain amount of lignin residues that may not present significant accessibility hindrance to the enzyme. Therefore, the role of unproductive enzyme adsorption is essential to the understanding of enzymatic hydrolysis of pre-treated biomass (Liet al., 2013). As the temperature increases, the rates of adsorption for lignin and cellulose are distinctive (Zheng et al., 2013). Increases in temperature improved the adsorption kinetics, as it increases the diffusion coefficient of the protein in solution (external mass transfer) to reach the adsorption surface. This is the standard case observed for cellulose. The chemical characteristic and pre-treatment approaches of lignin impact the enzyme adsorption and reaction. Porosity, adsorption kinetics and binding selectivity, along with chemical characteristics may affect the enzymatic adsorption on lignin samples (Zheng et al., 2013). Figure 2-2 shows the biochemical and thermochemical process of biomass to produces fuels and chemicals

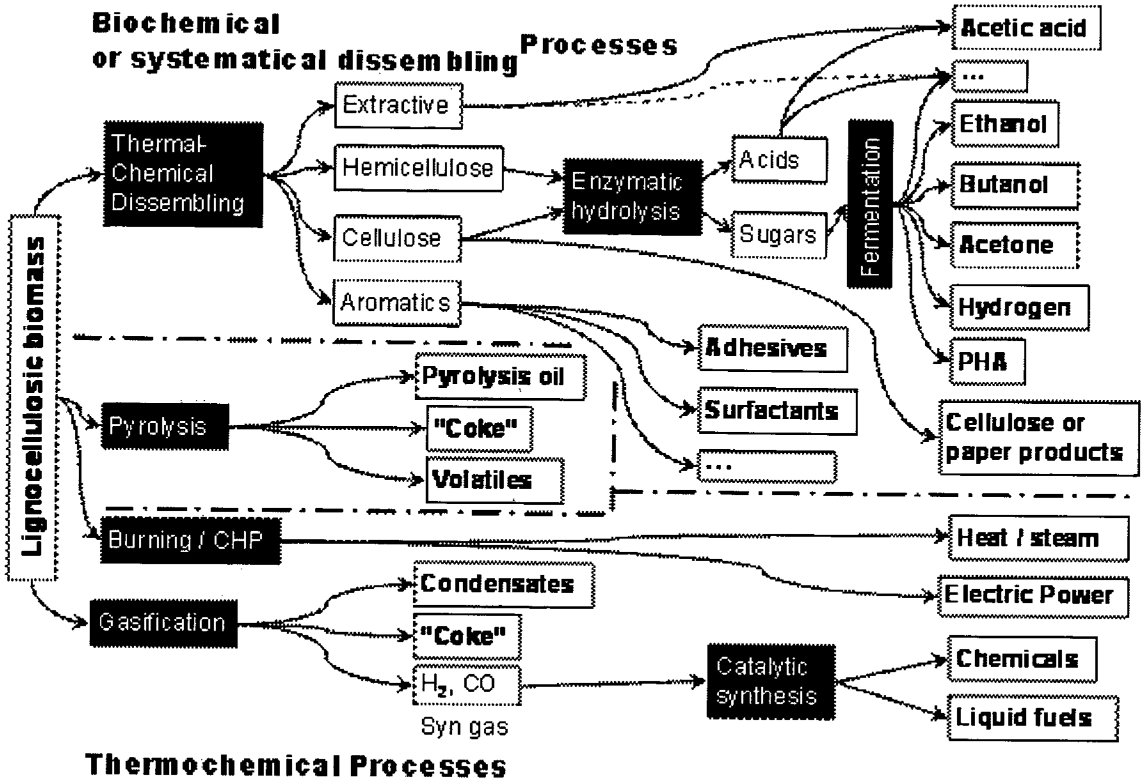

Figure 2-2: Biochemical and thermochemical processes of lignocellulosic biomass to produces fuels and chemicals

2.2 Xylose and glucose from biomass

Plant derived-materials of biomass called lignocelluloses contained of three main polymeric components which hemicelluloses, cellulose and lignin. Cellulose and hemicellulose are the two major carbohydrate components found in biomass. Cellulose is a highly crystalline and linear polymer of glucose units linked by b-1, 4-glucosidic bonds. Hemicelluloses are a complex, branched and heterogeneous polymers of largely pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose) and sugar acids (amino acids) (Zhang et al., 2008), (Galletti and Antonetti, 2011).

Glucose and xylose are universal substrates that can be converted to wide variety of renewable chemicals, bio-plastic cellulosic, ethanol and advanced bio-fuels like green gasoline, green diesel and bio-fuel. Both of sugar were produced by the hydrolysis process of biomass which then be fermented to produce ethanol, other bio-fuels, bio-jet fuel, or lactic acid. Table 2-2 below shows that the molecular weight of glucose is larger than xylose. The conversion of cellulose and hemicelluloses to monomeric sugars is harder to accomplish than the conversion of starch, mainly been used for ethanol production (Ohgrenet al., 2006). The use of sugar juice is unlikely to be the most economically feasible in the long term and lignocellulosic biomass can supply about 0.6 %, equivalent to a global market size of RM 48billion, which is expected to grow to as much as RM 110–175 billion by 2020 (Singh, 2011).

Table 2-2:Physical characteristics of xylose and glucose (Sjoman et al. (2007)

	Xylose	Glucose
Molar Mass (g/mol)	150.3	180.6
Equivalent Molar diameter (nm)	0.68	0.72
Diffusion Coefficient at 25 °c (× 10-6 cm^2/s)	7.495	6.728
Stokes diameter (nm)	0.65	0.73
Molar volume at normal boiling point (cm^3/mol)	155.0	189.2
Van der Waals volume (cm3/mol)	73.6	88.4
Hydration number in aqueous solution at 298K	6.8	8.4
Solubility parameter	31.0	32.0

2.3 *Sugar separation technology*

In the present study, sugar produced from the hydrolysis process of biomass been separated by evaporation process. However this current separations method evidence to be very expensive in order to produce pure xylose or glucose. Evaporation is an energy process for the concentration of xylose due to high used of latent heat of vaporization (Murthy et al., 2005). Besides that, in this recent study, chromatography method is the most popular method in separation sugar especially in producing xylitol from xylose. In a marketable xylitol production xylose is separated from the hemicellulose hydrolyzate stream by chromatography methods (Sjoman et al., 2007). The detoxifications methods used to recover sugar and acid from hydrolyzates included extraction, neutralization, over-liming, vacuum evaporation, steam stripping charcoal adsorption and ion exchange (Weng et al., 2009). These methods are the high production cost, complicated and long process, or extensive loss of fermentable sugars (Zhou et al., 2013). Main concentration of sugar products from lignocellulosic hydrolyzate were achieved by heating, vacuum evaporation and extraction (Huang et al., 2008). Both vacuum evaporation and heating required high-energy consumption. Alternative processes such as zeolite adsorption and reverse osmosis has been proposed to accomplish sugar separation (Luccio et al., 2000). Processes based on chemical affinity of sugar include electro dialysis using borates to complex sugars, ion exchange membranes and liquid membranes. Liquid membrane process is a technology combines solvent extraction and stripping process in single step based on facilitated diffusion (Luccio et al., 2000). Vacuum membrane distillation (VMD) based on liquid-vapour phase equilibrium is an increasingly popular and cost-effective membrane separation technology in separation of inhibitors and sugar from lignocellulosic hydrolyzates (Chen et al., 2013).

2.4 Application of biomass and sugar

Biomass energy production is eight times greater than the total annual world consumption of other energy sources and more economic to produce (Balat and Ayar, 2005). The transformation of biomass to energy already takes place in Malaysia, but on a smaller scale than in Europe. However, with the new renewable energy feed-in tariff system, biomass to energy plants of a similar scale to Europe will have to be assembled in Malaysia (Singh, 2011). Electricity yields from biomass is considered as renewable. The chemical energy collected from biomass may be made available for power production through different processing routes depending on the physical and chemical characteristics of the biomass and the economics of the different production chains (Brown et al., 2011).

The biomass conversion routes for production of electricity were shown in Figure 2-3 below:

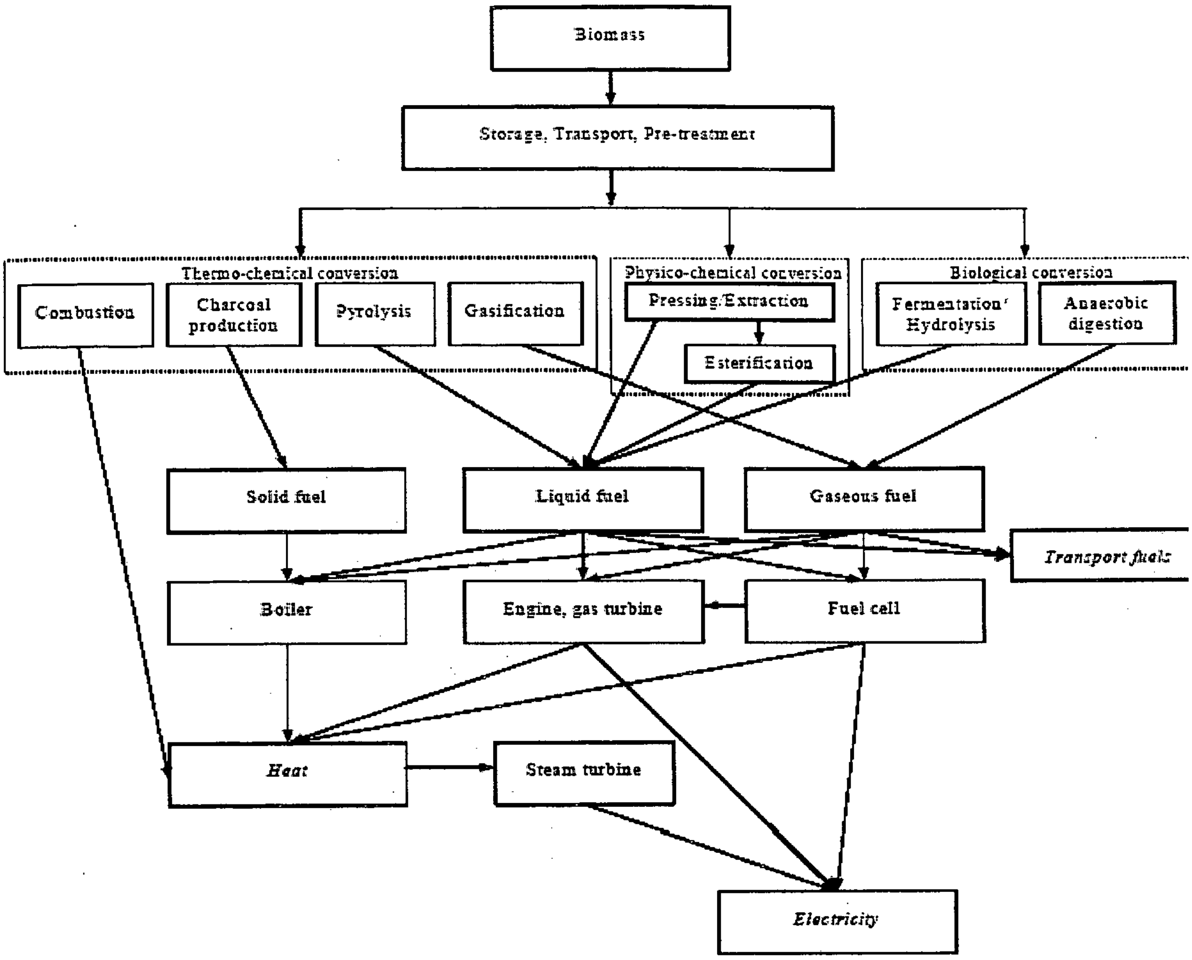

Figure 2-3: Routes for production of electricity from biomass (Bauen et al., 2004)

A bioelectricity production chain starts with collection of biomass fuel as residue or waste from others operations. The intermediate fuel is then been storage, transport and pre-treatment before been supplied to power plant. However, the generation of electricity may also involve the direct combustion of the biomass at a thermal power plant (Brown et al., 2011).

Nowadays energy sources are getting exhausted, and new kinds of energy are needed urgently. Ethanol has been acknowledged as a potential alternative to petroleum derived transportation fuels to reduce the net impact of greenhouse gases to the atmosphere. This ethanol can be produced by microorganism fermentation so the cost is low relatively. The microorganisms that have an ability to ferment both glucose and xylose are very important for an economically feasible process. Fermentation of pure xylose produce highest biomass concentration while fermentation on pure glucose produces lowest biomass concentration (Zhang et al., 2008). The effective conversion of all the sugars to ethanol and the concentration of ethanol in the fermentation broth prior to distillation are the factors that influence the production cost of ethanol. The low cost of lignocelluloses together with an efficient conversion of all sugars to ethanol could hypothetically reduce the production cost of ethanol produced from lignocellulose.

Bio-gasoline is a sustainable bio-fuel because it can be produced through microbial fermentation processes of refined glucose. Refined glucose obtained from fermentation of sugar of lignocelluloses biomass is more economically compared to glucose obtained from edible agricultural feedstock that may affects the food supply (Su et al, 2012). Fermentable sugar involves several step of processes such as size reduction, chemical pre-treatment for lignin removal, recovery of cellulosic residues, and hydrolysis of cellulose. The enzymatic hydrolysis of cellulose using cellulase as a biocatalyst in producing fermentable sugars such as glucose has recently raising the attention due to its energy-saving and eco-friendly process.

Xylitol is an application of xylose, which extracted from sugar cane bagasse, corncobs, etc. It is a five-carbon sugar alcohol produced from catalytic dehydrogenation of xylose consists of 1.5-2 % of d-xylose as the major constituent (Murthy et al., 2005). Typical xylitol is used as a natural sweetener in several food products and an ideal sweetener for diabetics since its metabolism does not require insulin. Other than that, xylitol has been shown to have a preventive effect against acute otitis in children by impairing the growth of oto-pathogen and lowers the adherence of streptococcus pneumonia and haemophilia influenza to the nasopharyngeal cells.

Xylitol is discovered naturally in fruits like strawberries, plums and pears, but in small quantities, which makes its extraction difficult and uneconomical. Xylitol can be produced by biological means from xylose, another sugar, by utilizing yeasts and bacteria (Murthy et al., 2005). Xylose is a versatile sugar compound and has many applications similar to xylitol. Typically use as a sugar source for diabetic patients, non-nutritive sweetener in pharmaceutical industry, and additive in colour photography, brightener in zinc electroplating and ethanol production during fermentation process. It was normally produced by the acid hydrolysis of rice husk and the hydrogenation of xylose produces xylitol, which is a sugar alcohol sweeter than sucrose. However, present separation methods verify to be expensive for concentration of xylose reaction liquor for subsequent production of pure xylitol at yields of 50–60% using the chemical reduction method (Murthy et al., 2005).

2.5 Membrane technology

Membrane separation is a new process performed to isolated mixtures between two different phase using thin barriers known as membranes coexist in one system. The membranes are classified according to their nature, geometry and separation regime. The membranes can be divided into organic (polymeric) membranes and inorganic (ceramic) membranes. Membranes separation process consists of effluent stream and influent stream which is permeate and retentate (Ahmed, 2010). Membrane technology has gained increasing attention due to its distinct technical and economical advantages, such as simple installation, easy operation, low energy loss and process cost, environmental friendly and high capacity in anhydrous product (Pan et al., 2008). Porous structure will be used in determining the synthetic membranes based on the size use in the process whereas the main transport rate of materials diffuse through membrane is determined by structure of membranes, size of components permeate and the driving force (Strathmann et al., 2006).

2.6 Membrane technology

Nanofiltration (NF) is the most recently developed pressure-driven membrane process for liquid-phase separations, which is gaining increasing importance world wide and widening scope for application. It is an advanced method for the concentration of organic and inorganic aqueous solutions (Murthy et al., 2005). Nanofiltration is the pressure-driven membrane filtration operates same as reverse osmosis but differentiated by the pore size in which nanofiltration has a slightly larger than reverse osmosis. The nominal pore size of nanofiltration is about 1 nanometer. The membrane filtration processes rated by molecular weight cut-off (MWCO) that classified into various membrane classifications. Nanofiltration has a MWCO 100 to 1000 Daltons that is smaller than ultrafiltration and larger than reverse osmosis. Nanofiltration sat in a place between reverse osmosis and ultrafiltration (Xu and Lebrun, 1998).

Types of membrane process are shown in Figure 2-4, which includes: Microfiltration (MF) Ultrafiltration (UF) and Reverse Osmosis and nanofiltration (RO/NF) (Merck Millipore, 2013). The primary difference between NF and RO is the size of dissolved contaminants that can be removed. NF membranes are typically used for hardness and organics (i.e. DBP precursors) removal. RO membranes are typically used for TDS and monovalent ion removal (e.g., seawater and brackish water desalting, F and Cl removal). Ultrafiltration (UF) has a molecular MWCO is about 100 kilo Dalton commonly used for protein and polysaccharides bio-separation or clarification pre-treatment for NF process, while NF is effective in separating the mixtures of small organic solutes such as oligosaccharides, low molecular weight (MW) peptides, inorganic salts, amino acids, and other low MW materials (Zhao et al., 2013).

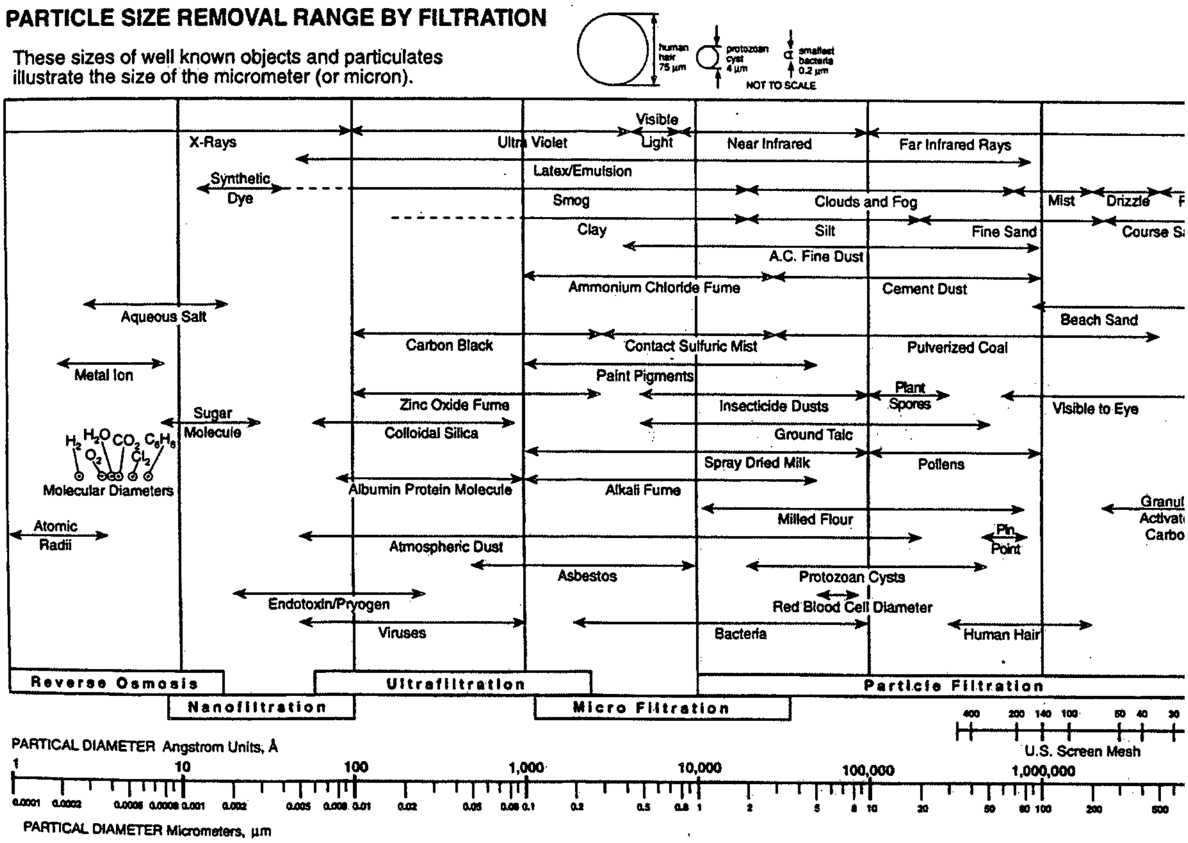

Figure 2-4: Particle size removal range by filtration at different MWCO value (Vertex Hydro pore Pty Ltd., 2011)

Microfiltration (MF) removes particles with a pore size of 0.05 to 5.0 0 µm. it is the physical retention of particles behind a filter medium in which particles are retained because they are larger than the pores in the filter. While the liquid can passes through the filter. Other factors affecting retention are fluid viscosity and chemical interactions between the membrane and the particles in the solution. Ultrafiltration (UF) works basically that same way as microfiltration; except for the pore sizes are considerably smaller. Solutes are retained behind the filter on the basis of molecular size while the bulk of the liquid and dissolved salts pass through. A pressure gradient across the membrane, known as trans membrane pressure, drives the filtration process. Ultrafiltration membranes are designed for the concentration and separation of complex protein mixtures. Reverse osmosis (RO) and Nano-filtration (NF) are the processes of separating very low molecular weight molecules (typically <1500 Daltons) from solvents, most often water. The primary basis for separation is rejection of solutes by the membrane on the basis of size and charge. Unlike UF membranes, RO and NF membranes retain most salts, as well as uncharged solutes. NF membranes are a class of RO membranes which allow passage of monovalent salts but retain polyvalent salts and uncharged solutes > ~400 Daltons. Reverse osmosis membranes (RO) have very small pore sizes and are designed to separate ions from each other. Membrane filtration permits complete removal of particles and microorganisms above a certain size as qualified by pre-established specifications and testing regimens.

Nanofiltration deals with dissolved materials in liquid is often referred as membrane softening since it is effectives at eliminating multivalent ions such as calcium and magnesium and synthetic organic compound by diffusion and sieving through semi-permeable membrane driven by high trans membrane pressure up to 3 Mpa not through any pore in the membrane. NF membranes have been discovered to be extremely effective in the fractionation as well as concentration of solutes from complex process streams. It is believed that sieving is the dominant rejection mechanism in NF for colloids and large molecules whereas the physicochemical interactions of solute and membrane become increasingly important for ions and low molecular weight organic (Murthy et al., 2005). Nanofiltration has a competences in removal both organic and inorganic compound (Ahmed, 2010). The most common nanofiltration membranes use to separates xylose and glucose nowadays are Desal-5 DK, Desal-5 DL, NF270, etc.

The presence of the negatively charged groups on the membrane surface causes the occurrence of the membrane charge. Ions having the same sign of charge as the membrane are excluded and the ions having the opposite sign of charge can be attracted and allowed to permeate (Bessarabov et al., 2002). The development of NF technology as a viable process in the last decade has led to a marked increase in its adoption in a number of industries, for treatment of pulp-bleaching effluents. The applications of the separation process using NF membrane are pharmaceuticals from fermentation broths, demineralization of milk and whey in the diary industry, metal recovery from wastewater, and virus removal.

2.7 NF hollow-fiber membrane

Common membranes module is hollow fiber, flat sheet and tubular. Hollow fiber is a mechanically self-supporting while flat-sheet membranes are usually cast on solid backing materials. Hollow fiber is prepared in spinning equipment using the dry-wet phase inversion method (Kapantaidakis et al., 2002). Due to high surface area to volume ratio and self-support capability, hollow fiber membrane was mainly apply in the liquid phase separation (Wang et al., 2009). Hollow fiber membranes are micro-thin tubules mostly about 1 mm thick and 200 micrometres in diameter with porous wall that allow liquid to flow through it. The advantages of hollow fiber membrane are environmentally friendly production, non-reactive materials, and huge filtering surface in small volume of space, and large absorbent capacity. To characterize the physical properties of hollow fiber there are different techniques such as surface morphology, contact angle, and state of polymer of the membrane may be used (Feng et al., 2013).

2.8 PES polymer as a dope solution

Polyethersulfone (PES) is a hydrophobic membrane for aqueous solution provides a removal of fine particles and other components. It is usually designed to remove particulates during general filtration activity. The typical pore size of PES is range from 0.03 micron to 5.0 micron. The chemical structure of PES uses showed in Figure 2-5. PES occupies high mechanical property and heat distortion temperature, wonderful oxidative, good heat-aging resistance, environmental endurance and processing, hydrolytic stability (Zhao et al., 2012), (Luo et al., 2004). PES has crystalline to some degree because of harder benzene ring and softer ether bond existed in the structure.

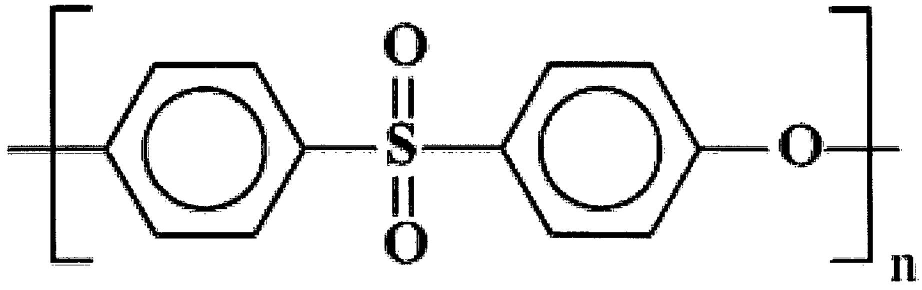

Figure 2-5: Molecular structure of Polyethersulfone (PES) polymer

2.9 General spinning parameter

The fiber formation process consists of four methods in which fusion spinning, dry spinning, wet spinning and dry-wet spinning. Fusion spinning is the simplest process for thermoplastic resins (Yo-Seung Ho et al., 2010). Dry-wet spinning involves various process variables that influence geometrical characteristics and the permeation properties of the hollow fiber. Dry-wet spinning is the most applied technique for the fabrication of hollow fiber membrane that most suitable for separation process.

The important factor that must be controlled in the fabrication of hollow fiber membrane is spinning parameters (Feng et al., 2013). The precipitation conditions, such as residence time and gas jet position, in the forced convection chamber have been shown to be important as they are responsible for creating a sufficiently thin and defect free active layer with a level of locked in molecular orientation (Shilton, 2013). The preparation of hollow fiber membranes is a complex process involving a various type of spinning parameter such as concentration of the polymer in the spinning dope, the type and the composition of the bore fluid, polymer extrusion rate, air gap distance, take up velocity, temperature, humidity, type of coagulant etc. (Kapantaidakis et al., 2002). For example, utilization of air gap during spinning could be considered as equivalent to the well-known method of adding small amounts of water to the dope in order to increase porosity (Kapantaidakis et al., 2002). With the increase of air-gap height, both the inner and outer radii of hollow fiber membranes will decrease (Zhang et al., 2008). The result was interpreted by indicating that the longer the nascent hollow fiber membrane was exposed to a humid air gap, the larger the amount of water content in the top layer. In the study of the morphology and permeation performance of hollow fiber member spun with different air-gap heights, the results showed that a short air-gap distance tended to form a thinner skin layer. Other than that, the interaction effects between the spinning