FACTORS AFFECTING WATER ABSORPTION OF HYDROPHILIC POLYMERIC MEMBRANE BASED ON CROSSLINKED EMPTY FRUIT BUNCH AND POLYVINYL ALCOHOL

MOHAMMAD ALIFF SHAKIR BIN MOHAMAD JAMIL KHIR

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by

MOHAMMAD ALIFF SHAKIR BIN MOHAMAD JAMIL KHIR

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LIST OF ABBREVIATIONS AND SYMBOLS

AD	Air Dry
CTR	Citric Acid
$CaCl_2$	Calcium Chloride
DSC	Differential Scanning Calorimetry
EFB	Empty Fruit Bunch
FTIR	Fourier Transform Infrared Spectroscopy
NaOH	Sodium Hydroxide
OD	Oven Dry
PVOH	Polyvinyl Alcohol
RH	Relative Humidity
SEM	Scanning Electron Microscope
TGA	Thermogravimetric
%	Percentage
^{o}C	Degree Celsius
cm	Centimetre
gsm	Grammage
kg	Kilogram
g	Gram
mL	Millimeter
m/s	Meter Per Second
L	Liter

T_g	Glass Transition Temperature
T_m	Melting Point Temperature

FAKTOR-FAKTOR KESAN PENYERAPAN AIR TERHADAP HIDROFILIK MEMBRAN POLIMER DIPERBUAT DARI SISA TANDAN KELAPA SAWIT DAN POLIVINIL ALKOHOL YANG DI SAMBUNG SILANG

ABSTRAK

Hidrofilik membran polimer diperbuat daripada serat sisa tandan kelapa sawit dan larutan polivinil alkohol. Terdapat tiga fasa utama dalam proses menghasilkan hidrofilik membran polimer iaitu fasa 1 (rawatan serat menggunakan rawatan hidrolisis dan alkali), fasa 2 (penghasilan filem dari polivinil alkohol yang disambung silang), dan fasa 3 (proses memasukkan larutan polivinil alkohol ke dalam serat sisa tandan kelapa sawit yang telah dirawat). Di fasa 1, rawatan hidrolisis mempunyai masa yang berbeza iaitu 20 min, 40 min, 60 min, dan 80 min. Kemudian, diteruskan lagi dengan rawatan alkali pada kepekatan 17 % NaOH, 22 % NaOH, 27 % NaOH, dan 32 % NaOH. Hasil kajian mendapati rawatan 60 min hidrolisis dan diikuti 27 % NaOH telah memberi hasil yang sesuai untuk menghasilkan hidrofilik membran polimer. Analisa bahan kimia menunjukkan kandungan hemiselulosa dan lignin ialah 4.73 % dan 4.66 %. Ia juga mencatatkan masa serapan yang terpantas iaitu 2.47 min dengan jumlah serapan air sebanyak 494 % dan juga serapan wap air yang tinggi iaitu dan 12.97 %. Pada masa yang sama, didapati panjang ukuran serat selepas rawatan adalah sesuai iaitu 0.70 mm. Serat sisa tandan kelapa sawit yang telah dirawat mempunyai peratusan amorfus sebanyak 44 % setelah dianalisa dalam ujian Pembelauan Serbuk Sinar-X. Seterusnya, pada fasa 2, filem dari polivinil alkohol telah dihasilkan dan disambung silang menggunakan asid sitrik. Peratusan asid sitrik yang dicampurkan dalam filem adalah 10 %, 20 %, 30 %, dan 40 %. Seterusnya, filem dari polivinil alkohol yang dicampur asid sitrik telah dipanaskan didalam ketuhar pada suhu 150 ^{o}C dalam masa 30 min untuk tujuan sambung silang. Hasil kajian mendapati 10 % asid sitrik yang digunakan telah mencapai keputusan yang terbaik dengan mencatatkan jumlah serapan air yang tertinggi iaitu sebanyak 183.36 %. Manakala, dalam ujian Spektroskopi Transformasi Fourier Inframerah menunjukkan terdapat pembentukkan sambung silang yang terhasil pada puncak 1180 cm^{-1} hingga 1200 cm^{-1}. Dalam ujian terma haba (analisis termogravimetri), hasil kajian menunjukkan terdapat peningkatan pada suhu degradasi bahan juga telah berlaku peningkatan iaitu dari 345.27 ^oC hingga 351.98 ^oC. Dengan itu, penggunaan asid sitrik sebanyak 10 % telah dipilih untuk digunakan dalam penghasilan hidrofilik membran polimer. Pada fasa 3, larutan polivinil alkohol yang mengandungi 10 % asid sitrik telah dimasukan ke dalam serat tandan kelapa sawit yang telah dirawat menggunakan penembak tekanan udara. Larutan polivinil alkohol tersebut dimasukkan ke dalam serat dalam jumlah yang berbeza iaitu, 1 lapisan semburan, 2 lapisan semburan, 3 lapisan semburan, dan 4 lapisan semburan. Kemudian, ia dimasukan ke dalam ketuhar pada suhu 150 ^oC selama 30 min untuk tujuan sambung silang dan menghasilkan hidrofilik membran polimer. Hasil kajian menunjukkan larutan polivinil alkohol dengan jumlah 3 lapisan semburan dapat menghasilkan hidrofilik membran polimer yang optima. Ianya mempunyai jumlah serapan air sebanyak 481 % dan mencatatkan masa serapan selama 98 saat serta mampu di tembusi wap air sebanyak 4.23 %. Dalam ujian pengembangan, hidrofilik membrane polimer menunjukkan ia mampu mencegah daripada berubah sifat fizikalnya walaupun dalam keadaan basah. Manakala, ujian pengimbas elektron mikroskop menunjukkan bahawa kehadiran liang pori yang terdapat dalam hidrofilik membran polimer masih jelas dan tidak tersumbat setelah dimasukkan larutan polivinil alkohol. Selain itu, dalam ujian Spektroskopi Transformasi Fourier Inframerah menunjukkan pengurangan pada puncak diantara 3200 cm^{-1} hingga 3500 cm^{-1}

membuktikan bahawa kehadiran kumpulan hidroksil telah hilang setelah di sambung silang. Akhir sekali, ujian analisis termogravimetri dan Kalorimetri Pengimbasan Perbezaan menunjukkan perubahan berlaku dari sifat asal bahan, di mana hidrofilik membrane polimer telah menjadi suatu bahan yang baharu. Hasil kajian menunjukkan hidrofilik membrane polimer telah berjaya dihasilkan dan berpotensi menjadi lebih baik dari segi sifat kimia dan fizikal berbanding serat yang digunakan dalam system penukar haba yang sedia ada di pasaran sekarang.

FACTORS AFFECTING WATER ABSORPTION OF HYDROPHILIC POLYMERIC MEMBRANE BASED ON CROSSLINKED EMPTY FRUIT BUNCH AND POLYVINYL ALCOHOL

ABSTRACT

The hydrophilic polymeric membrane (HPM) was made up from treated empty fruit bunch (EFB) fibers impregnated with polyvinyl alcohol (PVOH) solution which contains citric acid (CTR). The production of HPM involved 3 steps which was step 1 (EFB treatment process using prehydrolysis and alkali treatment), step 2 (formation of crosslinked PVOH film), and step 3 (impregnation of treated EFB fiber with PVOH solution contains CTR). In step 1, the EFB fibers were treated by pre-hydrolysis process with 20 min, 40 min, 60 min, and 80 min, then was continue with alkali treatment process at condition 17 % NaOH, 22 % NaOH, 27 % NaOH, and 32 % NaOH. Based on the results, treated EFB fibers with 60 min prehydrolysis and 27 % NaOH alkali treatment was found as the optimum conditioned for HPM production. In this conditioned, the chemical composition analysis of the treated EFB showed the percentage of hemicellulose and lignin content were 4.73 % and 4.66 % respectively. The time taken for water to absorb into the treated fibers was 2.47 min, the percentage of total water absorption was 494 % and moisture absorption was 12.97 %. The average fiber length for the treated EFB was 0.70 mm. Through X-ray Poweder Diffraction (XRD) analysis, it was found that the treated EFB fibers consist of 44 % amorphous region.Thus, the optimum conditioned which was 60 min and 27 % NaOH was chosen to be produce into HPM. In step 2, CTR was used as crosslink agent to produce PVOH film. The percentage of CTR studied were 10 %, 20 %, 30 %, and 40 % based on PVOH weight. The mixture was placed in the oven for crosslinking process at 150 ^{o}C for 30 minutes. From the result, the 10 % of CTR used, gave the highest water absorption which was 183.36 %. The FT-IR spectrum of crosslinked PVOH film showed that a peak between 1180 cm^{-1} to 1200 cm^{-1} was detected indicates that the crosslinking was occurred compared to uncrosslinked PVOH. In thermal analysis, the Thermogravimetric (TGA) results showed the increasing of thermal stability from 345.27 ^{o}C to 351.98 ^{o}C due to crosslink. Thus, 10 % of CTR were chosen as suitable amount for crosslinking the PVOH to produce HPM. In step 3, the treated EFB was impregnated with mixture of PVOH solution contained 10 % of CTR using pressurized air gun. To obtain the optimum amount of PVOH mixture used, the different spraying layers were applied which were 1 layer, 2 layers, 3 layers, and 4 layers. Then the sample was crosslinked in the oven at temperature 150^{o}C for 30 minutes to produce a complete HPM. The result showed that, the 3 layers spraying of PVOH solution contained CTR during forming the HPM, gave an optimum result by having 481 % water absorption, 98 seconds for time of water absorption, and 4.23 % of moisture transmission. The expansion test showed that with the impregnation of polyvinyl alcohol solution, the HPM able to maintain its physical structure in wet condition. The Scanning Elecron Microscopy (SEM) images showed that the pore structure of the HPM are still visible without forming any blockage as the PVOH solution was completely impregnated into fiber cavity. The reduction peak 3200 cm^{-1} to 3500 cm^{-1} in FT-IR analysis spectrum proved that the hydroxyl group in fiber were sacrifice in order to form crosslinking during the process. The TGA and Differential Scanning Calorimeter (DSC) analysis found that the HPM thermal analysis result were completely different from its raw material showing that it has changed into a new type of material. This indicated that the HPM was successfully surpassed the current fiber-based heat exchanger paper in term of chemical and physical properties.

CHAPTER 1

INTRODUCTION

1.1 General

Many South East Asian countries have been experiencing rapid growth of urbanization over the last few decades. Due to this reason, energy consumption kept on increasing, especially in urban areas years by years (Karin lundgren & Tord Kjellstorm, 2013). There was significant increase of population in past 30 years which led to high energy consumption. In order to deal with the hot and humid climate in most Asian countries, it is important to come out with a better solution to deal with the thermal discomfort. Previous research, has shown that there was a large increase in the total number of households with air-conditioners in Malaysia (Malaysia, 2000). Hot and humid condition created thermal discomfort for human to perform their daily routines, especially in closed buildings (Zain, Taib, & Baki, 2007). However, the air ventilation system in the air conditioner posed a health risk due to the system design which used a recycled air source. Menzies et al. (1993) stated that by reducing outdoor air supply in air ventilation system, the probability of air contamination in the building would also increase. Therefore, newer air conditioning systems have been developed to reduce this hot and humid air problems with better air ventilation to allow fresh air intake in closed building applications.

In Malaysia, there is an intensive mass production of palm oil, leading to increase of fibrous waste after harvesting. This waste material has been a massive environmental pollution that might increase the greenhouse effect due to emission of methane gas and carbon dioxide during anaerobic decomposition of solid waste (Lou & Nair, 2009). Fibrous waste such as empty fruit bunch, oil palm frond, and oil palm trunk have many potentials to be utilized for other purposes. Due to the large cellulose content, oil palm waste fiber could be the alternative source for paper making industry (Daud & Law, 2010). High cellulose content may provide compactibility with polar binders. Hence, a polar polymer such as polyvinyl alcohol might be used together to fabricate in composite or fiber product due to ability. Its ability to improve mechanical properties of wood or fiber product (Ching et al., 2015).

1.2 Project background

Heat exchanger is a tool or device that is able to facilitate energy transfer from hot air stream or fluid. The increase in energy content in air stream or fluid will also increase their temperature. The efficiency of heat exchanger depends on materials with good energy transfer capability. Some examples of materials with potential to be used in the heat exchanger are metals, polymers, fibers, and composite membranes.

All these materials have different rates of energy transfer capability. However, by having a good energy transfer alone does not mean that it was suitable to be used in the heat exchanger. Even though having a better system performance is important, other factors such as durability and service life of the heat exchanger should be considered. The study will focus on the fabrication and characterization of precursors and the heat exchanger membrane itself.

Fibers and polymer were used to fabricate the heat exchanger. The combination of these two materials is to complement each other. The fibers might have better energy transfer but low in durability. Addition of polymer, able to improve the durability of the membrane. Meanwhile, citric acid will be used as a curing agent to prevent dissolution of polyvinyl alcohol in water. In this research, material is one of important parameters that dictates the heat exchanger performance. Other parameters such as size core of heat exchanger, the plate design, numbers of channel, and area of ducting airflow ducting system are also important. All these should be investigated in future work to produce a commercial heat exchanger

.

1.3 Problem statement

The heat exchanger currently available in the market are mostly metal and fiber-based. Both of them have their advantages and disadvantages as well. Metal-based heat exchanger are were use in temperate countries due to it capability to transfer sensible heat effectively. However, it was not suitable to use metal-based heat exchanger in hot humid countries. This was due to metal non-porous structure that cause limitation which only able to transfer sensible heat but neglecting the latent heat. On the other hand, fiber-based heat exchanger are able to transfer both sensible and latent heat. Therefore, this work is intended to fabcricate new heat exchanger based on fiber-polymer membrane that is capable of transferring both sensible and latent heat.

1.4 Objectives

- To study the physical properties of empty fruit bunch fiber after prehydrolysis and alkali treatment process.
- To determine physical and chemical properties of crosslinked polyvinyl alcohol film using citric acid as curing agent.
- To investigate physical and chemical performance of hydrophilic polymer membrane and compare the physical performance with commercial fiber-based heat exchanger in wet condition.

CHAPTER 2

LITERATURE REVIEW

2.1 Heat exchanger

Heat recovery is a concept of energy recovery process (heat / mass) from higher temperature stream to a lower temperature stream (Riffat & Gan, 1998). High energy is contained within the hot incoming air stream. This high energy will be reduced or recovered during heat recovery system in order to produce lower air temperature . This process will ensure comfortable condition environment to live in. There are few types of heat exchangers that appear in various designs, with every design has their own specific capability. However, better performance of heat exchanger requires a higher maintenance, which is also uneconomical (Lazzarin & Gasparella, 1998).

There are two factors that needed to be taken into consideration, which are sensible heat and latent heat. Sensible heat can be defined as no change in physical state, regardless of any temperature changes. For latent heat, the object undergoes physical state change as the temperature rise or drop (Sharma & Sagara, 2005). For example, physical state may change from solid to liquid or liquid to gas. For some heat exchangers with better design, they are able to perform better due to their capability to transfer both sensible and latent heat. However, for normal performance heat exchangers, they just can transfer sensible heat only (Lazzarin & Gasparella, 1998).

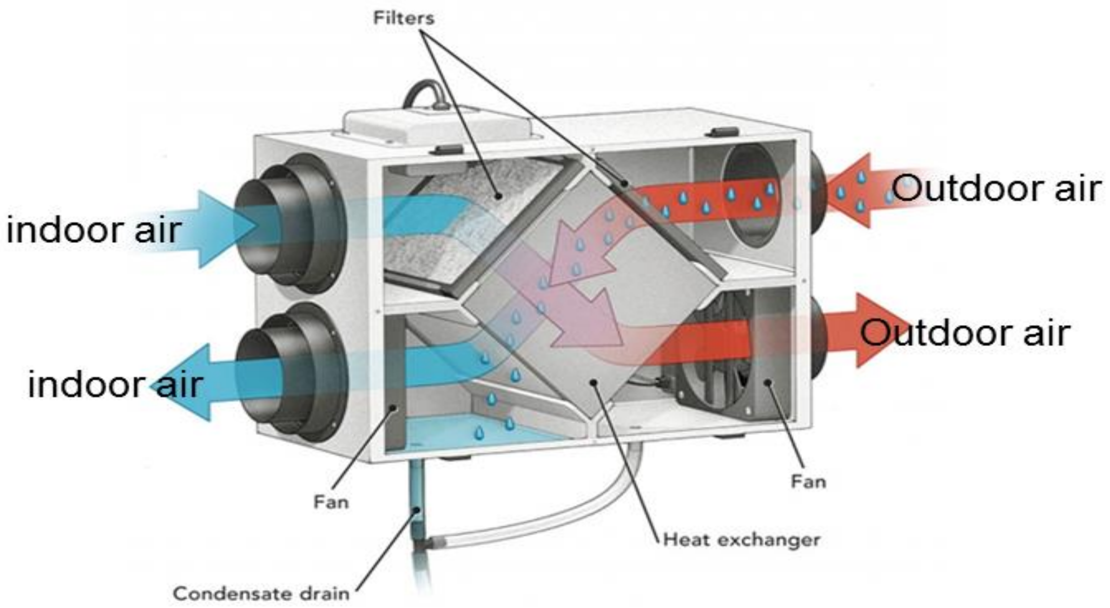

Figure 2.1 An energy recovery heat exchanger system design (Anonymous, 2017b)

Heat exchangers are able to carry out recovery process by reducing incoming exhaust of air about 60 % to 95 % and could help to improve air efficiency in the building ventilation. Since they can utilize energy contained in hot air, they can also save energy by producing an effective air ventilation, especially in an enclosed room such as a bedroom and living room. An effective air ventilation system means the air intake should be taken fresh from outside such as in Figure 2.1. If the air was consumed in closed room building, it will be circulated and used repeatedly which can be a contaminated (Figure 2.2). Apart from that, air in a closed room will become hotter and humid especially during the rainy season. By using heat recovery system, the outdoor fresh will be reduced of its temperature and humidity before being distributed in the building (Roulet et al., 2001).

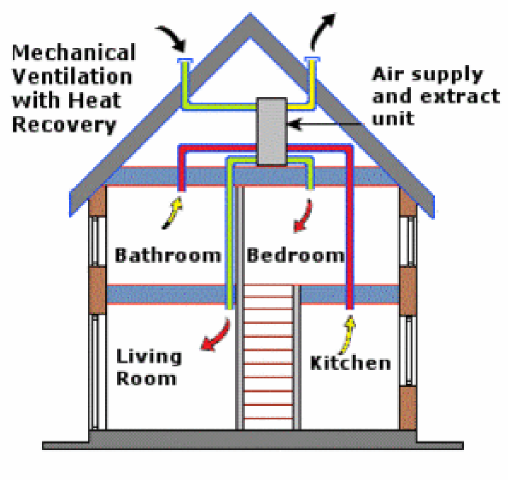

Figure 2. 2 An energy recovery heat exchanger system design (Anonymous, 2017b)

In the heat recovery system, both of the hot incoming air and out going stale air will pass through the duct. Energy transfer will occur inside the duct as the air flow passes through the heat exchanger core. It is important for the core to perform heat transfer process effectively. During the system run, there are 2 blowers being used to pull the incoming air and outgoing air. However, the speed of air flow from blower will influence the effectiveness of heat transfer process (Mardiana-Idayu & Riffat, 2012). As the system runs, the hot incoming air will be pulled inside and passes through the core to be pre-cooled by reducing its temperature and humidity (Figure 2.3). The heat transfer process will occur only when high temperature and low temperature condition meet together. After the air has been treated, it is ready to be passed to the the air conditioning system or distributed into rooms. However the air does not mix together due to design of the system, known as fixed plate heat exchangers (Mardiana-Idayu & Riffat, 2012). The water vapor diffuse by membrane goes to the bottom due to gravity, later to be blown out by the exhaust air (Figure 2.3). This cycle will ensure that the integrity of the membrane will not be compromised quickly during its service life.

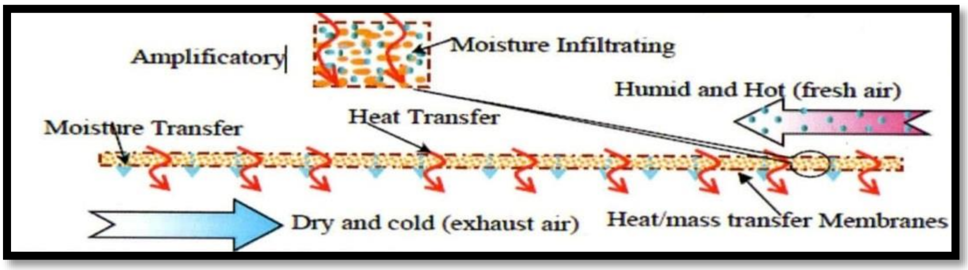

Figure 2.3 The energy transfer process of a hydrophilic polymeric membrane

2.1.1 Fixed plate heat exchanger

There are various types of heat exchangers, including the old version and the new version. Each version has its own advantages and comes with different features. For example, fixed plate, heat pipe, rotary wheel, and run around coil. In this research, fixed plate heat exchanger have been used as case study because it has potential for better performance (Figure 2.4). Fixed plate heat exchanger is cubic in form and constructed by stacking of plates. Due to plate stacking design, could be prevented mixing of incoming air and outgoing air which can cause cross contamination. Fixed plate heat exchanger provides the ability to carry out the process of heat transfer in greater efficiency due to close end air temperature differences that affected by counter-current flow system (Riffat & Gan, 1998). Previous studies have shown that the perfomance of fixed plate heat exchanger also depends on types of materials used to form the plates. For example, a treated paper has already been used in heat recovery system because of its hydrophilic properties that can lead to better moisture diffuse process. The membrane has also been used in heat exchanger to increase the energy recovery process due to its porous structure for better transfer of sensible heat and latent heat (Nasif et al., 2010). However, types of materials is not the only parameter, as there are also other parameters such as size of the core, plate design, and also size of channels in the core that also need to be considered.

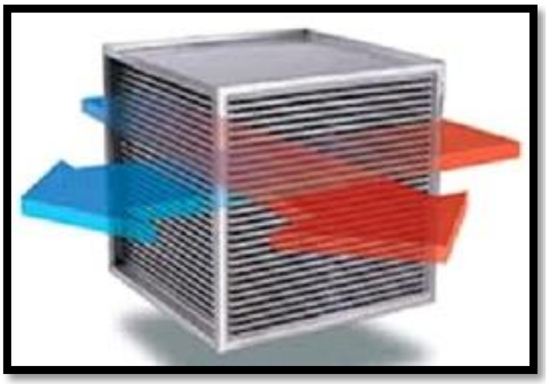

Figure 2.4 An energy recovery heat exchanger core design for fixed plate (Anonymous, 2017a)

2.1.2 Types of materials used in heat exchangers

In a heat exchanger, material and structure are the key factors that will dictate the performance of the system. A good capillary structure with high porosity and big pore diameter is able to enhance the heat transfer process of moisture because of its ability to hold or diffuse more mass transfer (Shuli Liu, 2008).

2.1.2 (a) Metal based

The use of metals as plating in the heat exchangers are more suitable for temperate countries. The types of metals used are copper, aluminum, and steel. However, metal-based heat exchanger is only able to heat transfer sensible heat by neglecting the latent heat. Generally, in temperate countries the air condition is cold and dry, while in Asia the air is hot and humid. The moisture in air is the main culprit. Metallic structure is usually less porous. As hot and humid air is passed through the core metal of heat exchanger, the moisture will be condensed on the plate surface due to inability of to transfer moisture. Surface structure will also affect the energy transfer in the system. By having a porous surface plate, the energy transfer would be better as compared to smooth surface plate (Tadrist et al., 2004). In addition, metal is usually heavy, and in case of steel, its needs proper protection to prevent rust.

2.1.2 (b) Polymer based

Polymers have already been used for making heat exchanger plates (Yhaya, 2016). Polymers are quite efficient in transferring the moisture which is the latent heat. In comparison with metal plate, polymer plate has the ability to deal with fouling and corrosion. However the capability of polymer can be further improved by constructing an appropriate design to be applied in heat exchanger (T'Joen et al., 2009). Polymers in general, usually have low thermal conductivity. In order to produce heat exchanger with a better heat transfer performance, the material used should have high conductivity similar or close to metal. However, having low conductivity doesn’t mean that the polymer are not capable enough to be applied as plates in heat exchanger. The design of system by increasing the size of core or increasing the number of channels will help polymer-based heat exchanger to encounter the low performance problem (Gendebien et al., 2013). The plates may be designed thinly or added with graphite to increase the conductivity. Polymers are also light weight, corrosion resistant, and easy to shape make them attractive for contructing heat exchanger.

2.1.2 (c) Natural Fiber based

It has been proven that, fiber is one of the suitable material that can be used as plates in heat exchanger to transfer heat and mass effectively due to its hydrophilic properties (Liu et al., 2009). Even though fibers are non-conductive, they are able to transfer heat by capturing moisture in the air during operation, provided the design is done properly. They have bigger potential to be used in heat exchanger system as compared to metal or polymer due to their hydrophilicity. By having multiple number of hydroxyl groups, they are a very hydrophilic in nature. Porosity in fibrous material able to absorb water or moisture from being condensed on plate surface. By having a large pore size in fiber structure, heat and mass can be transferred in effectively. This is due to the fiber structure that is less resistant to moisture transfer and has high absorption capacity (Mardiana-Idayu & Riffat, 2012; Li Zhi Zhang, 2014). However, natural fiber usually does not have strong mechanical properties and this may affect the life span of heat exchanger plate when using for long periods of time. Hence, the fiber plates can be easily damaged when in contact with water (Fend et al, 2004). This weakness needs to be overcome in order to maintain its mechanical properties when dealing with water.

2.1.2 (d) Membrane based

Membranes are another materials, that can be used to form plates in heat exchanger. They are capable to carry out both sensible heat and latent heat simultaneously during the system running (Zhang, 2008). In comparison with fibrous material, membranes also have micro-porous structure that able to perform a good heat transfer process (Min & Su, 2010). However, the efficiency of membranes also depend on the parameters such as membrane thickness and membrane gap spacing. Studies showed that even a thin layer of membrane was able to give better transfer process in the heat exchanger system (Min & Su, 2010). It was also important to have a suitable membrane gap spacers in heat exhchanger to enhance heat and mass transfer of the system (Zhang, 2008).

2.2 Performance parameters

As far as the heat exchanger is concerned, there are few variable parameters that need to be controlled in the system which are speed of air flow, air temperature, air humidity, and thickness structure of material. These four important parameters are crucial to ensure that the heat exchanger is able to transfer sensible heat and latent heat efficiently. However, the focus factor in this study was the structure of material which infuenced to reduce temperature and humidity as the air pass through the heat exchanger core (Zhang, 2009).

2.2.1 Thickness structure of material

The material thickness is also one of important parameter to develop the main core for heat exchanger. Recent studies had found that the effeciency of heat and mass transfer was reduced with the increase in the material thickness (Figure 2.5). Since, the thickness of material also were affected by structure of the material which turn to expand during heat and mass transfer process. As the thickness increase, the energy transfer process faced a lot of resistances that preventing smooth energy conversion. This has led to reduced sensible ad latent heat transfer rate and consequently reduced the system performances(Min & Su, 2010).

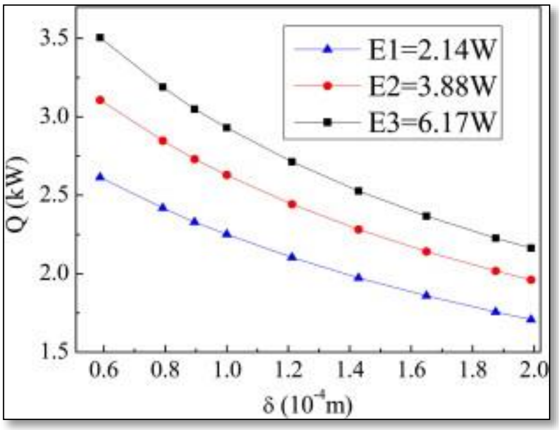

Figure 2.5 Total heat transfer rate plotted against the membrane thickness with the fan power as parameter (Min & Su, 2010)

2.3 Plant composition

2.3.1 Cellulose

Plant fibers are mainly composed of cellulose, hemicellulose, and lignin. Cellulose is the most abundant biopolymer available on the earth. It was formed by the combination of multiple glucose monomers at β-1,4 glycosidic bond (Figure 2.7) (Suganuma et al., 2008). The cellulose existed in any biomass such as wood, cotton, hemp, and other plant-based material. Cellulose microfibrils can be found as interwined microfibrils in the cell wall. It contributes to reinforce the plant by giving mechanical strength on plant structures (Morán et al., 2008; Siró & Plackett, 2010). Cellulose has been reported to form at or outside the plasma membrane by using freeze fracture technique (O'sullivan, 1997). Cellulose has 55.22 % of amorphous structure that may contribute to water absorption and the rest is 44.78 % crystalline (Fatin et al., 2015). In order to isolate crystalline region, usually acid hydrolysis had been used to remove the amorphous region (Bondeson, Mathew, & Oksman, 2006; Dong, Revol, & Gray, 1998).

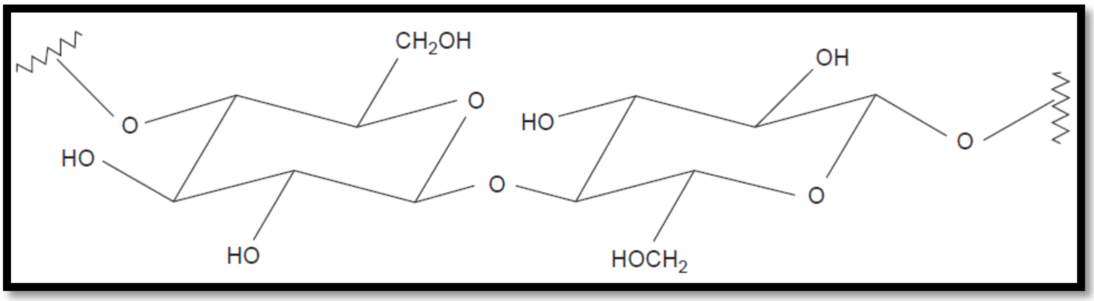

Figure 2.6 Fragment of cellulose chain (O'sullivan, 1997)

2.3.2 Hemicellulose

Hemicellulose is a combination of many types of cyclic saccharides such as xylose, mannose, and glucose. It consists of highly branched random structure which mainly from amorphous region (Moran et al., 2008). Hemicellulose occupies spaces between the fibril in both primary and secondary of cell wall. It is also soluble in hot water and attached to cellulose by hydrogen bond. Removal of hemicellulose may cause physical changes of fibers, making them less dense and rigid with the increase in moisture absorption (Pejic et al., 2008).

2.3.3 Lignin

Lignin is amorphous and consists of aromatic units such as guaiacyl, syringyl and phenylpropane (Moran et al., 2008). Lignin could not be easily accessed or degraded during treatment due to the presence of strong carbon-carbon linkages and other chemical groups such as aromatic groups, that are very resistant to chemical attack (Pejic et al., 2008).Lignin exists in the fiber as a random polymer network. It act as matrix by connecting cellulose and hemicellulose so that they can be held together (Spence et al., 2010). Removal of lignin may increase the bonding between fiber when formed into network as hydrogen bonds will occur without any interruptions from lignin. (Mwaikambo & Ansell, 2002; Spence et al., 2010). Pulping process involved alkali treatment where the lignin would be extracted out from the fibers. There are few pulping methods that can be applied in order to remove lignin in fibers which are chemical pulping, mechanical pulping, and chemi-mechanical pulping.

2.4 Paper making technology

In paper making technology, there are several processes involved such as pre-treatment, wood preparation, pulping process, chemical recovery, and bleaching. Paper can be produced from virgin pulp by mechanical pulping or chemical pulping. Both of these techniques are able to produce pulp for paper making. Excessive paper production, lead to deforestation, hence recycled paper was used as an alternative source for paper making. However, the mechanical strength of paper made from recycled paper was not strong enough as compared to paper made from virgin pulp due to the reduction in fiber length (Moshkelani ., 2013). Wood has long been used as the main ingredient in paper making because it is abundant and able to produce high quality paper. Alternatively, there are other resources such as straw, hemp, grass, cotton, and others which have potential to be used as raw materials for paper making. There is one significant difference between paper produced from wood and other materials which is the amount of paper that can be produced. This is because wood will give higher pulp yield as compared to other cellulosic material, which contain high amount of ashes. In the production of paper, there are two phases,which is from raw material to the pulp and from pulp to paper. Production types of a paper are depending on their final application (Moshkelani et al., 2013).

2.4.1 Pre-treatment (prehydrolysis)

Previous research reported that the high purity unbleached cellulose pulp could be obtained from empty fruit bunches via prehydrolysis treatment and soda pulping (Leh et al., 2008). The prehydrolysis is a water treatment process that usually applied before pulping. The process involved steam power, where the fibers are pressurized at high pressure and high temperature in digester. At this point, hemicellulose in the fibers will be hydrolyzed, lignin will be modified, surface area will be increased, and crystallinity of the cellulose and its degree of polymerization will be decreased (Kaar et al., 1998; Shamsudin et al., 2012). For lignin removal, the process will take place during pulping process. In principle, pulp can be obtain either via mechanical or chemical process. However, the pulp produced by chemical pulping is able to give better quality in optical and mechanical properties as compared to mechanical pulping (Daud et al., 2013). Therefore, a part of this work will study the effect of hemicellulose and lignin removal on fiber by adjusting the prehydrolysis time and the concentratation of sodium hydroxide.

2.4.2 Capillary action

Capillary action is an ability of a fluid to flow in narrow spaces without any external assistance forces. In order to achive equilibrium balance, the capillary action must be able to lift up and transfer the liquid against the gravity (Wong et al., 2001). It occurs when the inter-molecular forces take place between a liquid and its surrounding surfaces.The mechanism of capillary action is caused by cohesion force and adhesion force. The cohesion force pulls the liquid among themselves while for adhesion force is the ability of the liquid to attach on the solid surface. The speed of absorption and the forces for lifting the liquid against gravity depends on the diameter of capillary (Tan & Guo, 2013; Thomas et al., 2015). Previous study show that the chemical composition of hemicellulose and lignin will end up affecting the diameter of capillary of the fiber (Pejic et al., 2008). The capillary action will be affected by the diameter of the capillary. Capillary with smaller diameter will allow fluid to transfer further due to a huge amount of adhesion and cohesion forces (Tan & Guo, 2013; Thomas et al., 2015).

2.4.3 Paper making process

Paper manufactured from each paper mill may have undego different process, depending on its final applications. Paper making process can be divided into several operations, including pulping process, stock preparation, paper making, after process, and finished end (Rao et al., 2013). Pulping process, will extract the raw fibrous source by removing impurities such as lignin and silica. Pulping process was executed by using digester filled with chemical such as NaOH. In pulping process, the fibers will be cooked in digester at high temperature and high pressure. High quality pulp produce is dependent on the amount of chemical added, pressure applied, and temperature used during pulping process (Daud et al., 2013).

The purpose of stock preparation is to provide pulp solution for paper formation process. Pulp will be dispersed into water into certain consistency and additives were added to improve paper properties. Stock preparation will also determine the types of paper that will be produced. Paper additives are added during paper stock preparation which was before paper formation process. The amount of water to produce stock consistency will affect the grammage of paper during paper formation. It was important to make sure the pulps in solution were fully dispersed or it will result in defect after papermaking (Rao et al., 2013). After paper formation was completed, coating was applied to improve the surface structure of paper. Afterwards, paper was compressed at calendering process to increase the fiber bonding in paper which led to increase in paper density. At the end of process, paper will be trimmed and cut according to size before being dispacthed or sold (Rao et al., 2013).

2.5 Pulping process

In the pulping process, it started with the preparation of raw material. The pulping process can be divided into 2 types, which are chemical pulping and mechanical pulping. Both types of pulping have their own advantages and disadvantages. For example, mechanical pulping can result in 90% of fiber yield. Meanwhile, for chemical pulping, amount of pulp produced is low and the total yield is only about 50 %. However, the pulp produced by using chemical pulping have higher quality as strength and brightness are concerned (Bajpai, 2013).

In mechanical pulping, the mechanical energy was used in order to produce pulp. By applying mechanical force to wood fiber, fibers were separated until fragment. The mechanical force will remove the lignin out from the fiber (Thompson et al., 2001). The main objective of mechanical pulping is to maintain part of lignin to achieve high yield production with acceptable strength and suitable brigthness properties. However, mechanical pulping may cause defect to the fiber structure by reducing the length of fiber (McDonald et al., 2004). Mechanical pulping have low aging resistance where the paper produced may has tend to discolor. Even though mechanical pulp produced weak strength pulp, it was able to produce huge amount of paper at low cost (Bajpai, 2013).

Another method was chemical pulping. The chemical pulping was using alkali treatment such as Sodium Hydroxide or Sodium Sulphide at high temperature and high pressure by using digester (Chakar & Ragauskas, 2004). At current temperature, lignin does not melt. It is amorphous and crosslinked. The lignin will be extracted out from the fibers according to the amount or concentration of chemicals used.This method is commonly used in most commercial paper production in the world. The process extracts the fiber by using digester which cooks at high temperature and high pressure.

The objective of chemical pulping is to dissolve the lignin by using chemicals. However, if the concentration of chemicals was too high, it may cause cellulose degradation that cause reduction in fiber strength (Gurnagul et al., 1992; Knill & Kenned, 2003). The advantages of chemical pulping is that, it can produce clean pulp that is brighter and better than mechanical pulping (Bajpai, 2013).

After pulping, the process will be followed by next steps such as screening, washing, refining, and others. This process is aimed to produce a smooth, clean and high quality pulp. Although mechanical pulp has low brightness, it can be overcome by bleaching using peroxides and hydrosulphites. For chemical pulping, bleaching is intended to remove the remaining lignin that was not dissolved during pulping process. The examples of bleaching chemicals used during chemical pulping are oxygen, hydrogen peroxide, ozone, and others. After the pulping process was completed, the pulp was ready to be formed into paper sheet (Bajpai, 2013).

2.6 Polyvinyl alcohol (PVOH)

2.6.1 Polyvinyl alcohol potential as membrane

In chemical processing industry, the separation liquid mixtures was measured using pervaporation(PV) which known as rate of energy-efficient process. Pervaporation is a very high potential industrial process to separate liquid mixtures especially dehydration of organic solvents (Svang et al., 2006) .This process were used especially for separation of azeotropic or close boiling mixtures (Han et al., 2008). However, the main problem for industrial application of PV processes is the ability to synthesis or tailor membrane material with high pervaporation performance. Another fundamental issue is modeling pervaporation transport to optimize PV process. The model of mass transfer through the membrane has been studied quite extensively. Many models were proposed to predict the mass transfer process, such as solution-diffusion model, thermodynamics of irreversible process, Maxwell–Stefan theory, pore flow model, pseudo phase change solution-diffusion model, resistance-in-series model, molecular simulation and so on (Han et al., 2008). Among those models, the solution-diffusion is most widely model used in describing pervaporation transport including sorption and diffusion steps. For the diffusivity, the predictive methods of component diffusion in polymer solution have been commonly studied (Han et al., 2008). Membranes based on polyvinyl alcohol for dehydration of organic solvents have been studied. Previous research reported there are good pervaporation performance for dehydration of alcohol by using crosslinked membrane (Svang et al., 2006). The total permeation flux was not very high but the selectivity was excellent.

Polyvinyl alcohol is a well-known polymer that being used as membrane material due to high tensile and impact strength (Ahmad et al., 2012). As a hydrophilic material for pervaporation membranes, polyvinyl alcohol has drawn a great attention in past decade. Not only that, polyvinyl alcohol is a good film forming and has outstanding chemical resistant properties. It is a desirable material to be developed into membrane with good antifouling properties. However, the pure polyvinyl alcohol has a very poor stability in the aqueous solutions, which makes it impossible to use it directly for the separation of the aqueous and organic solutions. The precipitated polyvinyl alcohol film formed is still soluble in the water and cannot be used as a separation membrane for the aqueous mixtures. Therefore, there are numerous studies being done in order to understand how to increase the stability of this material. One of the methods is to crosslinking polyvinyl alcohol polymer. This method is usually achieved by reacting the polymer with a curing agent. Kim et al., (1993) have done studies on the effects of the crosslinking degree on the properties of polyvinyl alcohol membrane which are more focused on the degree of swelling and the pervaporation studies (Ahmad et al., 2012). Chuang et al., (2000) discussed the effect of acid on the formation mechanism of polyvinyl alcohol membranes. It was found that, the higher degree of crosslinking, the more rigid and compact structure of polyvinyl alcohol membrane will be produced. This has resulting to reduce the amount of water being absorb into the membrane (Das et al., 2010 : Fumio et al., 1990 : Muhlebach et al., 1997).There are many other research that study the effect of pervaporation performance after crosslinking of polyvinyl alcohol. Studies report that the additives of low molecular weight or secondary polymer are normally used as the additive in formation of PVA membrane (Ahmad et al., 2012).

2.6.2 Applications of polyvinyl alcohol

Polyvinyl alcohol is a non toxic synthetic polymer. It has wide range of usage such as in industrial, commercial, medical, and also in food application.Applications of polyvinyl alcohol including, resins, lacquers, surgical threads, and food-contact application (DeMerlis & Schoneker, 2003). Polyvinyl alcohol has been often used for packaging and coatings application. This was because it can be used for reinforcement with good physical properties such as high durability, good flexibility, and ecofriendly (Takahashi et al., 1998). In addition, the polyvinyl alcohol can be dissolved in water at room temperature. This can solve the problem of environmental pollution by using polyvinyl alcohol as raw material for making plastic bags to replace polyethylene. In fact, polyvinyl alcohol has already been used as main material for packaging in the medical sector. The problems faced by workers in the hospital was, there was direct contact between the contaminated patients clothes and worker during laundry. By using laundry bags made of polyvinyl alcohol, they were directly inserted into the washing machines without the need to unwrap as those would dissolved in water soon. This way, workers were protected from biohazard as there was no direct contact had occurred during laundry (Griffin, 1966). Generally polyvinyl alcohol is able to be crosslinked using curing agents, which may be accomplished by chemical reactions (e.g. radical polymerization, chemical reaction of complementary groups, using high energy irradiation, or enzymatic reaction) or by physical reaction (e.g. ionic interaction, crystallization of the polymeric chain, hydrogen bond between chains, protein interaction, or design of amphiphilic block and graft copolymers (Hennink & Van Nostrum, 2012). Polyvinyl alcohol is prepared by hydrolysis of polyvinyl acetate. It can be fully hydrolyzed(A) or partially hydrolyzed(B) (Figure 2.7).

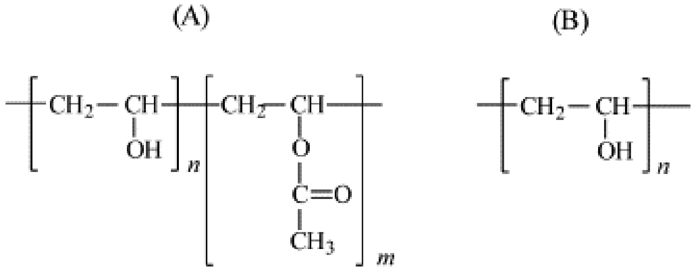

Figure 2.7 Two type of polyvinyl alcohol which is (A) partially hydrolyzed and (B) fully hydrolysed (Anonymous, 2017 c)

2.6.3 Polyvinyl alcohol as hydrophilic polymer

The hydrophilic polymer is a polymer capable of absorbing or attracting water (water loving). Hydrophilic polymer is able to dissolve in water, but its nature can be changed into hydrophobic (water hating) by adding the curing agent in esterification process. Crosslinking will consume the OH- groups on the polymer and will prevent the structure from breaking after having contact with water or moisture (Birck et al., 2014). Due to its solubility in water, polyvinyl alcohol often combined with other polymers in multi layer structure by locating it in the core layer to prevent contact with water. However, this solubility can be changed by crosslinking using curing agent. Example of curing agents suitable for polyvinyl alcohol are glyoxal (Conte et al., 2007), glutaraldehyde (Hasimi et al., 2008; Mansur et al., 2008), citric acid (Shi et al., 2008; Wang et al., 2014), succinic acid (Ajji, 2005) and tartaric acid. Some of curing agents are highly toxic while others are non toxic which found use in food application or medical application. For example, citric acid is one of the mostly used curing agent as food application that able to be acquired at low price. The curing agent must be able to perform crosslink to the hydroxyl groups in polyvinyl alcohol (Figure 2.8) (Dainelli et al., 2008; Martel et al., 2005).

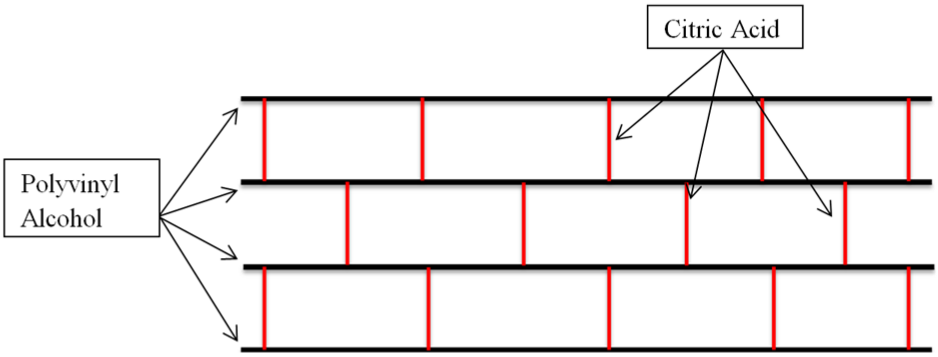

Figure 2.8 Crosslinked polyvinyl alcohol using citric acid

2.6.4 Polyvinyl alcohol compatibility with fiber

Polyvinyl alcohol is a polymer that has high compatibility with natural fiber and can be used to produce biodegradable products. Cellulose in fibers is hydrophilic due to presence of hydroxyl groups similar to polyvinyl alcohol (Dai & Shivkumar, 2007; Qin & Wang, 2006; Shao et al., 2003). In addition, natural fibers and polyvinyl alcohol have good interaction and it has been witnessed by many micrographs from previous research. It was shown that green composites made of bamboo using polyvinyl alcohol as binder had resulted in good bonding between the fiber and polyvinyl alcohol, which produced high tensile composites (Kim & Reneker, 1999; Boon Khoon Tan et al., 2015).