ACETONE SOLUBLE CELLULOSE ACETATE FROM OIL PALM EMPTY FRUIT BUNCHES (OPEFB) VIA A ONE STEP HETEROGENEOUS PROCESS FOR MEMBRANE APPLICATIONS

FAUZI

UNIVERSITI SAINS MALAYSIA

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by

FAUZI

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LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
CPO	Crude palm oil
CTA	Cellulose triacetate
DMSO	Dimethylsulfoxide
DS	Degree of substitution
DSC	Differential Scanning Calorimetry
DTG	Derivative thermogravimetric
ECF	Elemental chlorine free
ELM	Emulsion liquid membrane
FTIR	Fourier Transform Infra-Red
GA	Glutaraldehyde
GPC	Gel Permeation Chromatography
Mw	Molecular weight
O	Oxygen bleaching
OPEFB	Oil palm empty fruit bunch
P	Peroxide bleaching
PAA	Polyacrylamide
PAN	Polyacrylonitrile
PDMS	Polydimethylsiloxane
PS	Polysulfone

PV	Pervaporation
PVA	Poly vinyl alcohol
SEM	Scanning Electron Microscopy
SLM	Supported liquid membrane
TCF	Totally chlorine free
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TMS	Tetramethylsilane
XRD	X-Ray Difraction
Z	Ozone bleaching

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APPENDIX A	**Fauzi Muhammad Djuned**, Mohammad Asad, Mohamad Nasir Mohamad Ibrahin and Wan Rosli Wan Daud (2014). Synthesis of cellulose acetate from TCF oil palm empty fruit bunch pulp. *Bioresources*, 9(3), 4710-4721.	143
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APPENDIX C	**Fauzi Muhammad Djuned**, Wan Rosli W.D. and M.N. Mohamad Ibrahin (2012). Effect of process variables on the degree of substitution of cellulose acetate synthesized from oil palm empty fruit bunches. *Proceeding of MAMIP2012 Asian International Conference on Materials, Mineral and Polymer*, 23rd – 24th March 2012, Penang, Malaysia.	145
APPENDIX D	**Fauzi Muhammad Djuned** and Wan Rosli Wan Daud (2011). Potential utilization of the oil palm empty fruit bunches (OP-EFB) for producing cellulose acetate membrane. Proceeding of 4th USM-JIRCAS Joint International Symposium, 18-20th January 2011, Penang, Malaysia.	146

SELULOSA ASETAT TERLARUT ASETON DARIPADA TANDAN BUAH KELAPA SAWIT KOSONG (OPEFB) MELALUI PROSES HETEROGEN SATU LANGKAH UNTUK APLIKASI MEMBRAN

ABSTRAK

Selulosa asetat (CA) biasanya dihasilkan melalui tindak balas antara selulosa dan asetik anhidrida berlebihan dengan kehadiran mangkin asid sulfurik dalam proses pengasetilan dua langkah, kemudian diikuti oleh hidrolisis. Proses ini dapat dijimatkan secara ekonomi jika langkah hidrolisis dapat dikurangkan atau dilangkau. Dalam kajian ini, CA terlarut aseton dengan DS 2.52 telah berjaya disintesis daripada tandan buah kelapa sawit kosong (OPEFB) tanpa perlu langkah hidrolisis melalui pengasetilan heterogen selulosa menggunakan gabungan natrium bisulfat dan asid sulfurik sebagai pemangkin. Kaedah ini dapat dilakukan dengan menggunakan model matematik proses pengasetilan heterogen dengan masa tindak balas dan nisbah asetik anhidrida/selulosa (R) sebagai pembolehubah. Dari model yang diperoleh, R = 4.4 dan 1.5 jam masa tindak balas dengan DS 2.52 telah ditentukan sebagai keadaan optimum proses pengasetilan. Model ini telah disahkan oleh data eksperimen dan memberikan ralat kurang dari 2.5%, menunjukkan selulosa asetat boleh dihasilkan tanpa perlu langkah hidrolisis dengan keadaan tindak balas yang sesuai. Tindak balas pengasetilan telah dibuktikan oleh analisis FTIR melalui kemunculan puncak-puncak di 1753, 1384, dan 1240 cm^{-1} yang sepadan dengan karbonil C=O regangan ester, CH dalam -O(C=O)-CH3 dan regangan CO dari kumpulan asetil dalam spektrum FTIR. Analisis ^{1}HNMR menunjukkan bahawa antara tiga kumpulan OH dari selulosa OPEFB, pengedaran bahagian asetil lebih banyak pada kedudukan C6, diikuti oleh C2 dan C3. Analisis XRD dengan puncak

lebar di 2θ = 13° dan 2θ = 17° menunjukkan pengurangan penghabluran dalam OPEFB-CA yang ketara, keputusan ini turut disokong oleh kajian DSC yang dianggarkan bahawa penghabluran daripada OPEFB-CA adalah hanya 6.41 %. Filem OPEFB-CA mempunyai sifat mekanik yang baik di mana kekuatan tegangan dan modulus Young OPEFB-CA adalah lebih tinggi dari CA komersial. OPEFB-CA dengan DS 2.52 telah digunakan sebagai substrat untuk penyediaan membran asimetrik yang disalut dengan polivinil alkohol (PVA) untuk menghasilkan membran OPEFB-CA/PVA komposit. Membran OPEFB-CA/PVA komposit ini memberikan prestasi yang baik apabila digunakan dalam pervaporasi campuran etanol/air yang memberi fluks tinggi tetapi selektiviti yang agak rendah. Untuk meningkatkan prestasi membran, glutaraldehid (GA), ejen rangkai silang, telah ditambahkan kepada OPEFB-CA/PVA komposit menyebabkan peningkatan selektiviti dari 14.7 pada kepekatan suapan 90 % kepada 119.2 pada kepekatan suapan 99 %. Dalam usaha untuk menunjukkan bahawa membran rangkai-silang ini (OPEFB-CA/PVA/GA) boleh digunakan untuk proses pervaporasi dalam darjah yang lebih besar, pengiraan peningkatan skala telah dilaksanakan melalui simulasi. Hasil simulasi menunjukkan bahawa sistem pervaporasi menggunakan membran OPEFB-CA/PVA/GA komposit boleh menulenkan etanol berair sehingga 99.9 %.

ACETONE SOLUBLE CELLULOSE ACETATE FROM OIL PALM EMPTY FRUIT BUNCHES (OPEFB) VIA A ONE STEP HETEROGENEOUS PROCESS FOR MEMBRANE APPLICATIONS

ABSTRACT

Cellulose acetates (CA) are normally produced by reaction of cellulose with an excess of acetic anhydride in the presence of sulfuric acid catalyst in a two step process of acetylation, followed by hydrolysis. It would be of economic significance if the hydrolysis step could be reduced or totally eliminated. In this research, acetone soluble CA of DS 2.52 has been successfully synthesized from oil palm empty fruit bunches (OPEFB) without the need of the hydrolysis step via a heterogeneous acetylation of cellulose using a combination of sodium bisulfate and sulfuric acid as catalysts. This has been only made possible by using a mathematical model of the heterogeneous acetylation process of OPEFB cellulose by varying the reaction time and acetic anhydride/cellulose ratio (R). From the obtained model, R = 4.4 and a reaction time of 1.5 hours with a DS of 2.52 were determined as the optimum conditions of the acetylation process. The model has been verified by experimental data and gave less than 2.5 % error, indicating cellulose acetate can be produced without the necessity of the hydrolysis step with proper reaction conditions. Evidence of acetylation was provided by FTIR analysis with the appearance of peaks in OPEFB-CA such as those at 1753, 1384, and 1240 cm^{-1} corresponding to carbonyl C=O stretching of ester, C-H in -O(C=O)-CH_3 and C-O stretching of acetyl groups in the FTIR spectrum. ^{1}HNMR analysis showed that among the three OH groups of OPEFB cellulose, the distribution of the acetyl moiety shows a preference at the C6 position, followed by C2 and C3. XRD analysis show broad peaks at 2θ = 13° and 2θ

= 17° indicate a significant reduction in crystallinity in OPEFB-CA, which is further supported by DSC studies where it is estimated that the crystallinity of OPEFB-CA is only 6.41%. The OPEFB-CA films exhibited good mechanical properties where the tensile strength and Young's modulus of the OPEFB-CA are higher than the commercial CA. The obtained OPEFB-CA of DS 2.52 was then used as a substrate for the preparation of a porous asymmetric membrane coated with polyvinyl alcohol (PVA) to form a composite of OPEFB-CA/PVA membrane. This membrane composite of OPEFB-CA/PVA gave a good performance when applied in the pervaporation of ethanol/water mixture giving a high flux but rather low selectivity. To improve the performance of the membrane, glutaraldehyde (GA), a crosslinking agent was added to the OPEFB-CA/PVA composite resulting in an increase in selectivity from 14.7 at 90 % feed concentration to 119.2 at 99 % feed concentration. In an attempt to demonstrate that this crosslinked membrane (OPEFB-CA/PVA/GA) can be used in a larger degree of the pervaporation process, a scale up calculation has been carried out through simulation. The simulation result showed that the pervaporation system using OPEFB-CA/PVA/GA composite membrane can purify aqueous ethanol up to 99.9 %.

CHAPTER 1

INTRODUCTION

1.1 Background

Cellulose acetate (CA) is one of the most important cellulose derivatives in which all or part of the three hydroxyl groups in glucose rings are substituted by acetyl groups. The number of hydroxyl groups substituted by acetyl is expressed by a parameter called degree of substitution (DS). Depending on its DS, CA can be used for different applications, such as plastics (Tang et al., 1997; Tian et al., 2014) coating, film, textile (Reddy and Yang 2005; Entwistle and Rowe 1979) and synthetic polymeric membrane (Velu et al., 2014; Guilminot et al. 2007; Idris and Yet 2006; Sedelkin et al. 2006; Strathmann 2001; Wibowo et al. 2006; Yea et al. 2006). Fibers and membranes are usually made from cellulose diacetate with DS between 2.2–2.7, while films are made from cellulose triacetate with DS above 2.7 (Heinze et al., 2003). The widest usage of CA is acetone soluble CA with DS 2.4-2.5, usually called as diacetate or secondary acetate (Steinmeier, 2004; Fischer et al., 2008). Acetone soluble CA is more industrially important due to its low toxicity and the price of the acetone is relatively cheap (Sun et al., 2013).

Cellulose acetate is typically produced from a high quality chemical cellulose with an α-cellulose content more than 95% (Saka and Matsumura, 2004). The high quality chemical cellulose can usually be obtained from cotton and wood dissolving pulp which are expensive. In order to reduce the production cost, it is necessary to find alternative sources of cellulose as raw material. Lignocellulosic biomass has attracted the attention of many researchers as a renewable cellulose resource because it is available in large quantity and is routinely cultivated in the world. During the

past several years, many studies have been carried out to prepare cellulosic materials and cellulose derivatives from the agricultural by-products and other cellulose wastes such as wheat straw (Sun et al., 2004), sugarcane bagasse (Rodrigues Filho et al., 2000; Liu et al., 2006; Cerquera et al., 2007; Shaikh et al., 2009), cornhusk (Cao et al., 2007), cotton by-products (Cheng et al., 2009; 2011) and recycled newspaper (Rodrigues Filho et al., 2008). Among numerous biomass resources, oil palm wastes such as empty fruit bunches (OPEFB), trunk and frond form a promising feedstock for this purpose, especially in Indonesia and Malaysia as the two largest palm oil producers in the world. In 2013 Indonesia and Malaysia produced about 45 million tons of crude palm oil (CPO) in total (MPOB, 2013; GAPKI, 2014). Of all the oil palm residues, OPEFB is the most potential biomass from the palm oil industry due to its abundance where it is estimated that every ton of produced CPO yields 1.1 ton of OPEFB as by-product (Sudiyani, 2009).

Commercially, cellulose acetates are synthesized through the reaction of cellulose with an excess of acetic anhydride in the presence of sulfuric acid or perchloric acid as the catalysts in a two-step process; acetylation, followed by hydrolysis. The acetylation reaction takes place in a heterogeneous state until the end of reaction where the whole reaction mass becomes a viscous liquid. Due to the heterogeneous nature of the reaction, it is arguably unlikely to synthesize partially substituted cellulose acetates directly. Therefore, the hydrolysis step is required to produce cellulose acetate with the desired DS (Steinmeier, 2004; Cao et al., 2007). This typical industrial process of producing CA has some disadvantages where it requires very high quality cellulose raw material with high alpha cellulose content.

In an attempt to limit the use of sulfuric acid, Kuo and Bogan (1997) and later Ozaki et al. (2004) has successfully used a combination of sodium bisulfate and

sulfuric acid as catalysts. The use of bisulfate in the process, apart from improving the acetylation, could also allow the reaction to occur effectively even at room temperature, both of which are interesting features which could potentially allow the use of low grade raw materials in the production of CA.

The synthesis of CA is a two-step process viz. acetylation and hydrolysis, whereby CA is first produced at a high DS (due to excess acetic anhydride as the acetylating agent) followed by hydrolysis of the product to the required DS level. It would be of economic significance if the hydrolysis step could be totally eliminated. The objective of this study is to investigate the possibility of synthesizing acetone soluble CA in a one-step heterogeneous acetylation using cellulose from oil palm empty fruit bunch (OPEFB) which has been prepared via the environmentally friendly processes. Acetone soluble CA (DS 2.4-2.5) is the target of this research because of its industrial importance (Steinmeier et al. 2004, Fischer et al., 2008). To achieve this aim, mathematical modeling of the effects of DS on the process variables of reaction time and reactant ratio of acetic anhydride to cellulose will be exploited.

Cellulose acetate is one of the first materials used in membrane separation technology, and today, it has been universally recognized as the most important membrane polymer due to its availability in a wide variety of viscosity grades, low cost and good fouling resistance (Vidya and Mohan, 2010) and has an outstanding formability. They are also a cost-effective alternative to other filtration materials available in the market. In separation technology, CA is mostly applied as a porous membrane. Aside from membrane filters for laboratory usage, today CA is widely used in drinking water purification, seawater desalination, waste water treatment,

concentration of fruit juices, protein and enzyme sterilization and biological fluid filtration.

Cellulose acetate can also be used as a non-porous membrane for pervaporation process, but it is still limited to laboratory researches and mostly as a combination with other polymers. In recent years, numerous investigations on pervaporation using modified CA membrane for separation of many kinds of liquid mixtures have been carried out.

As part of the current study, an investigation was conducted to explore the possibility of utilizing cellulose acetate from OPEFB for membrane applications. The OPEFB CA was used to compose a CA/PVA composite membrane that can be applied to pervaporation of ethanol/water mixtures.

1.2 Problem Statement

To produce a good quality CA membrane, CA should be dissolved in a polar organic solvent with high volatility such as acetone. The solubility of CA in acetone depends on its DS, where CA with high DS (>2.7) is very difficult to be dissolved, while the low DS CA (<2.2) is fragile and also difficult to be dissolved, the most soluble CA is diacetate with DS of ca. 2.5. CA is usually synthesized by reacting cellulose with excess acetic anhydride in a heterogeneous state which produce cellulose triacetate (DS>2.8). It is then put through a controlled, partial hydrolysis to reach a sufficient number of acetate groups to give the product the desired properties. It would therefore be of economic significance if the hydrolysis step could be reduced or totally eliminated. For this purpose, this study investigates an alternative acetylation process that can be used to produce CA in a single step process without

necessitating the hydrolysis process so that use of reactant and time of reaction can be minimize.

Cellulose acetate can be applied in almost all of membrane separation process, whether as a porous or as non-porous membrane, with the latter usually used in pervaporation process. Pervaporation is a very attractive separation process due to its ability to separate an azeotrope mixture, hence making it a suitable candidate for the purification of an ethanol/water mixture. Most ethanol pervaporation system used poly vinyl alcohol (PVA) as membrane because of its good flux performance, however its selectivity is left to be desired. In an attempt to increase its selectivity while at the same time maintaining its flux performance, this study uses OPEFB-CA as a supporting membrane for PVA to form a composite of OPEFB-CA/PVA membrane for the pervaporation of ethanol/water mixture. In a further attempt to increase its performance, the OPEFB-CA/PVA membrane will be crosslinked with glutaraldehyde (GA) to form the composite membrane of OPEFB-CA/PVA/GA. The presence of CA that crosslinked to PVA is expected to inhibit the excessive permeation of ethanol through the membrane, subsequently, membrane selectivity can be increased.

1.3 Objectives

The general objective of this study is to utilize the oil palm empty fruit bunches (OPEFB) for the production of cellulose acetates that can be applied in membrane separation processes, while the specific objectives of the study are as follow:

1. To produce an acetone soluble CA of DS ca. 2.5 from OPEFB through a one-step heterogeneous acetylation process and examine its characteristics and properties.

2. To develop a mathematical model of the acetylation process and to use the model in determining the optimum condition of the process.
3. To apply the OPEFB-CA for membrane separation processes by making composite membranes of OPEFB-CA/PVA and OPEFB-CA/PVA/GA for purification of ethanol and examine the membrane performance.
4. To study the possibility of applying the composite membrane of OPEFB-CA/PVA/GA for pervaporation of ethanol/water mixture in industrial scale through simulation calculation.

CHAPTER 2

LITERATUR REVIEW

2.1 Cellulose

Cellulose is the most abundant naturally occurring reproducible organic compound (Kamide, 2005). Cellulose can be obtained from wood, cotton and other plants as natural linear polymer chains (Lewin and Pearce, 1985). It is the main constituent of wood and meets up to 40 – 45 % of the dry matter, which are mostly in the secondary cell wall (Sjöström, 1993), more than 90 % of raw cotton (up to 99.9 % of purified cotton) and flax (Kamide, 2005). Cellulose is also a kind of carbohydrate, and contains carbon, hydrogen and oxygen, also known as polysaccharides which shows that it has a lot of sugar (Smook, 1992).

2.1.1 Source of cellulose

Cellulose for industrial conversion comes from wood and a number of minor sources such as agricultural lignocellulosic biomass. Although most papers and rayons are made from wood pulp, sometime cotton is an ingredient as well. The importance of cellulose recycling is increasing, especially for paper products. On a more biological level, the majority of cellulose is in plant secondary cell walls, where it is usually the principal material. Primary cell wall have lower cellulose content, less crystalline, and have lower molecular weight. Some cellulose comes from the hairs on seeds, like cotton, kapok, and milkweed. Bast fibers such as hemp, ramie, linen, and jute are obtained from the stems of plants (French et al., 2001). One of the most potential alternative sources of cellulose is oil palm empty fruit bunch (OPEFB) that will be discussed further in section 2.2.

Cellulon, a commercial bacterial cellulose product was recently introduced. The fibers are produced through an aerobic fermentation of glucose from corn syrup in a stirred fermentor. It has a small particle diameter (10 μm) that gives it a smooth mouthfeel to formulations in which it is included and has a surface area 300 times greater than typical wood cellulose. Cellulon has an unusual level of water binding and work with other viscosity builders to improve their effectiveness (French et al., 2001).

2.1.2 Chemistry of cellulose

Cellulose is a polymer of β-D-glucose with an empirical formula demonstrated as $(C_6H_{10}O_5)_n$ in form of pyranose. The formation of cellulose in plants can be expressed by a sequence of chemical reactions. Initially, glucose is formed from a photosynthetic reaction of water and carbon dioxide as shown in Eq. 2.1, and the water molecule from adjacent β-anomers of the two cyclic forms of glucose is eliminated to form macromolecule of cellulose as shown in Eq. 2.2 (Hocking, 2006).

$$6\ H_2O\ +\ 6\ CO_2\ \rightarrow\ C_6H_{12}O_6\ +\ 6\ O_2 \qquad (2.1)$$

$$n\ C_6H_{12}O_6\ \rightarrow\ (C_6H_{10}O_5)_n\ +\ n\ H_2O \qquad (2.2)$$

The glucose monomers linked to each other by a 1-4 glycosidic linkage as shown in Fig. 2.1. Formation of cellulose from the β-anomers is the one that make it a linear polymer, which sustains strong intermolecular hydrogen bonding between neighbouring polymer chains. With some 10,000 anhydroglucose units (AGU) per chain (Mw ≈ 1.5 million), individual molecules length can be up to 0.012 mm. The close intermolecular association and high molecular weight give fibers composed of cellulose great mechanical properties and makes it insoluble in water. Both factors also introduce significant resistance to hydrolysis because of the relative

inaccessibility of the acetal links between adjacent glucose units. The insolubility, strength and hydrolytic stability properties are important features of the structural role of cellulose in the plant as well as being important for the papermaking process and for the properties of paper (Hocking, 2006).

Chemically, cellulose is a two-dimensional high molecular weight polymer with no conjugation, therefore it is insoluble and relatively stable in water or aqueous alkali, is white (colorless) in color, and is tasteless or odorless. However, it is soluble in high concentration of aqueous mineral acids, and may be regenerated into fragments of the solid fibers with lower molecular weight on dilution with water. It is also relatively stable towards oxidation (Hocking, 2006).

Cellulose can be degraded by either acid or alkali. The glycosidic bond is vulnerable to hydrolysis catalyzed by acid. High yield of glucose can be obtained when hydrolysis proceeds for a long time, in days or weeks (French et al., 2001). Glucose, decomposed from cellulose, is β type (Fig. 2.2), which was proven by β-glucocidase against cellobiose. It has a six-membered ring structure (pyranoid). β-glucopyranose has a steric structure as illustrated in Fig. 2.3 (Kamide, 2005).

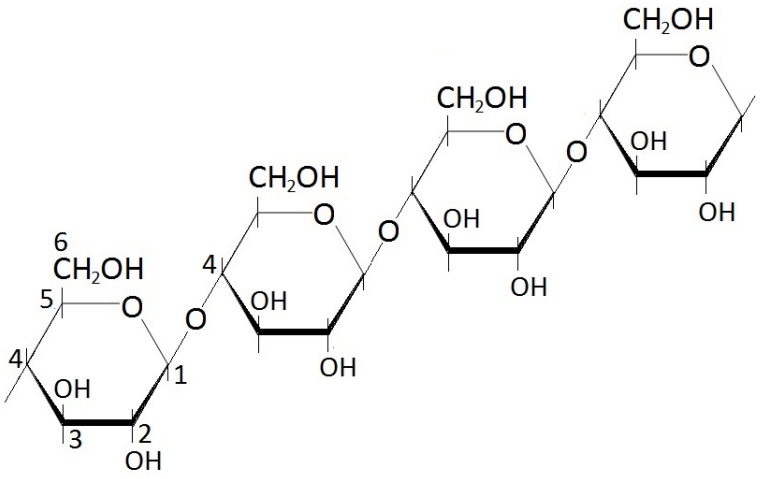

Fig. 2.1 The Haworth structural formula of cellulose shows the β-1,4 linkages between glucose units.

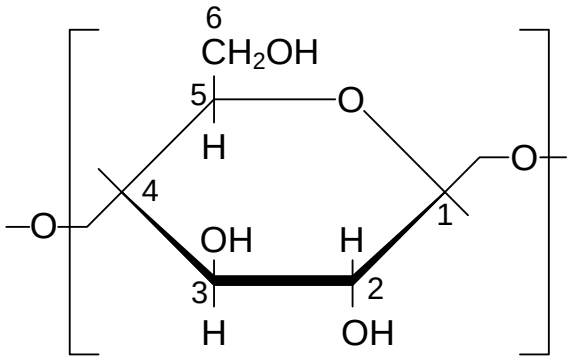

Fig. 2.2. Glucopyranose unit of cellulose

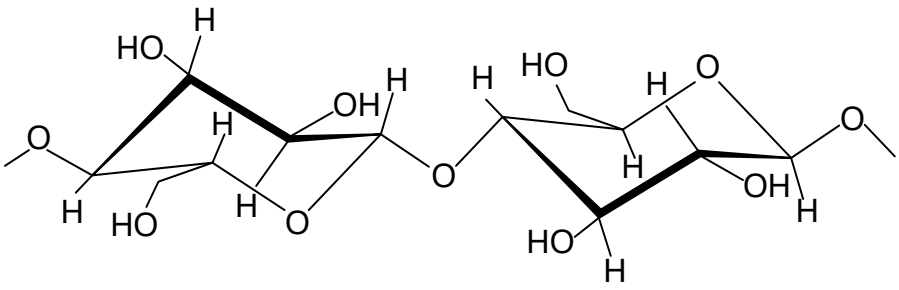

Fig. 2.3. Steric configuration of cellulose.

Each glucose unit of cellulose contains three free hydroxyl groups, if reagents are able to penetrate both crystalline and amorphous regions, substitution reaction (esterification or etherification) will take place. Generally, industrially important chemical modifications of this polymer involve reaction with the hydroxyl groups at the positions of 2, 3 and 6 on glucose ring. These reactive sites behave like alcohols in term of chemical reactivity. Etherification and esterification are particular importance for cellulose. Due to the insoluble and crystalline nature of cellulose, the reactions with the hydroxyl groups usually take place under heterogeneous conditions. Under such mild heterogeneous conditions, the reactivity of hydroxyl groups may depend on whether they are involved in hydrogen bonds (French et al., 2001).

2.2 Oil Palm Empty Fruit Bunch (OPEFB) As a Source of Cellulose

Oil palm empty fruit bunch (OPEFB) is one of several wastes of palm oil plantations and oil palm mills; others are oil palm trunk, frond, fruit fibers and shells. A study conducted by Hassan et al. (1997) showed that one ton of fresh palm fruit can produce 70.48 kg or 7.05 % empty fruit bunch. Fig. 2.4 shows the photograph of OPEFB and its fiber form.

2.2.1 Potential and availability

Nowadays, about 25% of world's total edible oil and fat production come from palm oil, which means palm oil has become the world's largest source of edible oil. Thus, oil palm has now become a major economic crop which triggered expansion of plantation area in Indonesia and Malaysia (Shuit et al., 2009; Sumathi et al., 2008). In 2008, Malaysia produced 17.7 million tonnes of palm oil on 4.5 million hectares of land (Global oil and fat magazine, 2009), and Indonesia produced 17.37 million tonnes of crude palm oil (Sudiyani, 2009). Fig. 2.5 shows the growth of palm oil production in Indonesia and Malaysia from 1999 to 2008. Palm oil industry yields large amount of biomass such as palm frond, empty fruit bunch, palm kernel shell and fiber and palm oil mill effluent.

Fig. 2.4 Oil palm empty fruit bunch (OPEFB) (left) and OPEFB fibers (right)

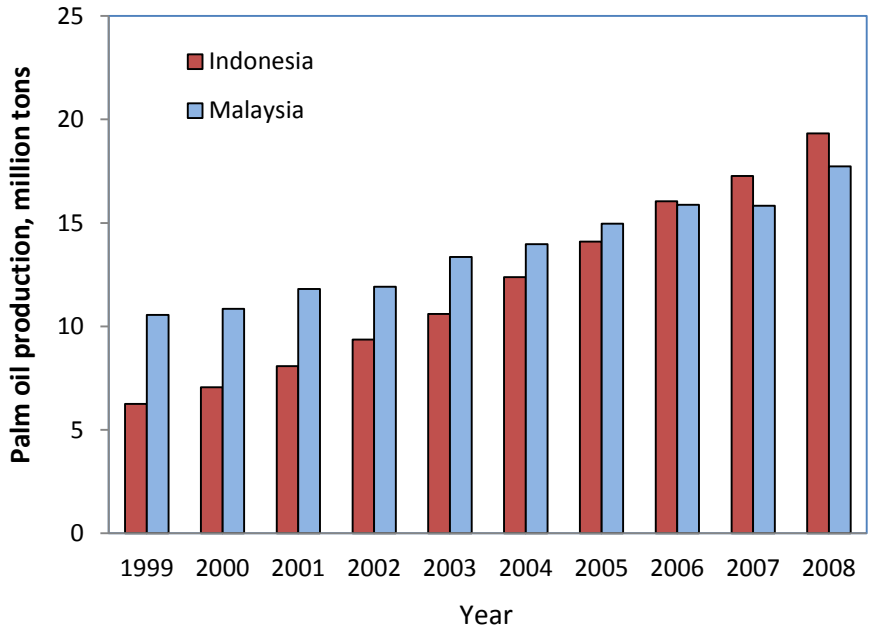

Fig. 2.5. Production of palm oil in Indonesia and Malaysia from year 1999 to 2008. (Source: Muhammad Dujned and Wan Rosli, 2011)

In 2005, there were about 55.73 million tons of oil palm biomass produced in Malaysia, which empty fruit bunches and fibers contributed the most (17 million tons and 19.6 million tons respectively), the others were shell (9.2 million tons), palm

kernel (2.11 million tons), and fronds and trunks (21.1 million tons) (Shuit et al., 2009). The growth of palm oil industry in Indonesia and Malaysia keeps increasing from year to year, where in 2013 Indonesia and Malaysia produced about 45 million tons of crude palm oil (CPO) (MPOB, 2013; GAPKI, 2014). Oil palm empty fruit bunches (OPEFB) is the most potential biomass from palm oil industry, with every ton of CPO produced yielding 1.1 ton of OPEFB as by-product (Sudiyani, 2009).

2.2.2 Chemical composition of OPEFB

OPEFB is one kind of lignocellulosic materials. Generally the main constituents of the lignocellulosic are cellulose (40 – 50 %), hemicellulose (20 – 30 %) and lignin (15 – 20 %) (Lasure and Zhang, 2004). Chemical and physical properties of OPEFB may vary by site and age of the plant (Sreekala et al., 1998). Table 2.1 shows the chemical composition of OPEFB from different locations in Malaysia.

Table 2.1 Chemical composition of OPEFB from different sources

Source of OPEFB	Chemical composition (after normalization), %			Reference
	Cellulose	Hemicellulose	Lignin	
Teluk Intan, Perak, Malaysia	60	24	17	Wan Rosli et al., 2004
Dengkil, Selangor, Malaysia	54	30	16	Ariffin et al., 2008
MPOB, Malaysia	60	22	18	Abdullah et al., 2011

2.3 Pulping process for the production of chemical cellulose

Chemical cellulose for production of cellulose acetate is generally obtained from acid sulfite or prehydrolyzed kraft pulping process (Saka and Matsumura, 2004). The Soda process was widely used in the past, but it was, however, replaced by kraft process.

2.3.1 Acid sulfite pulping

Sulfite pulping process is a full chemical pulping process, using mixtures of sulfurous acid and/or its alkali salts (calcium, magnesium, sodium or ammonium) to solubilize lignin through the formation of sulfonate functionalities and cleavage of lignin bonds. Sulfite process is the most important pulping process since 1900 until it was surpassed by kraft pulping in the 1940s. It now accounts for less than 10% of pulp production (Biermann, 1996).

The cooking liquor in acid sulfite process is prepared by burning sulfur to produce SO_2 and dissolving the gas in water to produce sulfurous acid (H_2SO_3). Wood chips are then cooked with the prepared cooking liquor which consisted of sulfurous acid and alkaline base sulfite. The sulfite cooking liquor is heated partly to the desired temperature and held with the wood chips until uniform liquor penetration is achieved, particularly in acid sulfite processes. The cationic base chemicals (calcium, magnesium, sodium or ammonium) are used in the cooking liquor to prevent discoloration of pulp. The species of the base used in cooking is determined by appropriate choice of cooking condition, resultant pulp yield and quality. The soluble base such as sodium, magnesium and ammonium can be used in cooking process at any pH within the range of 1.5 to 4.0, while the cooking process with the traditional calcium acid sulfite must be carried out at a low pH of about 1.5

due to the relative insolubility of calcium (Biermann, 1996; Saka and Matsumura, 2004).

The wood chips are cooked at temperature 130 – 150 °C under pressure of 75 – 125 psi for 4 to 8 hours. The raw cooking acid after SO_2 absorption is a mixture of SO_2 and combined SO_2 in the desired proportion. The compositions in the cooking liquor are 5 – 10 % in the total SO_2, 3 – 6 % in the combined SO_2 and 0.5 – 1.5 % in the free SO_2. The range of liquor to wood chip ratio is 3.5 to 6.1 (Saka and Matsumura, 2004).

2.3.2 Prehydrolyzed kraft pulping

Kraft pulping is a full chemical pulping method using sodium hydroxide and sodium sulfide at pH above 12 with temperature 160 – 180 °C corresponding to about 800 kPa steam pressure for 30 minutes to 3 hours to extract the lignin as much as possible from wood fibers. It is useful for any wood species, gives a high strength pulp, tolerant to bark, and has an efficient energy and chemical recovery cycle. The disadvantages of this process are the difficulty with which the pulps are bleached compared to sulfite pulps, low yields due to carbohydrate losses, and generates sulfur emissions that are extremely odiferous (Biermann, 1996).

There are several important variables that must be considered during kraft cooking;

1. Wood species (though all species can be pulped) and chip geometry.
2. Effective alkali to wood weight ratio.
3. Concentration of effective alkali and liquor/wood.
4. Sulfidity.
5. H-factor, a function of cooking time and temperature.

The typical kraft pulps contain carbohydrates, mainly pentosans that interfere with the acetylation of cellulose. To reduce the pentosan content in pulps, the prehydrolyzed kraft pulping was developed by exposing the wood chips to acid hydrolysis prior to the alkaline pulping. The wood chips are pretreated with direct steaming at the temperature of 160 – 170 ºC for 1 to 3 hours. The action of the steam releases organic acids such as formic and acetic acids from the wood which hydrolyze hemicelluloses selectively to the soluble sugars. After prehydrolyzed, wood chips are cooked with sodium hydroxide and sodium sulfide to produce pulps suitable for raw material of cellulose acetate production. The pulp yield of this process is generally 5 to 7 % lower than ordinary kraft pulping process (Saka and Matsumura, 2004).

2.3.3 Soda pulping

Soda pulping, invented in England by Burgess and Watts in 1851, uses sodium hydroxide as the cooking chemical. Due to the little enthusiasm in England for this new process, Burgess brought the method to the U.S. in 1854 and the first mill started in 1866. Many of the early soda mills converted to the kraft process once it was discovered. The soda process still has limited use for only easily pulped non-wood materials such as straws and some hardwoods, but is not a major process (Biermann, 1996). However, due to environment issues, the use of soda process began to be reconsidered, especially for non-wood materials. Non-wood biomasses contribute about 8 – 10 % to pulp and paper production (Jiménez et al., 2006) and have grown considerably worldwide over the past few decades. From 1999 – 2003, wood pulp production rose by 4% while the non-wood pulp increased by 10% (Jiménez et al., 2009).

One type of non-wood materials that is effectively to be utilized for pulp, as confirmed by several studies, is oil palm empty fruit bunches (OPEFB). Since 1980s, several studies have been carried out on the suitability of this material as a source for pulp and paper. Alkaline pulping of OPEFB using only sodium hydroxide appears to be the most interesting pulping process when its effectiveness and environmental friendliness is taken into consideration (Wan Rosli et al., 2004; Jiménez et al., 2009).

Soda pulping process is usually conducted at cooking temperature of 160 – 170 °C with an alkali concentration of 20 – 30 % based on dry weight raw material for 60 – 120 minutes, the process gives pulp yield in the range of 30 – 45 % (Wan Rosli et al., 2004; Jiménez et al., 2009). Anthraquinone can be used as a pulping additive to increase delignification and to decrease carbohydrate degradation. It works by going through a cycle which leads to the reduction of lignin and the oxidation of the reducing end-group of cellulose from an aldehyde to a carboxylic acid. Anthraquinone is typically used at about 0.1 % on wood and results in a 1 – 3 % increase in pulp yield (Biermann, 1996).

2.3.4 Bleaching process

Bleaching is defined as a process to increase the brightness of the wood or lignocellulosic pulps using chemical agents. The strategy of chemical pulps bleaching was very much different than mechanical pulp bleaching. Chemical pulp is more concerned with the removal of lignin, but excessive use of chemicals will shorten the cellulose molecule chains that lead to weak fiber strength. While that, mechanical pulps is achieved by chemically altering the portion of lignin molecules that absorbs light. To distinguish it with the chemical pulps bleaching, mechanical pulps bleaching is called brightening (Biermann, 1996).

The main objective of bleaching is to remove the colour bodies associated with the lignin and other impurities that remain in pulp after the pulping operation. At the same time, it is possible to remove hemicellulose and resinous materials. Hemicellulose loss is something that needs to be avoided in the case of papermaking process, however, to produce the dissolving pulp, hemicellulose must be removed to obtain high α-cellulose pulp (Sjostrom, 1993).

Chlorine-based bleaching species is still an option because it attacks lignin selectively with minimum carbohydrate degradation (Hinck, 1985). However, the bleaching rules using chlorination and alkali extraction is allegedly involved in generating polychlorinated dioxin and dibenzofurans to the environment, which are toxins and carcinogens. As a result, research to reduce the use of chlorine base bleaching is encouraged, and it can be replaced by the totally chlorine-free bleaching (TCF) and elemental chlorine free (ECF) (Smook, 1992).

ECF bleaching involves bleaching which replaces all chlorine elements in bleaching system with chlorine dioxide. TCF bleaching is a bleaching sequence using chemicals that do not contain chlorine, including chlorine dioxide. The TCF bleaching sequence usually consists of bleaching stages of oxygen (O), ozone (Z) and peroxide (P), and will be described in more detail in the next section.

2.3.4.1 Oxygen bleaching (O)

Oxygen bleaching is the delignification of pulp using oxygen gas under high pressure (80 – 100 psi) and sodium hydroxide (3 – 4 % based on dry pulp). Oxygen bleaching has been used commercially since the late 1960s. This is an odourless and relatively environmentally friendly process compared to chlorination at high consistencies (20 – 30 %) or medium consistencies (10 – 15 %). Delignification is

performed at 90 – 130 °C for 20 – 60 minutes. The key to the use of oxygen delignification is the discovery that small amounts of magnesium ion (0.05 – 0.1 % on pulp) must be present to protect the carbohydrates from excessive degradation. This is the cheapest bleaching chemical to use, but in terms of selectivity, it is considered less selective for lignin removal. A considerable decrease in cellulose viscosity occurs at the same time in this process (Biermann, 1996).

Most of the kraft pulping will use oxygen bleaching system using oxidized white liquor as a source of alkali to maintain the balance of sulfur or sodium in the chemical cycle. Mostly, the air system is used for the oxidation of white liquor because it is more economical. There are two types of oxygen bleaching system, high consistency and medium consistency system. In high consistency system, pulp available in the range of 25 % and 28 % consistency is performed in a pressurized reactor. While, medium consistency system is provided in the 10 – 14 % consistency reacted with caustic or oxidized white liquor. Both systems performed well. However, the medium consistency system is more widely used due to low costs and safer operating condition (Smook, 1992).

The main problem in oxygen bleaching is inviting random degradation reaction persist due to lack of selectivity in bleaching. However, some studies in the 1960s found that a mixture of magnesium can be used to protect the cellulose from further degradation (Smook, 1992; Lindström, 1988). Peroxide decomposition reaction of hydroxyl radicals will be inhibited by the use of magnesium compounds. Although the method of propagation of magnesium salts was found, severe degradation of polysaccharides have restricted its use in oxygen bleaching (Sjöström, 1993). This does not mean the use of magnesium salts is not necessary, because by adding it, viscosity loss can be minimized. Chemically, this is caused by oxidation of

the cellulose anhydroglucose unit. Reliable heavy metal ions will be precipitated with magnesium hydroxide, $Mg(OH)_2$, formed in the pulp suspension, thereby reducing the decomposition of oxygen. In addition to magnesium, DTPMPA chelating agent (diethylene triamines pentamethylene phosphonic acid) is also claimed to be able to protect the cellulose from degradation (Lindström, 1988).

2.3.4.2 Ozone bleaching (Z)

Ozone is an unstable gas, toxic and blue with a molecular weight of 48 gram/mole. It will change to dark blue and unstable at -111.9 °C temperature, and solidifies at -192.5 ºC. Ozone is more easily soluble in water than oxygen, especially when elevated temperatures decreased, but has a higher solubility in organic solvents like some kind of concentrated acetic acid and carbon tetrachloride (Liebergott, 1992). Ozone has a tendency to decompose in water, and generate some materials that produce reactive oxidizing species unelected including superoxide and hydroxyl radical. Ozone molecules can exist in various mesomeric structures (Sjöström, 1993).

Ozone bleaching has been used as a single bleaching or combined in various stages of bleaching with other bleaching types such as oxygen, peroxide, chlorine dioxide and hypochlorite (Liebergott, 1992). Ozone bleaching is also one that does not relieve any residual toxic. In addition, waste products can also be reused in the bleaching system (Byrd, 1992).

There are three types of bleaching treatment for ozone bleaching, which are in low, medium and high consistency. Low consistency system (0.5 – 3 %) exposed to pulp suspension and dissolved in water to the reaction in a situation where pressure is applied. Viscosity and strength of pulp produced higher than medium and high consistency system, but the required ozone concentration was higher (Johnson,

1993). This type of system is widely used in the industry as because of the consistency of ozone in oxygen is depleted and the impression on left-over pulp is good (Liebergott, 1992). The advantage of the high consistency system is its high selectivity property, which affect both the quality and viscosity of the pulp (Kappel et al., 1994).

2.3.4.3 Peroxide bleaching (P)

Peroxide (typically as hydrogen peroxide) is commonly used in the bleaching of chemical pulp and mechanical pulps, and not common for chemical pulps. This perception changed as pulp mills look for more environmentally friendly process (chlorine-free systems). It is an expensive bleaching agent, but may be used more frequently as the use of elemental chlorine decreases (Biermann, 1996). At 60 ºC, peroxide is an effective material as a bleaching agent to remove lignin which increases the brightness without causing excessive loss of product (Smook, 1992).

The presence of some metal ions, such as Fe^{3+}, Mn^{2+} and Cu^{2+} in the form of colloid, complex or bonded with acid groups catalytically decompose hydrogen peroxide, so peroxide bleaching is carried out with agents that deactivate these metal ions. In this case, sodium silicate (5 % on wood) can be used as the agent (usually after the addition of magnesium ion). The mechanism for inactivating the ions by sodium silicate cannot be explained clearly, it may precipitate the ions, but, strictly it is not a chelating agent. Buffering action is required to keep the pH high even as organic acids are produced as a result of some carbohydrate degradation. Sodium silicate also acts as a buffering agent (Biermann, 1996).

The peroxide bleaching of chemical pulps is run with 0.5 – 3 % peroxide and 0.05 % magnesium on pulp at temperature of 60 – 70 °C, pH of 8 – 10, and

consistency of 10 – 20 % for a retention time of 2 – 4 hours, with brightness gain of 6 – 20 %. Hydrogen peroxide with sodium hydroxide and/or sodium peroxide (NaOOH) is used to produce the high pH that is necessary to produce the active perhydroxyl ion, HOO^-. Some carbohydrate degradation occurs and is responsible for about half of the peroxide consumed (Biermann, 1996).

2.4 Cellulose Derivatives

The use of cellulose depends not only on its natural physical properties, but also on its availability for modifications to the cellulose derivatives through substitution reaction. Each anhydroglucose units of cellulose consists of three reactive hydroxyl groups that can be substituted fully or in part with simple or complex group. Esterification and etherification are two major substitution reactions carried out in industry for the manufacturing of many products, which is called cellulose esters and cellulose ethers (Cook, 1968; Zugenmaier, 2008).

Cellulose esters are commonly derived from natural cellulose by reaction with organic acids, anhydrides, or strong inorganic acids such as nitric acid. Cellulose esters of almost any organic acid can be prepared, but because of practical limitations esters of acids containing more than four carbon atoms have not achieved commercial significance (Immergut, 1981; Gedon and Fengi, 2001). Cellulose acetate is the most important organic ester because of its broad application in fibers and plastics, while cellulose nitrate is the most important inorganic ester.

Cellulose esters from aliphatic and aromatic acids containing more than four carbon atoms and aliphatic diacids are difficult and expensive to prepare due to the poor reactivity of the corresponding anhydrides with cellulose, thus these esters show little interest commercially. However, recently the mixed esters of cellulose

succinates prepared by reaction of cellulose with succinic anhydride and catalyzed by sodium acetate shows some industrial interest. The additional expense incurred in manufacturing succinate esters is compensated by the improved film properties observed in waterborne coatings (Gedon and Fengi, 2001).

Mixed cellulose esters such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) esters have numerous applications, in sheeting, film products, molding plastics, melt dip coatings and lacquer coatings. The properties of CAP esters ordinarily lie between those of CA and CAB. The CAP esters have traditionally covered a narrow composition range compared to the range of CAB esters. Through proper variation of acetyl and butyryl contents, the esters can be adapted to a broad range of applications. CAP and CAB are thermoplastic. If properly formulated, these esters can be processed by methods such as injection molding and extrusion and can be dissolved and casted into films from a variety of solvents. The mixed esters are generally more compatible with various plasticizers and synthetic resins than the acetates, and their films possess excellent clarity and toughness. For example, cellulose acetate butyrate is compatible with, acrylic, polyester vinyl, and alkyd resins, depending on the amount of butyryl substitution and the degree of hydrolysis of the esters (Gedon and Fengi, 2001).

Cellulose ethers can be obtained by the reaction of cellulose with an alkyl or arylalkyl halides or sulfates, with ω-halocarboxyilic acid or its salt, with an alkene oxide or with an activated olefin with polar substituents, in the presence of alkali or alkali cellulose. Among the commercial cellulose ethers are methyl cellulose (MC), ethyl cellulose (EC) carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC). Methyl cellulose and its derivatives are widely used in the manufacturing of cement, adhesives and ceramics. CMC is widely used in the food industry, to

enhance the growth of ice crystals in cold foods, toppings for desserts, thickener in beverage and as a water-binding agent in cake. In the pharmaceutical field, the CMC is used in the manufacturing of tablets and lotions as a binder. In addition, CMC can also be used in cosmetic products, paper products, adhesives, lithographs, ceramics, detergents and textiles (Immergut, 1981).

2.5 Cellulose Acetate

2.5.1 Introduction

Cellulose acetates (CAs) are one of the most important esters of cellulose, which are produced by reaction of cellulose with acetic anhydride and acetic acid catalyzed by sulfuric acid. The most common form of cellulose acetate has an acetyl group on approximately 2.4 – 2.5 of every three hydroxyls. This cellulose diacetate is known as secondary acetate, or simply as ‘‘acetate’’. The solubility of cellulose acetate depends among other things on the degree of substitution (DS), CA with DS of 2 – 2.5 are soluble in methyl acetate, dioxane and acetone, higher acetylated types are soluble in dimethyl sulfoxide, dichloromethane and chloroform (Fisher, 2008).

2.5.2 Raw materials

The basic raw materials for production of cellulose acetate are cellulose, acetic acid, acetic anhydride and sulfuric acid. The high purity cellulose can be obtained from wood pulps with α-cellulose content of more than 95% and cotton linters (Saka and Matsumura, 2004). Cotton linter is the best raw materials for synthesis of cellulose acetate due to their high quality and purity of cellulose. Particularly for the production of cellulose acetate, cotton fibers and a highly purified