# PRODUCTION OF CELLULOSE ACETATE: EFFECT OF PRETREATMENTS AND ACETYLATION CONDITIONS ON RECYCLED PAPER DUST

**By**

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## LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| ± | about |
| % | percent |
| $(CH_3CO)_2\,O$ | acetic anhydride |
| < | less than |
| > | more than |
| °C | degree Celsius |
| ACPD | acid pretreatment  carton box paper dust |
| ACPD CA | cellulose acetate synthesized from acid pretreatment carton box paper dust |
| ACPD CA 19:1 | cellulose acetate synthesized  from acid pretreatment carton box paper dust produce by changing ratio of acetic acid-water |
| ACPD CA 50 degree | cellulose acetate synthesized from acid pretreatment carton box paper dust by using 50 degree pretreatment modification |
| AGU | anhydroglucose unit |
| AmimCl | 1-allyl-3-methylimidazolium |
| ASTM | American Society for Testing and Materials |
| C | chlorination |
| CA | cellulose acetate |
| ca. | circa |
| CAB | cellulose acetate butyrate |
| CAP | cellulose acetate propionate |
| CAPh | cellulose acetate phthalate |
| C CA | commercial cellulose acetate |
| $CH_3COOH$ | acetic acid |
| cm | centimetre |
| CMC | carboxymethycellulose |
| CN | cellulose nitrate |

| | |
|---|---|
| -COCH$_3$ | acetyl group |
| cP | centipoise |
| CPD | carton box paper dust |
| CPD CA | cellulose acetate synthesized from carton box paper dust |
| D | chlorine dioxide |
| DP | dissolving pulp |
| DP CA | cellulose acetate synthesized from dissolving pulp |
| DP CA 19:1 | cellulose acetate produce from dissolving pulp by changing ratio of acetic acid-water |
| DP CA 50 degree | cellulose acetate from dissolving pulp by using 50 degree pretreatment modification |
| DS | degree of substitution |
| DTG | Derivative Thermogravimetry |
| E | mild (less than atmospheric HCE) |
| e.g. | *exempli gratiā* (for example) |
| E˚ | pressure hot caustic extraction (HCE) |
| etc. | *et cetera* |
| FAO | Food and Agriculture Organization |
| FTIR | Fourier Transform Infrared Spectroscopy |
| g | gram |
| H | hypochlorite |
| H$_2$O | molecular water |
| H$_2$SO$_3$ | sulfurous acid |
| H$_2$SO$_4$ | sulfuric acid |
| HCl | hydrochloric acid |
| HEC | hydroxyethyl |
| HPMC | hydroxypropylmethyl |
| HPMCPh | hydroxypropylmethyl-cellulose phthalate |

| | |
|---|---|
| $I_2$ | molecular iodine |
| $I_c$ | crystallinity index |
| Inc. | incorporation |
| KHP | potassium hydrogen phthalate |
| KI | potassium iodide |
| $KMnO_4$ | potassium permanganate |
| kV | kilovolts |
| L | liter |
| LCD | liquid crystal display |
| M | molarity |
| mA | milliampere |
| max | maximum |
| mg | milligram |
| min | minute |
| ml | mililiter |
| mm | milimeter |
| mPa.s | milipascal-second |
| MS | molar substitution |
| $Na_2CO_3$ | sodium carbonate |
| $Na_2S_2O_3$ | sodium thiosulphate |
| NaOH | sodium hydroxide |
| $NaS_2$ | sodium sulphide |
| nm | nanometer |
| NTPM | Nibong Tebal Paper Mill |
| O | oxygen |
| o.d. | oven dry |
| OCPD | oxygen-alkaline pretreatment carton box paper dust |

| | |
|---|---|
| OCPD CA | cellulose acetate synthesized from oxygen-alkaline pretreatment carton box paper dust |
| OCPD CA 19:1 | cellulose acetate from produce from oxygen-alkaline pretreatment carton box paper dust carton box paper dust by changing ratio of acetic acid-water |
| OCPD CA 50 degree | cellulose acetate from oxygen-alkaline pretreatment carton box paper dust carton box paper dust by using 50 degree pretreatment modification |
| OH | hydroxyl group |
| P | hydrogen peroxide |
| PCDD | polychlorinated dibenzo-p-dioxins |
| PCDF | polychlorinated dibenzofurans |
| pH | potentiometric hydrogen ion concentration |
| ppm | parts per million |
| psi | pound per square inch |
| RC | regenerated cellulose |
| rpm | round per minute |
| Sdn Bhd. | sendirian berhad |
| SEM | Scanning Electron Microscopy |
| TG | Thermogravimetric Analysis |
| TPD | tissue paper dust |
| TPD CA | cellulose acetate synthesized from tissue paper dust |
| X | cold caustic extraction |
| XRD | X-ray Diffraction |
| Z | ozone |
| α | alpha |
| β | beta |
| γ | gamma |
| μm | micron |

# PENGHASILAN SELULOSA ASETAT: KESAN PRA-PENGOLAHAN DAN KEADAAN-KEADAAN PENGASETILAN KE ATAS HABUK KERTAS TERKITAR

## ABSTRAK

Di dalam kajian ini, selulosa asetat telah dihasilkan daripada habuk kotak kertas (CPD) dan habuk kertas tisu (TPD) dengan tujuan untuk mengekstrak nilai daripada aliran sisa kertas serta memaksimumkan dan mempelbagaikan penggunaan selulosa terkitar. Kualiti selulosa asetat yang dihasilkan dibandingkan dengan selulosa asetat yang dihasilkan daripada pulpa terlarut komersial. Untuk mendekati pulpa yang biasa digunakan untuk pengasetilan, pra-pengolahan asid dan oksigen-alkali telah dijalankan ke atas habuk kertas kotak. Kedua-dua pra-pengolahan, pra-pengolahan asid (yang mengolah habuk kotak kertas dengan acid sulfurik pH 2 untuk satu jam dengan 80°C.) dan oksigen-alkali (yang mengolah habuk kotak kertas dengan natrium hidroksida di bawah tekanan gas oksigen (70 psi) pada 100°C selama 30 minit.) telah memperbaikkan sifat kimia habuk kertas kotak secara signifikan berbanding dengan CPD. Sifat-sifat bagi kesemua selulosa asetat yang dihasilkan telah dikaji dengan penentuan darjah penukargantian (DS), Analisis *Fourier Transform Infra Red* (FTIR), Analisis Terma Gravimetrik (TG) dan pembelauan sinar-X (XRD). DS untuk selulosa asetat yang disintesis daripada pulpa terlarut (DP CA), habuk kotak kertas (CPD CA) dan habuk kertas tisu (TPD CA) masing-masing adalah 2.15, 1.94 dan 2.03. Berbanding dengan CPD, kedua-dua habuk kertas yang terolah telah menunjukkan sifat kimia yang lebih mendekati pulpa yang digunakan untuk pengasetilan. Oleh sebab itu, DS, darjah penghabluran serta suhu degradasi maksimum telah meningkat untuk kedua-dua habuk kertas terolah. Namun demikian, kesemua selulosa yang dihasilkan telah menunjukkan DS dan kestabilan terma yang lebih rendah berbanding dengan selulosa asetat komersil (C CA). Oleh sebab itu, dua pengubahsuaian kondisi pengasetilan telah dijalankan dengan tujuan untuk memperbaiki sifat-sifat selulosa asetat yang dihasilkan. Cara pengubahsuaian suhu pengaktifan kepada 50°C telah memberikan kesan positif kepada DP tetapi tidak

memberikan sebarang perubahan secara statistikal bagi kedua-dua habuk kotak terolah. Sebaliknya, cara pengubahsuaian nisbah asetik asid dengan air kepada 19:1 telah meningkatkan DS bagi selulosa asetat yang dihasilkan daripada DP dan habuk kotak kertas yang telah menjalani pra-pengolahan. Namun demikian, suhu degradasi maksimum selulosa asetat DP dan habuk kertas yang diolah dengan acid telah menurun, manakala suhu degradasi maksimum untuk selulosa asetat habuk kertas yang diolah dengan oksigen-alkali telah meningkat. Di antara kesemua selulosa asetat yang dihasilkan, hanya filem yang disediakan dari selulosa asetat yang dihasilkan dengan cara pengubahsuaian nisbah asetik asid dengan air sahaja tidak menunjukkan sebarang liang semasa diperhatikan di bawah pengskanan elektron mikroskopi (SEM). Kesemua selulosa asetat yang telah dihasilkan menunjukkan penyusutan darjah penghabluran berbanding dengan bahan asli yang digunakan kerana kawasan berhablur telah termusnah selepas pengasetilan.

# PRODUCTION OF CELLULOSE ACETATE: EFFECT OF PRETREATMENTS AND ACETYLATION CONDITIONS ON RECYCLED PAPER DUST

## ABSTRACT

In this study, cellulose acetate was produced from recycled paper dust of carton box (CPD) and tissue paper (TPD) with the aim to extract value from the waste stream and also to maximize and diversify the utilization of recycled cellulose. The quality of the resultant cellulose acetate was compared to the cellulose acetate produced from the commercial dissolving pulp. In order to approach acetylation pulp properties, acid and oxygen-alkaline pretreatment have been carried out on the carton box paper dust. Both the acid pretreatment (which carried out by treating the paper dust in pH 2 sulfuric acid solution for 1 hour at 80°C) and the oxygen-alkaline pretreatment (which treated the dust in sodium hydroxide solution under oxygen gas pressure (70psi) at 100°C for 30 minutes), have improved the chemical properties of the paper dust significantly in comparison to CPD. All the cellulose acetates produced were then characterized by determining the degree of substitution (DS), Fourier Transform Infrared (FTIR), Thermal Gravimetric Analysis (TG) and X-ray diffraction (XRD). The DS of cellulose acetate synthesized from dissolving pulp (DP CA), corrugated paper dust (CPD CA) and tissue paper dust (TPD CA) were 2.15, 1.94 and 2.03 respectively. The chemical properties of both pretreated pulps show a better approach to acetylation grade pulp; thus, there is an increment in DS, the degree of crystallinity and the maximum degradation temperature when compared to CPD CA. However, all the cellulose acetates produced showed a lower DS and thermal stability than commercial cellulose acetate (C CA), hence modifications of acetylation procedure have been done with the intention to improve the properties of cellulose acetate. The modification method with 50°C pretreatment, which treated the raw material under 50°C during activation stage has shown a positive effect on DP but not statistically different for both pretreated pulps. On the other hand, the modification method by changing the ratio of acetic acid and water to 19:1 during hydrolysis stage has

improved the DS for cellulose acetate synthesized from DP and pretreated pulps. Nevertheless, the results of TG showed that the maximum degradation temperature of the resultant cellulose acetate from DP and acid pretreated pulp (ACPD) has decreased, whereas that of cellulose acetate synthesized from oxygen-alkaline pretreated pulp (OCPD) has increased. Among all the cellulose acetates produced, only the film prepared from the cellulose acetate synthesized under modification method by changing the ratio of acetic acid-water showed no pores when observed under scanning electron microscopy (SEM). The degree of crystallinity of all the cellulose acetate has decreased in comparison to the original material as the crystallite region is broken after acetylation reaction.

# 1    INTRODUCTION

Cellulose acetate (CA) is one of the earliest synthetic fiber and most commercially important cellulose derivatives. Generally, cellulose acetate is a biopolymer prepared by reaction of cotton linter or wood pulp cellulose with acetic anhydride using glacial acetic acid as solvent in the present of sulfuric acid as the catalyst.

Cellulose acetate has a wide range of applications ranging from impact resistant plastic to soft fabric. Textile, cigarette filtered, photographic and packaging films, liquid crystal display (LCD), tools handle and production of membrane for separation processes such as dialysis, reverse osmosis, gas separation and hemodialysis are some of the applications of cellulose acetate (Cao et al., 2007; Cerqueira et al., 2007). The wide range of applications and user-friendly characteristic has make cellulose acetate a special product.

Cellulose acetate is easily bonded with plasticizers and is soluble in most conventional and alternative solvents. Besides that, it can selectively absorb and remove low levels of organic chemicals, its hypoallergenic properties guarantee safety in contact with skin and food. Cellulose acetate also has advantages such as flexible, weather resistant and water resistant. Cellulose acetate is an environmentally friendly product made from renewable resource, which is biodegradable and hence can be composted (Micheal, 2004). The lower the degree of substitution the easier cellulose acetate being biodegraded (Gu et al., 1993; Buchanan et al., 1993; Samios et al., 1997) According to Buchnan et al. (1993), cellulose acetate films with the degree of substitution 1.7 could degrade more than 80 percent in 4-5 days and cellulose acetate film with the degree of substitution 2.5 require 10-12 days for degradation using aerobic biodegradation.

1.1  Justification

In general, fully bleached dissolving pulp or so-called chemical cellulose with high alpha cellulose content (normally more than 95 percent), low hemicellulose and lignin are required to prepare cellulose acetate (He et al., 2008; Matsumura & Saka, 1992). The production of dissolving pulp requires higher production cost but lower yield as in comparison to paper grade pulp thus it occupies only a small part of the world pulp production. According to the FAO Pulp, Paper Capacity Survey 2002-2007, dissolving pulp occupies only about 1.6 percent of the world pulp production. The high production cost and low supply of dissolving pulp indicated that the raw material for cellulose acetate is fairly expensive to be obtained (Barkalow et al., 1989; Cao et al., 2007; Yang et al., 2008).

The two major sources for the production of dissolving pulp are cotton linters and wood pulp with the latter being the most important. Since the production of dissolving pulp only give the yield of ca. 30 percent, thus relatively more raw materials especially woods are required to provide sufficient supply to the market, this phenomenon is actually in contravention of environmental conservation, which are tremendously emphasized nowadays. Thus, there is a trend of using alternative resources such as non wood agro wastes and recycled materials for the production of cellulose acetate (Cerqueira et al., 2007; He et al., 2008; Rodrigues Filho et al., 2008).

On the other hand, during converting the paper product in paper and box factories, a lot of paper dust is generated. These airborne paper dusts will pollute the working environment by contaminating the air in the factory and affecting the health of staff workers. To solve this problem, the authority of factory might have to allocate a large sum of fund for installing a cyclone dust collector in order to provide a healthy working environment for the workers. Since the fiber length of the paper dust is too short to be recycled for papermaking. Therefore, the dust collected most possibly will be incinerated with or without generating

energy for the factory. In addition, the dust might also face the possibility to be deposit in landfill.

In the context of preserving the environment which has been tremendously emphasized nowadays, the incineration and landfill of fiber dust are considered as resource wastage. Maximizing and diversifying the utilization of recycled cellulose to produce value-added products might be one of the best ways to avoid resource wastage as well as to extract value from the waste stream (Rodrigues Filho et al., 2008). From the environmental viewpoint, the feasible of cellulose acetate production from an alternative resource-recycled paper dust may lessen the dependent on the dissolving pulp as raw material and maximize the usage of recycled cellulose.

1.2  Objective

This research was conducted to produce cellulose acetate from paper dust generated in paper and paper converting factories. Therefore, the objectives of the research are:

1.  To study the viability of paper dust from corrugated carton box and tissue paper in producing cellulose acetate.

2.  To investigate the effect of acid and alkaline pretreatment on corrugated paper dust properties.

3.  To study the effect of different acetylation conditions on corrugated carton box dust.

4.  To examine the properties of cellulose acetate synthesized from paper dust and compare with commercial cellulose acetate.

## 2 LITERATURE REVIEW

### 2.1 Lignocellulose

Lignocelluloses which include all woods and plant materials are used as sources in producing furniture, paper products and as building material. The cellulose from the lignocellulosic material can even be converted into various types of cellulose derivatives which have an extensive range of end products such as explosive, film, textile, lacquer, etc. Wood or other plant materials are renewable resources, which are widely distributed on the earth. The major components of the lignocelluloses consist of cellulose, hemicellulose and lignin. Besides the three major components, there is also a small amount of extraneous component known as extractive present in wood (Sjöström, 1993).

### 2.2 Chemical Component of Wood and Fibers

### 2.2.1 Cellulose

Cellulose, which has the function as supporting material for the cell walls, is the main constituent of wood (Alén, 2000). Cellulose is relatively hygroscopic but is insoluble in water and diluted acid. Cellulose solution can be attained under severe degradation with high concentration acid. Cellulose is non-melting with the thermal decomposition at 180°C and the ignition point is >290°C (Krassig et al., 1986).

As referred to Figure 2-1, the basic structural repeating unit for cellulose is cellobiose, which linked by oxygen atom with β (1-4)-glycosidic bonds. Cellobiose consists of two molecules of glucose. Each ring is called anhydroglucose unit (AGUs) or β-D-glucopyranose unit. The second ring of the cellobiose is inverted over from the general plane of the first ring but both are chemically identical. These rings are puckered but not planar. The chains of

5

AGU include a reducing end unit, a non reducing end unit and intermediate units. There are three hydroxyl groups attach to an AGU in the position 2, 3 and 6. These hydroxyl groups make cellulose hygroscopic and readily adsorb and desorb water with changes in relative humidity (Steinmann, 1985; Krassig et al., 1986; Sjöström, 1993).
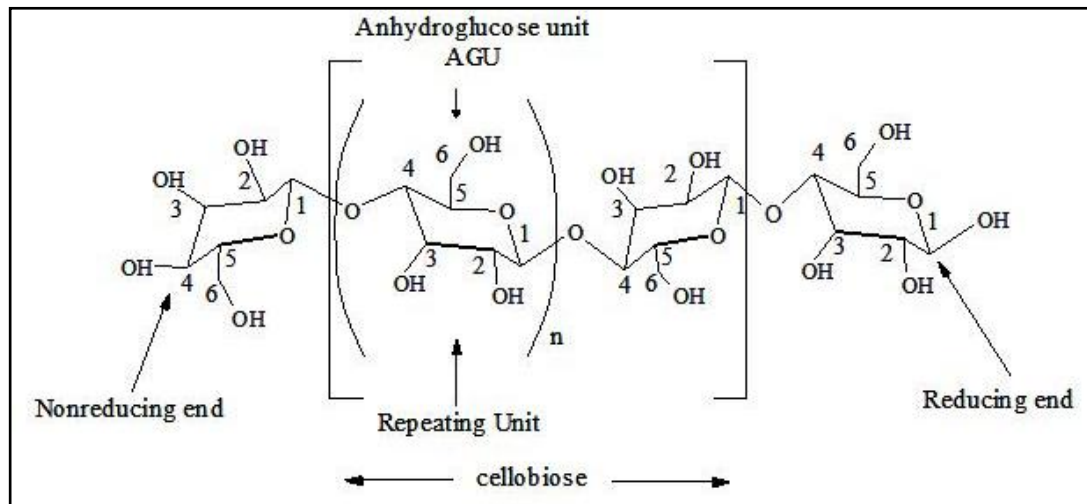


Figure 2-1: Cellulose structure (Steinmann, 1985; Krassig et al., 1986)

The degree of polymerization (n) of cellulose $(C_6H_{12}O_5)_n$ is in the range of 2000-15 000. The longest cellulose molecule is around 10 micron (μm) (1/1000 cm) and the diameter is 0.001 micron (μm) (1/10,000,000 cm) (Steinmann, 1985; Haygreen & Bowyer, 2003). Cellulose consists of crystalline region and also disordered or so-called amorphous region. These regions are blended into each other hence there is no clearly defined boundary for them. The extensive hydrogen bonding between cellulose chains has led to strong intermolecular bonding between adjacent cellulose and the hydrogen bonding is enhanced by the steric configuration of the AGUs. The crystalline orders of cellulose are held together by hydrogen bonding owing to the favors of the structure in organize the individual cellulose chains in a bundle (Steinmann, 1985; Krassig et al., 1986; Sjöström, 1993).

The crystalline region is more difficult to be penetrated in comparison to the amorphous region. For that reason, most of the reactions on cellulose are heterogeneous in nature. The reaction medium firstly will react with the amorphous regions which are mainly located on the surface of the elementary crystallites in the fibrils. Subsequently under favorable conditions it will react with the interlinking regions between elementary crystallites to penetrate from both ends into crystallites (Krassig et al., 1986).

The reactivity of cellulose can be improved by activation treatments. Swelling, solvent exchanges, inclusion of structure-loosening additives, degradation or mechanical grinding are treatments that will increase accessible surfaces by opening fibrillar aggregation. Swelling with water and other polar liquids is most frequent applied to treat the cellulose which had lost of reactivity due to hornification. Water can swell the less ordered surfaces and interlinking regions of the fibrillar element thus enhanced the accessibility to cellulose (Krassig et al., 1986).

2.2.2    Hemicelluloses

Hemicellulose are heteropolysaccharides which consisting mainly mannan and xylan (Sjöström, 1993). Similar as cellulose, hemicellulose has the function as supporting material in cell walls. However, it has a shorter chain with a low degree of polymerization (100-200). The monomeric components of hemicellulose consist of hexoses (D-glucose, D-mannose, and D-galactose), pentoses (D-xylose, L-arabinose and D-arabinose), or deoxyhexoses (L-rhamnose or 6-deoxy-L-mannose and rare L-fucose or 6-deoxy-L-galactose) and  small amounts of certain uronic acids (4-O-methyl-D-glucuronic acid, D-galacturonic acid, and D-glucuronic acid) (Sjöström, 1993; Alén, 2000).

The hemicellulose content and also the percentage of individual hemicellulose in softwood and hardwood are different. Softwood contains more mannose and galactose unit while hardwood has more xylose units and acetylated hydroxyl groups (Alén, 2000).

Due to the lack of crystallinity and lower degree of polymerization, the chemical and thermal stability of hemicellulose are basically lower than cellulose. Thus, the hemicellulose are more easily degraded and dissolved than cellulose (Smook, 1992). In addition, the solubility in alkali of hemicellulose is usually varied from cellulose (Alén, 2000), in which the caustic solutions can cause extensive swelling and dissolution of low molecular mass hemicelluloses.

2.2.3    Lignin

Lignin is an amorphous, highly-polymerized substance in woody plant. Lignin can be defined as polyphenolic material formed from enzymic dehydrogenative polymerization of three phenylpropanoid units (p-hydroxycinnamyl alcohols) which are the trans-Coniferyl alcohol, trans-Sinapyl alcohol and trans-p-Coumaryl alcohol (Figure 2-2). Ether linkages (C-O-C) and carbon linkage (C-C) join the phenylpropanoid units together where two thirds or more of the linkages are the ether linkage and the rest is carbon linkages (Alén, 2000).



| Coniferyl alcohol | Sinapyl alcohol | p-Coumaryl alcohol |
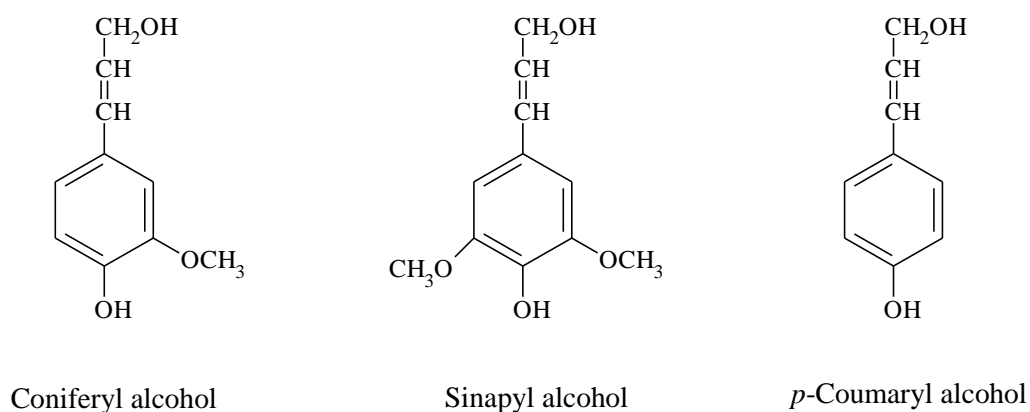
Figure 2-2: Three phenylpropanoid units of lignin

The different structure of phenylpropane units which are not linked to each other in any systematical order had led to the irregular chemical structure of lignin. However, the chemistry of lignin is extremely complex and many aspects of it are still remaining unclear (Casey, 1960; Sjöström, 1993; Alén, 2000).

Lignin can basically be grouped into three: softwood, hardwood and grass lignins. Softwood lignin referred as "guaiacyl lignins" is a polymerization product of trans-Coniferyl alcohol (more than 90%) and the remained are trans-p-Coumaryl alcohol. "Guaiacyl-syringyl" lignin which is the hardwood lignin had the ratio about 50 to 50 of trans-Coniferyl alcohol and trans-Sinapyl alcohol. Grass lignin which contained p-hydroxyphenyl units derived from trans-p-Coumaryl alcohol and some other aromatic acid residues (about 40% trans-Coniferyl alcohol, 40% of trans-Sinapyl alcohol and about 20% other precursors) also classified as "guaicyl-syringyl" lignins (Alén, 2000).

Lignin is removed during pulping process and delignifying process. In the sulfite pulping process, sulfonation and hydrolysis are the reactions for delignification. These reactions will increase the hydrophilicity of lignin make it more soluble. In kraft pulping, hydroxyl and hydrogen sulfide ions will cause the cleavage of ether linkages which led to the liberation of phenolic hydroxyl groups and thus increase the hydrophilicity of lignin. The lignin will later be dissolved in cooking liquor as sodium phenolates. As for delignifying process, the most common chemicals used nowadays are chlorine, chlorine dioxide and oxygen (Sjöström, 1993). However, chlorine free chemical would be preferable in the future due to the environment consideration. In mild oxidation conditions, lignin will form vanillin but under drastic conditions of oxygen delignifying process, lignin is completely converted into water soluble products (Brauns, 1954).

### 2.2.4 Extractives

Extractives can be regarded as a nonstructural wood constituent. They only occupied a minor fraction in wood by occupying certain morphological sites in the wood structure. For example, the fats and waxes are in the ray parenchyma cells, the resin acids are in resin canals while the phenolic extractives are located mainly in the heartwood and in bark. Extractives are soluble in water or neutral organic solvents (Smook, 1992; Sjöström, 1993).

### 2.3 Cellulose Derivatives

Cellulose which is not soluble in water can be converted into chemical derivatives which are soluble in water or organic solvent. In fact, it has been known for over 150 years. The one primary hydroxyl (HO-6) and two secondary hydroxyl (HO-2 and HO-3) groups of AGUs in cellulose can undergo esterification, etherification, oxidation or halogenations. Thus it can be substituted with many different groups and in a wide varying degree of substitution (DS) (zero to three) (Serad, 1992). These substitute reactions are used in industry to produce an extensive range of product. Almost all the commercial important cellulose derivative is either esters or ethers. Table 2-1 shows some of the uses of cellulose derivatives (Ishizu, 1990).

Table 2-1: Some of the Uses of Cellulose Derivatives

| Field | Uses | Cellulose Derivatives |
|---|---|---|
| Textiles | Fibers | CA, RC |
| Plastics | | CA,CAP,CAB,CN |
| Film | Packing, tape | RC,CA |
| Paper making | | CMC, HEC |
| Photography | Film | CA |
| Printing | Ink stabilizers | CN |
| Magnetic recording | Binders | CMC |
| Cigarettes | Binders | CMC |
| | Filters | CA |
| Cosmetics | Emulsion stabilizers, hair conditioners | CMC, HEC |
| Membrane separation | Reverse osmosis | CA |
| | Ultra filtration | CA |
| Agricultural chemicals | Disintegrants | CMC, CA, HPMC |
| Building materials | Sound absorbing material | CA |
| Explosives | Gunpowder | CN |

CA=cellulose acetate; CAP=cellulose acetate propionate; CAB=cellulose acetate butyrate; CN=cellulose nitrate; RC=regenerated cellulose; CMC=sodium carboxymethycellulose; HPMC= hydroxypropylmethyl; HEC=hydroxyethyl.

Source: Ishizu, A. (1990)

2.3.1    Cellulose Ester

Cellulose esters are generally prepared by synthesizing natural cellulose with mineral acids, organic acids, anhydrides or acid chlorides. The functional group of ester is as shown in Figure 2-3. Esters of cellulose can either be inorganic or organic based on the atoms linked to the cellulosic oxygen. The atom link to the cellulosic oxygen of organic ester is

carbon whereas inorganic esters are esters where the atom linked to cellulosic oxygen is non-carbon.

$$R—\overset{\overset{\displaystyle O}{\|}}{C}—O—R'$$
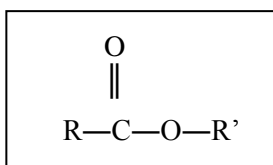
R and R'= hydrocarbon groups

Figure 2-3: Functional group of esters

2.3.1.1 Organic Ester

Organic esters are generally prepared by reacting cellulose with reagent such as organic acids, anhydride and acid chlorides. The esterification mechanisms of cellulose are shown in Equation 2-1 - Equation 2-3. Equation 2-1 shows the esterification with organic acid by nucleophilic addition. Equation 2-2 and 2-3 show the acid-catalyzed esterification (Balser et al., 1986).
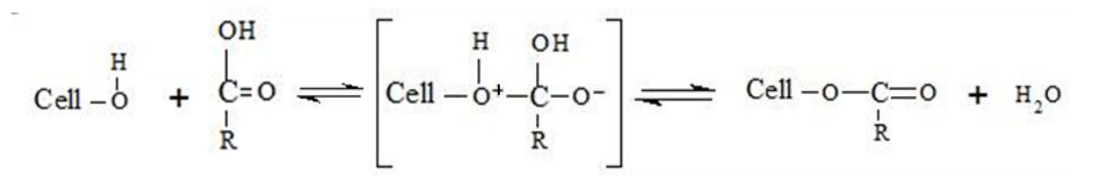


Cell-OH = cellulose                                                                      Equation 2-1



Cell-OH = cellulose                                                                      Equation 2-2

$$\text{Cell}-\overset{\underset{|}{H}}{\text{O}} \ + \ \begin{bmatrix} \text{OH} \\ | \\ \text{C-OH} \\ | \\ \text{R} \end{bmatrix}^{+} \ \rightleftharpoons \ \begin{bmatrix} \text{Cell}-\text{O}-\overset{\underset{|}{\overset{|}{\text{OH}}}}{\underset{\text{R}}{\text{C}}}-\text{OH} \\ \underset{\text{H}}{|} \end{bmatrix}^{+} \ \rightleftharpoons \ \text{Cell}-\text{O}-\underset{\underset{\text{R}}{|}}{\text{C}}{=}\text{O} \ + \ H_2O \ + \ H^{+}$$
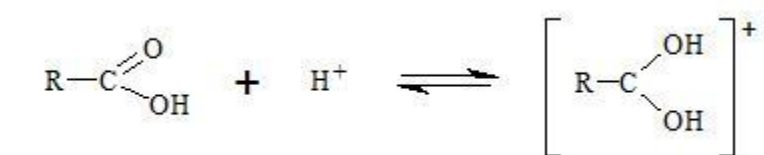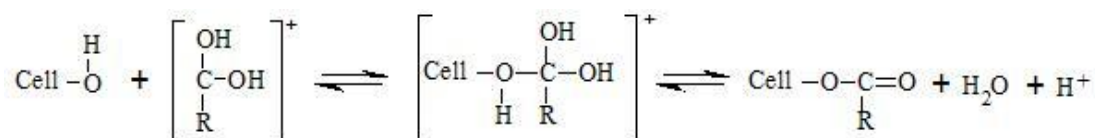
Cell-OH = cellulose                                                    Equation 2-3

Commercially important organic esters are cellulose acetate, cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). These organic esters have been recognized for some time and have extensive production. Besides that, there are also other organic ester such as cellulose acetate phthalate (CAPh), hydroxypropylmethyl-cellulose phthalate (HPMCPh) and also esters which are not used industrially such as cellulose palmitate, cellulose stearate, esters of unsaturated acids such as crotonic acid or esters of dicarboxylic acids (Ishizu, 1990; Balser et al., 1986).

Cellulose acetate is widely known and is one of the most commercially important organic esters. It is a white, transparent and amorphous product that can be obtained commercially as powder or flake (Eicher, 1986). Cellulose acetate butyrate (CAB) is a white flaky or granular material mixed ester similar to cellulose acetate in its general appearance (Yarsley et al., 1964). Cellulose acetate butyrates (CAB) are used in application such as tabulator keys and tool handles due to the tough injection moulding. It is also used as plastic, film sheeting and lacquer for cables, fabrics and furniture (Saunders, 1973).

Cellulose acetate propionate (CAP) also is a mixed esters of acetic and propionic acid. Similar to cellulose acetate butyrate it has the preparation alike to esterification of cellulose acetate (Rouse, 1964). Cellulose acetate propionate is used as injection moulding and extrusion because of its toughness and dimensional stability. Besides, cellulose acetate propionate which has 40-50% propionyl also been used in wood furniture coatings (Edgar, 2007).

2.3.1.2 Inorganic Ester

The oldest and most commercially important inorganic ester is cellulose nitrate (Bruxelles & Grassie, 1965). Equation 2-4 and Equation 2-5 show the general esterification mechanism using inorganic acid. Cellulose oxonium is formed in the first step of reaction (Equation 2-4) followed by nucleophilic substitution of an acid residue and the splitting off of water (Krassig et al., 1986; Balser et al., 1986).

$$\text{Cell—OH} \quad + \quad \text{H}^+ \quad \leftrightarrows \quad \text{Cell—O}^+ \begin{smallmatrix} \nearrow \text{H} \\ \searrow \text{H} \end{smallmatrix}$$

Equation 2-4

$$\text{X}^- \ + \ \text{Cell—O}^+\!\begin{smallmatrix} \nearrow \text{H} \\ \searrow \text{H} \end{smallmatrix} \ \leftrightarrows \ [\ \text{X}^- \ \longrightarrow \ \text{Cell} \longrightarrow \text{O}^+\!\begin{smallmatrix} \nearrow \text{H} \\ \searrow \text{H} \end{smallmatrix}\ ] \ \leftrightarrows \ \text{X—Cell} \ + \ \text{O}\begin{smallmatrix} \nearrow \text{H} \\ \searrow \text{H} \end{smallmatrix}$$
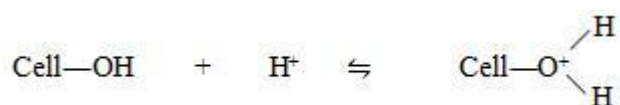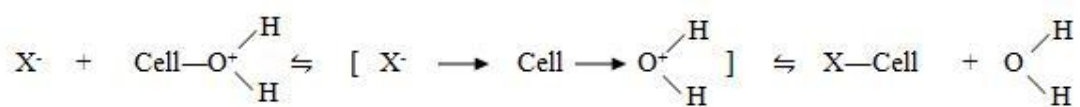
Equation 2-5

The largest market uses for cellulose nitrate is lacquer finishes and the second largest is for explosive and propellants. Besides, cellulose nitrate is used in different application such as plastic, ester films and cement depends on the DS and the solvent used. (Bruxelles & Grassie, 1965; Sjöström, 1993). There are also other inorganic esters such as cellulose sulfates, cellulose nitrite, cellulose phosphate and so on.

2.3.2    Cellulose Ether

Cellulose ether is prepared through the reaction of purified cellulose with alkylating reagents such as alkyl and aryl halides, alkene oxides, and unsaturated compounds activated by electron-attracting groups under heterogeneous conditions. Generally, the reaction is in the presence of inert diluents and a base which normally is sodium hydroxide (Sjöström,

1993). Sodium carboxymethycellulose (CMC), hydroxyethylcellulose (HEC) and hydroxypropylmethylcellulose are high volume cellulose ethers produce in industry (Majewicz et al., 2007)

There are four types of reactions in preparing cellulose ether. Equation 2-6 describes the Williamson etherification. Equation 2-7 is the etherification of cellulose without alkali consumption. The generating of new hydroxyl groups during the reaction will make the reaction proceeds further leading to oligomeric alkylene oxide chains. On the other hand, the reaction in Equation 2-8 is seldom applied in industry. In this reaction, cellulose is added to an activated double bond in the alkaline medium where Y is an electron-attracting substituent. Equation 2-9 shows the etherification with diazoalkanes which have no industrial significance (Brandt, 1986).

Cell—OH   +   R—X   +   NaOH   $\longrightarrow$   Cell—OR   +   $H_2O$   +   NaX
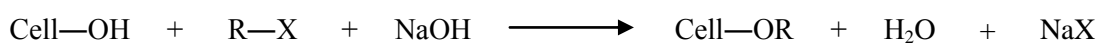
Cell-OH = cellulose

R-X = inorganic acid ester

X = halogen or sulfate (chlorides usually applied in industry)

<div align="right">Equation 2-6</div>
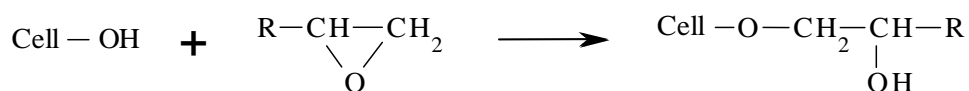


Cell-OH = cellulose

R = H, $CH_3$ or $C_2H_5$

<div align="right">Equation 2-7</div>

Cell—OH  +  CH$_2$=CH—Y  $\longrightarrow$  Cell—O—CH$_2$—CH$_2$—Y
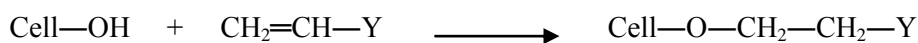
Cell-OH = cellulose

Y= CN, CONH$_2$, or SO$^{3-}$ Na+

<div align="right">Equation 2-8</div>

Cell—OH  +  R—CHN$_2$  $\longrightarrow$  Cell—O—CH$_2$—R  +  N$_2$
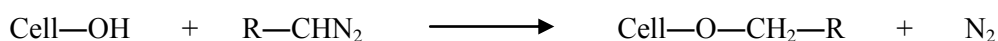
Cell-OH = cellulose

<div align="right">Equation 2-9</div>

The important parameter for cellulose ethers is the degree of substitution (DS). Cellulose ether attained at very low DS is water solubility, whereas higher degree cellulose ethers soluble in organic solvent. Most water-soluble derivatives have DS of 0.4-2.0 while organo-soluble ethylcellulose has a DS of 2.3-2.8. However, in certain cases such as using alkylene oxide as a reagent, cellulose ether was characterized by molar substitution (MS) which is the moles reagent combined per mole of anhydroglucose unit. This is due to the generating of a new hydroxyl group upon reacting which can then further react to give oligomeric chains. In general, hydroxyalkyl ethers have MS values between 1.5 and 4.0. The ratio of MS to DS is a measure of the average chain length of the oligomeric side chains (Majewicz et al., 2007).

Ether has been developed into a variety of products which are commercially important for different uses as summarized in Table 2-2 (Durso, 1978; Brandt, 1986; Majewicz & Podlas, 1992; Sjöström, 1993; Majewicz et al., 2007).

Table 2-2: Types of Commercial Cellulose Ethers and Their Functions

| Cellulose Ether | Reagent | Solvent | DS | Functions |
|---|---|---|---|---|
| Methylcellulose | Methylchloride, dimethyl sulfate | Water | 1.5-2.4 | Thickener, water-binder, latex paint, paint remover |
| Ethylcellulose | Ethyl chloride | Organic Solvents | 2.3-2.6 | binder, coatings and ink, protective film-former, additives |
| Carboxymethylcellulose | Sodium chloroacetate | Water | 0.5-1.2 | Thickener, water binder, granulation aid, stabilizer, film former |
| Hydroxyethycellulose | Sodium chloroacetate | Water | 0.5-1.2 | Thickener, water binder, Stabilizer in paper sizing |
| Cyanoethylcellulose | Acrylonitrile | Organic Solvents | 2.0 | Improving sheet strength , Heat resistance, Electrical resistance |

DS = degree of substitution

2.4  Cellulose Acetate and Cellulose Triacetate

Cellulose acetate is also known as acetate or secondary acetate. It is a white and transparent material obtained by the combination cellulose and acetic acid in the presence of sulfuric acid. It is nontoxic, odorless, tasteless and less flammable than nitrocellulose (Eicher, 1986; Gedon & Fengl, 1992). Cellulose acetate is partially acetylated cellulose which has two acetate groups in each of its anhydroglucose unit (AGU). On the other hand, fully

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acetylated cellulose is known as cellulose triacetate, primary acetate or high-acetyl cellulose acetate (Malm & Hiatt, 1954). The differences of cellulose acetate and cellulose triacetate are shown in Table 2-3 (Ward, 1978; Balser et al., 1986).

Table 2-3: The Properties of Cellulose Acetate and Cellulose Triacetate

|  | Cellulose Acetate | Cellulose Triacetate |
| --- | --- | --- |
| Density, g cm$^{-1}$ | 1.28-1.32 | 1.27-1.29 |
| Thermal stability, ˚C | ca.230 | >240 |
| Solubility |  |  |
| Acetone | Soluble | Insoluble |
| Tetrachlorethane | Soluble | Soluble |
| Chloroform | Insoluble | Soluble |
| Usage | Transparent sheets |  |
|  | Textiles | Transparent Sheets |
|  | Cigarette Filters | Textiles |
|  | Molded Plastics | Photographic Film |
|  | Tool Handles | Electrical Insulation |
|  | Toys |  |

Source: Ward (1978) and Balser et al. (1986)

2.4.1    Historical Background

The first cellulose acetate was prepared in 1865 by Paul Schützenberger, a French chemist by synthesizing cotton cellulose with acetic anhydride in a sealed tube at 180˚C until the cotton dissolved (Gedon & Fengl, 1992). The result was white amorphous powder which is soluble in alcohol and degraded to a very low molecular weight by high reaction temperature (Malm & Hiatt, 1954). According to Yasley et al. (1964), in 1879, Franchimont

used various types of catalysts to increase the esterification reactions. Franchimont had found that external heat is unnecessary when stronger dehydrating agent such as sulphuric acid is used as a catalyst and his products can be also classified into two types based on their solubility in hot and cold alcohol. Erwig and Koenigs had further developed Franchimont work by using zinc chloride as condensing agent (Yarsley et al., 1964).

Cellulose hydrate, which was heated with acetyl chloride in the presence of crystalline zinc acetate and obtained by precipitating cellulose from solution in zinc chloride or cuprammonium, was patented in the UK by Charles Cross and Edward Bevan in 1894. While in 1898, Weber had described the action of acetyl chloride and acetic anhydride on regenerated cellulose in the presence of magnesium acetate as the production of cellulose tetra-acetate. The triacetate produced by treating modified or normal cellulose with acetic anhydride, acetic acid and suitable catalyst or condensing agent such as sulfuric acid was first used by Lederer (Yarsley et al., 1964).

In 1905, George Miles in America enabled to distinguish between fully esterified acetate as chloroform-soluble derivatives and his new hydrolyzed acetate as acetone-soluble derivatives. Almost at the same time, Bayer Company in Germany also showed that mild hydrolysis of the primary acetylation products yielded cellulose acetate insoluble in chloroform but soluble in acetone. The production of acetone soluble cellulose acetate had brought a turning point to its industry. This is because the usage of cellulose acetate previously produced had been seriously hindered by the fact that it was only soluble in relatively toxic or costly solvent such as chloroform or tetrachloroethane (Yarsley et al., 1964; Malm & Hiatt, 1954).

The Swiss brothers Henry and Camille Dreyfus used cellulose acetate for lacquer and film production at Basle in 1910. At the outbreak of World War I, a factory was established at Spondon, Derby, under the direction of the brother Dreyfus and supported by British

government to meet the growing demand for cellulose acetate for aircraft construction (Plastics Historical Society, 2006).

The production of cellulose acetate on an industrial scale began during World War 1, for military application: as fire-resistant lacquers used to cover airplanes, airship, and balloons, in preparing nonfogging and unbreakable glass, and composite nonsplintering glass (with transparent acetylcellulose sheet glued between two pieces of glass), etc. After the war, large capacity for production of cellulose acetate was produced, along with the production of sheets, lacquers and plastics and for the production of fiber from cellulose acetate (Rogovin & Kostrov, 1968).

### 2.4.2 Preparation and the Mechanism of Cellulose Acetate

#### 2.4.2.1 Activation

Accessibility of cellulose is important due to the heterogeneous reaction of acetylation. Therefore, the greater the accessibility of cellulose, the easier it is for the reactants to diffuse into the interior of the cellulose. Pretreatment will open up the cellulosic structure and allows the acetylating agent penetrate uniformly and simultaneously the whole and not the surface of fiber. Adequate shredding of cellulose sheet and adequate swelling of cellulose are necessary pretreatments before acetylation (Balser et al., 1986).

Water, aqueous acetic acid and glacial acetic acid are the most common used activating agent. Water is more effective for pretreatment as cellulose acetylation is a topochemical reaction because water swells the fibers more than other agents and alters the hydrogen bonding between the polymer chains to provide greater surface for reaction. However, remaining water from the pretreatment will react and destroy anhydride during acetylation. Therefore, when water or aqueous acids are used, the cellulose must be dehydrated by displacing the water with acetic acid before the start of acetylation (Edgar, 2007).

The efficiency of activation is increased by the increased temperature, time, the amount of catalyst and lower acetic acid-cellulose ratio (Balser et al., 1986). The temperature of pretreatment may range from 20˚C to the boiling point of acetic acid (118˚C) or above but it is usually more effective at 50˚C or below because losses of acetic acid through evaporation can be avoided (Malm & Hiatt, 1954; Yarsley et al., 1964).

Mild acetylation will occur when acetic acid was used during the activation. The mild acetylation of the pretreatment will make the actual acetylation less violent and more controllable thus it will subsequently reduce the risk of cellulose structure degradation and increase the possibility of uniform acetylation (Yarsley et.al, 1964).

2.4.2.2  Acetylation

There are several methods in producing cellulose acetate. According to Yarsley et al. (1964), the methods used may be classified into two classes namely the solution or homogeneous acetylation and the non-solution or heterogeneous acetylation accordingly to the diluent used. Balser et al. (1986) also stated the same in classification of cellulose acetate producing methods as Yarsley but further elaborated the solution process into the glacial acetic acid process and methylene chloride process. On the other hand, Sjöström (1993) and Ishizu (1990) distinguished the methods as solution and fibrous processes.

Basically, these methods can be differentiated into two: (i) the reaction which completed in liquid phase as the cellulose ester passes into solution when it is formed; and (ii) the reaction which the cellulosic material retains its original fiber structure during the whole reaction due to the resultant acetate produced is insoluble in the reaction medium. Based on the definition, solution process (glacial acetic acid process and methylene chloride process) or homogeneous acetylation belongs to the first reaction while the heterogeneous acetylation or fibrous process belongs to the second reaction. However, the three basic systems commercially used in cellulose acetate and cellulose triacetate production are acetic acid

system, methylene chloride system and heterogeneous system (Steinmann, 1985; Balser et al., 1986; Serad, 1992).

Catalyst is normally used in acetylation in order to improve the diffusion of acetylating reagents. There are different catalysts suggested to accelerate the reaction of esterifying cellulose. The only known catalyst preferable and commercially used for esterifying cellulose is sulfuric acid. In cellulose acetylation with sulfuric acid as the catalyst, cellulose sulfate acid ester (cellulose sulfate) are formed but can be removed by adding dilute aqueous acetic acid solution.

Perchloric acid is also a well-known acetylation catalyst but only used in fibrous method to prepare cellulose triacetate. Perchloric acid does not combine with cellulose to form esters and thus a complete cellulose acetylation with DS of 3 might be obtained. Nevertheless, perchloric acid is not used industrially as it is extremely corrosive and its salts are explosive in nature. Zinc chloride also can be used as a catalyst for esterification. However, the large quantities (0.5-1 part per part of cellulose) required and high acetylation temperatures make it uneconomical for commercial use (Balser et al., 1986).

2.4.2.2.1        Acetic Acid System

Acetic anhydride is currently used as the reactant in most industrial processes of cellulose acetate. In an acetic acid system, cellulose is acetylated with acetic anhydride where sulfuric acid is used as the catalyst and acetic acid as solvent (Steinmann, 1985). This system is also known as the solution process.

In this system, the cellulose which reacts heterogeneously with acetic anhydride is initially reacting mainly in the amorphous regions of the cellulose. The reaction is an exothermic reaction. At the end of reaction, cellulose sulfate is formed instead of triacetate. Therefore, the residual sulfate linkage is then desulfated by adding aqueous acetic acid.

Subsequently, it is hydrolyzed to a desired degree of substitution and then be precipitated (Tanghe et al., 1963; Edgar, 2007).

Theoretically, 3 units of anhydride per unit of glucose will form a cellulose triacetate and 3 units of acetic acid (Equation 2-10). In order to prepare cellulose acetate, cellulose triacetate is further hydrolyzed as illustrated by Equation 2-11.
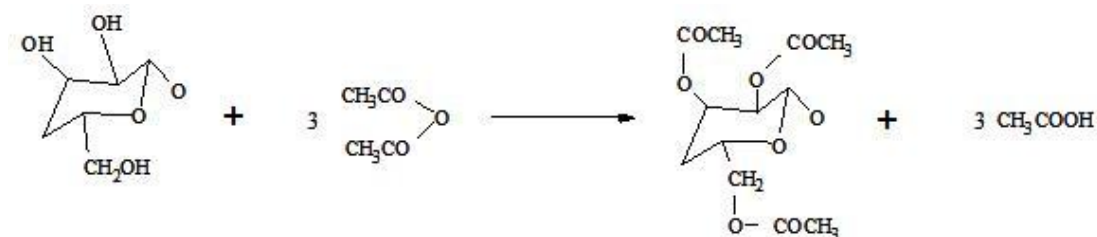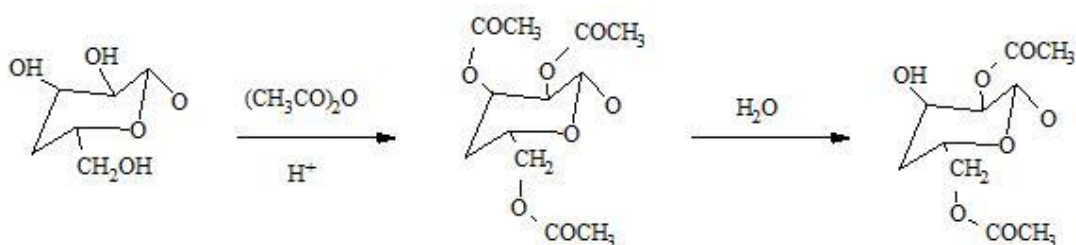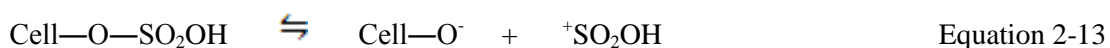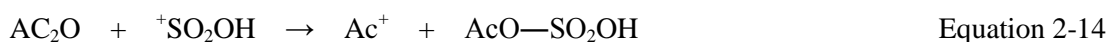


Equation 2-10



Equation 2-11

However, when sulfuric acid is used as a catalyst, the sulfuric acid will combine with cellulose in the presence of acetic anhydride to form cellulose sulfate (Equation 2-12). The acetic anhydride removes the water just as soon as the water is formed and thus the Equation 2-12 was driven to the right.

$$\text{Cell—OH} \quad + \quad H_2SO_4 \quad \rightarrow \quad \text{Cell—O—SO}_2\text{OH} \quad + \quad H_2O \qquad \text{Equation 2-12}$$

For the cellulose sulfate formed, its sulfate linkage is not 100% covalent. Part of the present polarization causes some ion separation in sulfate linkage (Equation 2-13).

$$\text{Cell—O—SO}_2\text{OH} \quad \rightleftharpoons \quad \text{Cell—O}^- \quad + \quad {}^+\text{SO}_2\text{OH} \qquad \text{Equation 2-13}$$

Ion ${}^+\text{SO}_2\text{OH}$ from ion separation in sulfate linkage will cleave the molecule of acetic anhydride and formed an acetylium ion (Equation 2-14). The strong acetylium ion ($Ac^{+)}$ will then react with the negatively charged alkoxide ion and formed Cell—OAc (Equation 2-15). Equation 2-16 showed that the —$SO_2OH$ group in cellulose sulfate had been replaced by —OAc.

$$AC_2O \quad + \quad {}^+\text{SO}_2\text{OH} \quad \rightarrow \quad Ac^+ \quad + \quad \text{AcO—SO}_2\text{OH} \qquad \text{Equation 2-14}$$

$$\text{Cell—O}^- \quad + \quad Ac^+ \quad \rightarrow \quad \text{Cell—OAc} \qquad \text{Equation 2-15}$$

$$\text{Cell—O—SO}_2\text{OH} \quad + \quad Ac_2O \quad \rightarrow \quad \text{Cell—OAc} \quad + \quad \text{AcO—SO}_2\text{OH} \qquad \text{Equation 2-16}$$

Besides that, there is another mechanism for acetylating cellulose, which is through the acetylsulfuric acid intermediate. Acetylsulfuric acid can be formed with the reaction of sulfuric acid with acetic anhydride (Equation 2-17) and also via replacement of sulfate with acetyl (Equation 2-16). As shown by the Equation 2-18, cellulose has been acetylated by the acetylsulfuric acid. The regenerated sulfuric acid will combine with cellulose to start again as Equation 2-12 (Steinmann, 1985).

$$Ac_2O \;+\; HO—SO_2OH \;\rightarrow\; AcO—SO_2OH \;+\; HOAc \qquad\qquad \text{Equation 2-17}$$

$$Cell—OH \;+\; AcO—SO_2OH \;\rightarrow\; Cell—OAc \;+\; H_2SO_4 \qquad\qquad \text{Equation 2-18}$$

The availability of cellulose hydroxyl groups gradually decreases as the acetylation near to completion. Hence, the amount of acetylsulfuric acid constantly increases as most of the sulfuric acid will react with acetic anhydride since the cellulose hydroxyl is no longer available. However, it is more difficult for sulfate groups on cellulose to be replaced by acetyl groups when the amount of acetylsufuric acid increases. Therefore, there will be some residual sulfate groups remain on the cellulose after the completion of the acetylation. These sulfate groups are then removed during hydrolysis.

Nevertheless, cellulose triacetate can be obtained if the liberated sulfuric acid is neutralized by slow addition of a dilute aqueous acetic acid solution, which contained sodium or magnesium acetate or triethanolamine. Besides that, the liberated sulfuric acid also can be removed by a simple transesterification in which magnesium oxide or magnesium carbonate is added to neutralize the catalyst (Rouse, 1964; Ward, 1978; Serad, 1992).