PRODUCTION OF BRAILLE PAPER FROM RECYCLED FIBER TREATED WITH CELLULOSE ACETATE AND OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY (RSM)

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By

SOO MEI CHONG

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LIST OF ABBREVIATIONS AND SYMBOLS

$(CH_3CO)_2O$	acetic anhydride
2k	two-level factorial design
2^{k-1}	half two-level factorial
ACPD 1-19 CA	cellulose acetate synthesized from acid pretreatment carton box paper dust produce by changing ratios of acetic-acid water
AGU	anhydroglucose unit
ANOVA	analysis of variance
ASTM	American Society for Testing and Materials
AQ	anthrahydroquinone
C	concentrate of cellulose acetate bath
C_2H_5Cl	Ethyl Chloride
CAPD	cellulose acetate synthesized from paper dust
CAEFB	cellulose acetate synthesized from oil palm empty fruit brunch
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
CCD	central composite design
CDA	cellulose diacetate
CE	coefficient estimation
CH_3CH_2COOH	propionic acid
CH_3Cl	methyl chloride

Cl – CH_2-COOH	chloroacetic acid
CMC	carboxymethyl cellulose
CO_2	carbon dioxide
$COCH_3$	acetyl
Conc.	concentrate
CTA	cellulose triacetate
D	dipping time
dl/g	deciliters per gram
DP	degree of polymerization
DS	degree of substitution
EFB	oil palm empty fruit bunch
Eq.	equation
etc	*et cetera*
GHG	green house gas
gm	gram
gsm	grammage
H_2O	water
HAMC	hydroxyethyl methyl cellulose
HCI	hydrochloride
HPC	hydroxypropyl cellulose
KHP	potassium hydrogen phthalate
$kPa.m^2/g$	kilo pascal square metre per gram
kV	kilovolt
M	molarity
MCC	microcrystalline

min	minute
mL	mililiter
mL/min	mililiter per minute
MSW	municipal solid waste
N	normality
Na_2CO_3	sodium carbonate
NaCl	sodium chloride
NaOH	sodium hydroxide
^{o}/s	degree per second
^{o}C	degree Celsius
OD	oven dry
OH	hydroxyl
OPEFB	oil palm empty fruit bunch
PI	predicted interval
psi	pound-force/sq.inch
RSM	response surface methodology
Sdn Bhd	Sendirian Berhad
SEM	scanning electron microscopy
T	pressing temperature
TAPPI	Technical Association of Pulp and Paper Industry
TEC	triethyl citrate
TG	thermogravimetric analysis
US$	US dollar
wt%	weight percent

PENGHASILAN KERTAS BRAILLE DARIPADA GENTIAN SEKUNDER YANG DIRAWAT DENGAN SELULOSA ACETAT DAN PENGOPTIMUMAN MENGGUNAKAN UJIKAIJI PERMUKAAN SAMBUTAN

ABSTRAK

Dalam kajian ini, habuk kertas dan pulpa kimia tandan buah kelapa sawit kosong yang belum terluntur telah digunakan untuk menghasilkan selulosa acetat . Kertas kitar semula yang diperbuat daripada gentian sekunder dirawat dengan selulosa acetat yang disintesis daripada kertas habuk untuk menghasilkan kertas yang kegramman rendah (~80 gsm) dan keras yang sesuai digunakan dalam mesin Braille. Rawatan selulosa acetat yang dihasilkan daripada kertas habuk ke dalam kertas pembuatan telah dikaji secara statistik dengan mengguanakan rekabentuk uji kaji dua-tingkat pemfaktoran separuh. Tindak balas ketiga-tiga pembolehubah-pembolehubah rawatan – masa pencelupan, suhu penekanan dan tempoh masa penekanan ke atas ketiga-tiga sifat (kepadatan, indeks pecahan dan kadar pembasahan permukaan) telah dikaji siasat. Merujuk kepada model-model faktoran yang dibina, tempoh masa pencelupan merupakan pembolehubah yang paling berpengaruh diikuti dengan suhu penekanan, manakala tempoh masa penekanan tiada kesan yang signifikasi keatas semua sifat kertas. Pengoptimuman keadaan rawatan ke atas sifat-sifat kertas telah dijalankan dengan menggunakan rekabentuk ujikaji metodologi permukaan sambutan (Respose Surface methodology, RSM) yang berdasarkan rekabentuk komposit pusat (central composite design, CCD). Keempat-empat sifat, iaitu kepadatan, indeks pecahan, kelicinan dan kadar pembasahan permukaan telah dianalisis. Model anggaran polinomia bagi semua sifat telah dikembang sebagai fungsi kepada ketiga-tiga pembolehubah individu iaitu suhu penekanan, masa rawatan dan kepekatan selulosa asetat. Kertas yang dirawat berdasarkan keadaan optima (T: 163^{o}C, D: 2.8 minutes and C: 2.7%) menghasilkan kertas yang mempunyai kepadatan

sebanyak 0.5450 g/cm^3, kadar pembasahan permukaan sebanyak 0.012^o/s, indeks pecahan sebanyak 2.84-kPa m^2/g, dan kelicinan kertas sebanyak 475 mL/min. Semua nilai eksperimen tidak berbeza secara signifikasi keatas nilai jangkaan yang dikira daripada model-model anggaran. Kertas kitar semula yang telah dirawat dengan selulosa asetat yang diperbuat daripada gentian sekunder telah didapati mempunyai sifat-sifat kertas yang lebih baik daripada kertas Braille komersia dari segi kadar pembasahan permukaan dan indeks pecahan. Rawatan kertas kitar semula dengan selulosa acetat yang diperbuat daripada tandan kosong kelapa sawit (CAEFB) juga dijalankan. Sifat kertas yang telah dirawat dengan menggunakan selulosa acetat yang disintesis daripada tandan kosong kelapa sawit telah dibandingkan dengan sifat kertas yang telah dirawat dengan selulose acetate yang disintesis daripada habuk kertas. Kesan rawatan kedua-dua jenis selulosa acetat telah dibanding secara statistik dengan menggunkan ujikaji-t: pasagan dua sampel untuk purata (t-test: Paired Two Sample for Means). Hasil daripada statistik, didapati sifat kepadatan, kadar pembasahan permukaan dan kelicinan kertas buatan yang dirawat dengan menggunakan selulosa acetat yang disintesis daripada tandan kosong kelapa sawit adalah lebih baik daripada yang dirawat dengan selulosa acetat habuk kertas. Ini mungkin disebabkan kertas yang dirawat dengan selulosa acetat disintesiskan daripada pulpa dara tandan kelapa sawit.

PRODUCTION OF BRAILLE PAPER FROM RECYCLED FIBER TREATED WITH CELLULOSE ACETATE AND OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY (RSM)

ABSTRACT

Paper dust and oil palm empty fruit bunch (EFB) unbleached chemical pulps were derived to a low-grade cellulose acetate in this study. Papers made from secondary fiber were then treated with the resultant cellulose acetate (CA) to produce paper that is suitable to be used on Braille embosser but in lower grammage (~80 gsm) and higher paper stiffness. The treatment of cellulose acetate derived from paper dust (CAPD) into handsheet was studied statistically by employing a half two level factorial design. The effects of the three independent variables of treatment - dipping time, pressing temperature and pressing time on three response variables (paper density, burst index and rate of surface wettability) was investigated. The factorial models obtained showed that dipping time is the most influential variable followed by pressing temperature, whereas the pressing time was insignificant to all responses. The optimization of treatment conditions on the paper properties were carried out by employing response surface methodology (RSM) based on central composite design (CCD). Four response variables, namely density, burst index, smoothness, and rate of surface wettability were analyzed. Polynomial estimation model of each response was developed as functions of three independent variables, which are pressing temperature (T), dipping time (D), and concentration of cellulose acetate (C). The paper which was treated based on the calculated optimum condition (T: 163°C, D: 2.8 minutes and C: 2.7%) , possessed density of 0.5450 g/cm^3, rate of surface wettability of 0.012°/s, burst index of 2.84-kPa m^2/g, and paper smoothness of 475 mL/min. All the experimental values were significantly no different from the predicted values calculated from estimation models. The cellulose acetate treated Braille papers made from recycled fiber was found to have better properties than those of commercial Braille paper in terms of rate of surface wettability and burst index. The treatment of cellulose acetate derived from oil palm empty fruit bunch (CAEFB) into handsheet was also carried out. The properties of handsheet that treated with CAEFB were then compared to those treated with CAPD. The effect of the two cellulose acetate treatments was compared statistically by using t-test: Paired Two Sample for Means. From the result of statistic, it was found that the paper density, rate of surface wettability and surface smoothness of handsheet that treated with CAEFB was better than that treated with CAPD. This might due to the former was derived from relatively purer virgin pulp from EFB.

1 INTRODUCTION

1.1 General

Cellulose acetate (CA) is a kind of thermoplastic, and it is one of the most important and widely used cellulose derivatives (Ibrahem et al., 1983). The application of cellulose acetate in papermaking had been reported since 1977, when Litzinger patented an extrusion process of making cellulose acetate fibers, which was suitable to be used in conventional papermaking methods (Rustemeyer, 2004).

Recently, the production of cellulose acetate from lower grade pulp such as secondary fiber, agrowaste fiber, and non-wood biomass pulp, has been reported (Filho *et al.* 2008). However, the cellulose acetate produced showed relatively poor quality in terms of transparency, thermal stability, filterability, and solubility. These inferior properties were due to the presence of impurities in the materials, which include lignin, hemicellulose, and low molecular weight cellulose. Nevertheless, the resultant cellulose acetate with a high degree of substitution (DS) could be obtained when applying a longer acetylation time. The potential applications of this lower-grade cellulose acetate are numerous, including: a variety of coating applications, pressure-sensitive tapes, wood-sealers, packaging, and paper and paperboard for food contact applications (Eastman, 2006).

In the world of blind or visual-impaired people, listening and touching are the main ways to gain knowledge. The Braille system is a type of tactile symbol based on the Braille cell, which composed of one to six dots in a specific position (Rex et al., 1995). Braille dots are produced by using a special typewriter known as an embosser.

To ensure that the Braille dots produced have sufficient stiffness and height for effective reading, Braille paper basically requires a relatively high grammage of 120 to 140 gsm and an apparent density of more than 0.75 g/cm^3. In order to meet the requirement of high density, fully bleached virgin paper, which principally has a better inter-fiber bonding ability (Casey, 1981), is normally used as raw material. However, to approach environmental sustainability, utilization of recycle paper for the production of Braille paper is recommended. Nevertheless, some modifications are required to be done during the papermaking process to attain the desired properties of Braille paper. One of the methods to improve paper properties is via a simple penetration or coating method by dipping paper sheets into a polymer solution (Ibrahem et al., 1983).

Paper dust is a type of cellulose waste generated in the course of converting operations in a paper mill and cannot be recycled for papermaking, as it has rather short fiber length. Although cellulose is one of the most abundant natural resources, it is valuable and should be fully utilized.

In current study, researcher attempts to use cellulose acetate synthesized from secondary fibers as treatment material on recycle paper with the aim to produce handsheet in low grammage (~80gsm) but high in stiffness, which made the products suitable to be used on Braille embosser. In order to retrieve and to maximize the resource value, the research starts from the study of the effect of cellulose acetate treatment variables in the production of Braille paper from secondary fiber studied based on half two level factorial design (2^{k-1}). Paper dusts used to form a low-grade cellulose acetate. Recycle papers are then treated with the resultant cellulose acetate with the aim to improve the properties of the papers. The three independent variables in the treatment process are dipping time (D), pressing time (P), and pressing temperature (T). The data collected for responses (density, burst index and rate of surface wettability) are statistical analyzed by a half two-level factorial (2^{k-1}) design.

The research was followed by studying the effects of the treatment process variables [the pressing temperature (*T*), dipping time (*D*), and concentration of CA bath (*C*)] on paper properties. An experimental design called response surface methodology (RSM) based on central composite design (CCD) were employed in the investigation. The quality of the handsheet is then evaluated based on four response variables, namely density, burst index, smoothness, and rate of surface wettability. The estimated models of the four responses generated were used to identify the optimum process conditions.

In addition, the paper properties of handsheet treated with cellulose acetate synthsized from oil palm empty fruit bunch (CAEFB) are also studied. The comparison of the paper properties between handsheet treated with CAEFB and cellulose acetate prepared from paper dust (CAPD) are statistically analyzed by using t-test.

1.2 Objectives:

i. To generate low grade cellulose acetate from recycle paper dust and virgin unbleached oil palm empty fruit bunch pulp.
ii. To investigate the effects of cellulose acetate treatment variables (dipping time, concentration of cellulose acetate solution, pressing temperature and pressing time) on paper properties (burst index, paper density, wettability and smoothness) by employing statistical experimental designs.
iii. To determine the optimum conditions of cellulose acetate treatment on paper properties based on the polynomial estimation models acquired from central composite design (CCD).
iv. To study the paper properties of the handsheet treated with cellulose acetate synthesized from paper dust (CAPD) and cellulose acetate synthesized from oil palm empty fruit bunch (CAEFB) and to compare their differences.

2 LITERATURE REVIEW

2.1 Cellulose Acetate

Cellulose acetate in general is a semi-synthetic polymer obtained from the esterification of cellulose by using acetic anhydride, with the present of sulphuric acid as a catalyst. Presently, commercially available cellulose acetate can be roughly divided into two categories according to the degree of acetylation thereof. The first is cellulose triacetate (CTA) which has the degree of acetylation of not less than 59%. The other is cellulose diacetate of a wide range. Among them, those having a degree of acetylation of about 50% to 59% are referred to as cellulose diacetate (CDA). The cellulose acetate (CA) mentioned in this research refers to cellulose diacetate (CDA) (Kiyose et al., 1999).

Cellulose diacetate or cellulose acetate is known as the second oldest man-made fiber commercially manufactured (Friday, 1990). This polymer was, firstly, invented by Schützenberger in 1865 by heating cellulose in a sealed glass tube with acetic anhydride. In 1879, Franchimont found that the cellulose acetate can be produced at room temperature in the present of sulfuric acid as a catalyst. As for CTA, the first patent was applied by Charles Cross and Edward Bevan in 1894, which targeted to replace collodion and nitrocellulose with the hardly inflammable cellulose acetate (Rustemeyer, 2004).

The commercial success of research work remained poor until the discovery of cellulose acetate by Miles in 1904 and Eichengrün in 1905. The mechanical properties of the cellulose acetate produced are similar to collodion, and it is also soluble in acetone, methyl acetate and ethyl acetate. Cellulose acetate was then became a rather successful commercial product, such as “Cellit” that was produced under F. Bayer & Co. since 1905; “Cellonit” since 1912; and “Celanese” that was introduced after War World I by Dreyfus brothers (Rustemeyer, 2004).

Cellulose acetate remains as one of the major fibers in linings, fashion-ended uses and robe-wear (Friday, 1990). In 1998, the world’s production of cellulose acetate multifilament yarns achieved more than 300 thousand tons per annum, and it continued to increase with an approximately 2 to 3% annually (Pocienė et al., 2004).

2.1.1 Utilization of cellulose acetate

2.1.1.1 Airplane lacquers

The first important application of cellulose acetate was in the field of plane-wings-coating. The normal material for the outer skin of aircraft before the use of aluminum was a heavy linen fabric such as rubber. The craft wings were treated with a substance commonly called “dope” which made from cellulose acetate. This dope provides resistance to water, wind, oil and petrol. At the same time, it adds tautness, resiliency and non-flammability on the plan’s wings. The demand of the cellulose acetate in the aircraft industry was increased after the outbreak of the World War I in 1914 (Winter, 1975, Rustemeyer, 2004).

2.1.1.2 Textile

By the late 1930s, cellulose acetate silk industry grew well in the family of textile fibers. At that time, the family of textile fibers included man-made fibers, viscose rayon and natural fibers, such as cotton, silk, flax and wool (Rustemeyer, 2004). In 1950s, cellulose triacetate textile fiber was commercialized and gained a place in the family of textile fibers. The demand of combined cellulose triacetate textile fiber peaked at 938 million pounds world-wide in 1971 and declined after the introduction of synthetic fibers, such as polyester and acrylics in the textile market (Lewin and Pearce, 1985).

The products made from acetate yarns are comfortable, attractive, fully biodegradable, have good drapes, pleasant handle, have no problem with static electricity, “silky” gloss and easily dyed. Furthermore it does not shrink after washed, does not form pills on surface and low in cost (Pocienė et al., 2004, Lewin, 2006).

The traditional market for cellulose acetate and cellulose triacetate fabrics is in women’s apparel, such as dresses, blouses, lingerie, robes and housecoats. Others than women’s apparel, other textile products include decorative household applications, curtains, caskets and also liner in men’s suits (Lewin, 2006).

2.1.1.3 Cigarette tow

The first usage of cellulose acetate in cigarette filters was in 1952. Because of the unique properties of cellulose acetate that suited it as filters in cigarette, the demands of cellulose acetate filter tow has seen a tremendously near to linear growth. Today, nearly 95% of the world’s cigarette is sold with a cellulose acetate filter. The properties of cellulose acetate that include high surface-to-volume proportions, moisture-regain, non toxic, and plasticizer have made it an efficient smoke-removal with low pressure drop properties, which helps to improve the taste of the cigarette and to reduce the risk for lung diseases among smokers (Lewin, 2006, Rustemeyer, 2004).

2.1.1.4 Plastic Application

Combinations of cellulose triacetate and cellulose acetate with plasticizers as well as mixed esters are used to fabricate transparent thermoplastics. The thermoplastic of these cellulose acetate gives excellent clarity and good mechanical properties, such as non yellowing, resistant to embrittlement and provides pleasant electrical insulation. Cellulose acetate which fabricated by most of the thermoplastic processes is molded into brush handles, combs, barrettes, toys and spectacle frames. In additional, cellulose acetate is used in the manufacturing of automotive parts like steering wheels (i.e. cellulose acetate propionate, CAP), signal glasses and others (Lokensgard, 2010, Rustemeyer, 2004).

2.1.1.5 Film

One of the applications of cellulose acetate is as films and sheets in the packaging and displaying industries. Cellulose acetate film was proposed for photographic film in 1901 and able to replace celluloid and cellulose triacetate after improvement. With a better quality of the handling characteristic such as rupture and splicing, cellulose acetate becomes the preferred material for photographic film as well as for professional motion picture films. Besides it is used in the production of magnetic recording tapes and photographic film. Other important usages of the acetate films were the formation of security glass for automobiles and electrical insulator films. The cellulose acetate films that allowed the passage of moisture and gases are also used in commercial packaging of fruits and vegetables (Rustemeyer, 2004, Lokensgard, 2010).

2.1.1.6 Membrane

Cellulose acetate has been widely used in the membranes for separation in various fields. These include drinking water treatment, sewage treatment, waste-water treatment and for blood dialysis in medical used. The properties of cellulose acetate such as hydrophilic, relatively low cost, environmental friendly, easily fabricated into films, membranes and fiber are fitted to be used for these applications, especially in the manufacturing process that involve electrospinning techniques (Zhou et al., 2011, Nakatsuka et al., 2009).

2.1.1.7 Coating treatment material

Researches have been conducted to study the usefulness of cellulose acetate as one of the materials to improve paper properties. The physical, mechanical, water resistance and printability properties of paper can be improved by modifying the inter and intra fiber bonding in the paper. One of the methods is penetration of paper sheet in cellulose derivative's solution. This treatment method is very important, especially for paper that produced from agricultural residue, which has poor properties. Factors that involves in these coating treatment methods include concentration of the cellulose acetate dipping bath, dipping time, curing time, temperature, and so on (Kassem and Nada, 2009, Ibrahem et al., 1983, Nada et al., 1997).

2.1.2 Cellulose Derivatives

The usefulness of cellulose not only depends on its superb physical properties, but also on its readiness to be modified into derivatives (Ott et al., 1954). The purposes to transform cellulose into derivatives are: (a) restructure cellulose from its original form; (b) modify its chemical and/or physical properties; and (c) make cellulose amenable to analysis by specific analytical technique (Fraser-Reid et al., 2008). Various modes of chemical modification on the cellulose are available, which include reaction of hydroxyl groups (esterification and etherification), intermolecular cross linking reactions, and macrocellulosic free radical reactions. These cellulose derivatives are grouped according to their processes and substituents (Varshney and Naithani, 2011).

In general, all cellulose modification reactions happen at the available free hydroxyl groups or at the most reactive hydroxyl (OH) groups of the cellulose macromolecule. The three OH groups are not completely equivalent, because of their vary in accessibility within the crystalline organization as well as in their relative reactivity. C-6 is the most accessible and reactive OH group, and the regular reaction sequences among the three OH groups are C-6 > C-2 > C-3. The level of derivation is measured in terms of the degree of substitution (DS) (Varshney and Naithani, 2011, Chatterjee and Gupta, 2002). Degree of substitution is the average number of hydroxyl groups replaced by the substituent, with the maximum of three. The type, distribution and uniformity of substituent groups determine derivative's properties (Varshney and Naithani, 2011).

Cellulose derivatives, from its natural origin, have diverse physicochemical properties due to kind of substituent, and molecular weight. Degree of substitution (DS) and degree of polymerization (DP) are used widely in different industrial sectors. The applications of cellulose derivatives include additives in building material, chemical in textile, pharmaceutical, food, cosmetic product and packaging industrial (Varshney and Naithani, 2011, Granström, 2009).

2.1.2.1 Cellulose Ether

In general, cellulose ether produced by alkalizing high-purity cellulose fibers in suspension, with high alkalinity and low water content conditions. Most of the commercial cellulose ethers produced is in heterogeneous conditions in organic solvent suspension (Fraser-Reid et al., 2008).

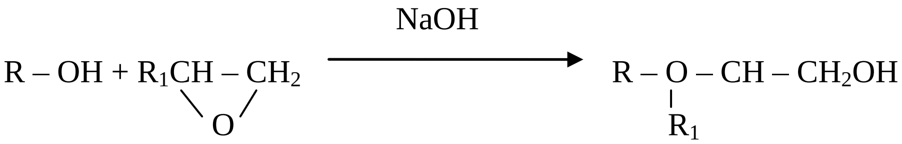
There are many possible variations in the process to produce cellulose ethers. Feller (1990) mentioned these processes in general involve the converting of purified cellulose, which derived from wood, cotton and related scrap materials into alkali cellulose, follow by reaction with an etherifying reagent such as methyl chloride. While, Fraser-Reid (2008) reveals that cellulose ethers are made from alkalized cellulose in: (a) a typical Williamson synthesis using alkyl halides; (b) using ring opening reactions with oxiranes, or (c) by reacting with vinyl compounds.

Below are the simplified general equations for the synthesis steps of cellulose ether, where equation 2.1 refers to the formation of alkali cellulose; equation 2.2 and 2.3 refer to the two optional formations of cellulose ether (Feller, 1990).

$$R - OH + NaOH \longrightarrow RONa + H_2O \qquad \text{Equation 2.1}$$

$$R\text{-}ONa + ClCH_3 \longrightarrow R - O - CH_3 + NaCl \qquad \text{Equation 2.2}$$

Or



$$R - OH + R_1\underset{\diagdown\ O\ \diagup}{CH - CH_2} \xrightarrow{NaOH} R - \underset{\overset{|}{R_1}}{O} - CH - CH_2OH$$

Equation 2.3

Where

R = anhyroglucose radical

R_1 = H or CH_3

There are four major cellulose ether categories that include carboxymethyl cellulose (CMC); methylcellulose and hydroxyethyl methyl cellulose (HAMC); hydroxyethyl cellulose and hydroxypropyl cellulose (HPC). Figure 2.1 shows chemical reaction between cellulose with its derivatives. In addition, Figure 2.2 until Figure 2.5 are the idealized structures for the four major celluloses (Fraser-Reid et al., 2008).

The unique characteristic of cellulose ethers, are related to the behavior during dissolution, the structure and rheological properties of the solutions, and the ability to interact and blends with other solids. These behaviors depend upon the type and numbers of subtituents, distribution of subtituents, and molecular mass (Fraser-Reid et al., 2008).

The applications of cellulose ethers include used as thickeners and dispersants in agricultural and food products, as well as in ceramics, cements, films, lacquers, textiles, pharmaceuticals, paints, detergents, and cosmetics (Fraser-Reid et al., 2008). Table 2.1 shows the application, DS, solubility and etherifying agents of some commercial cellulose ethers in the market.

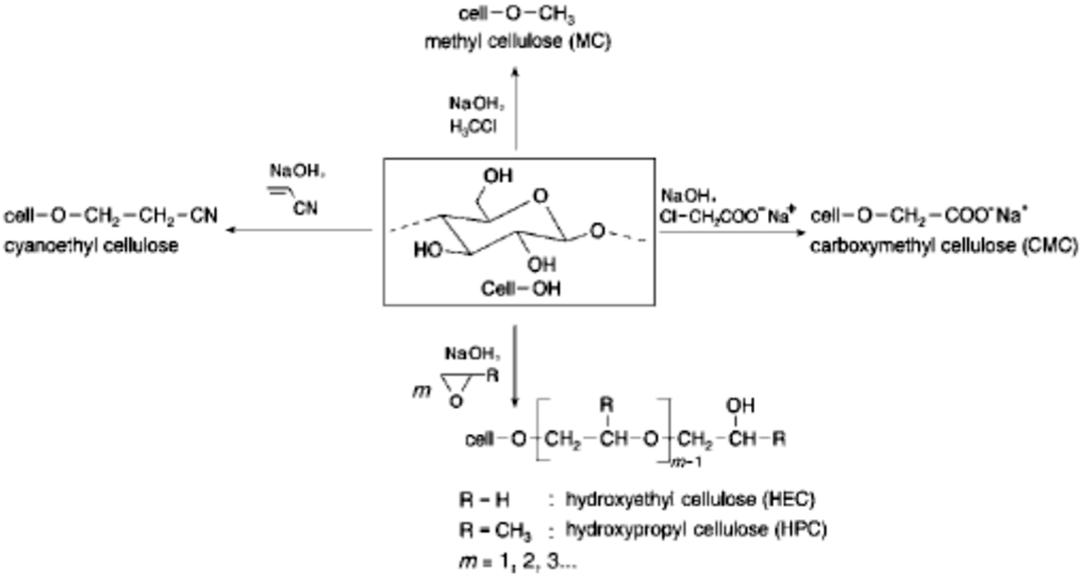


Figure 2.1: Examples of commercial cellulose ethers (Source: Klemm et al., 2005)

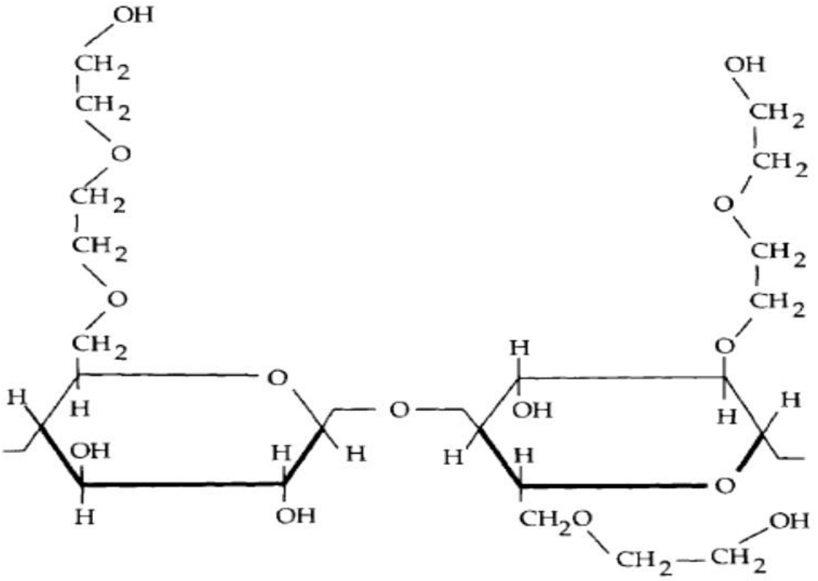


Figure 2.2: One of the possible structures for a cellulose segment of cellulose substituted with hydroxyethyl groups, named Hydroxyethylcellulose with DS 1.5 (Source: Feller, 1990)

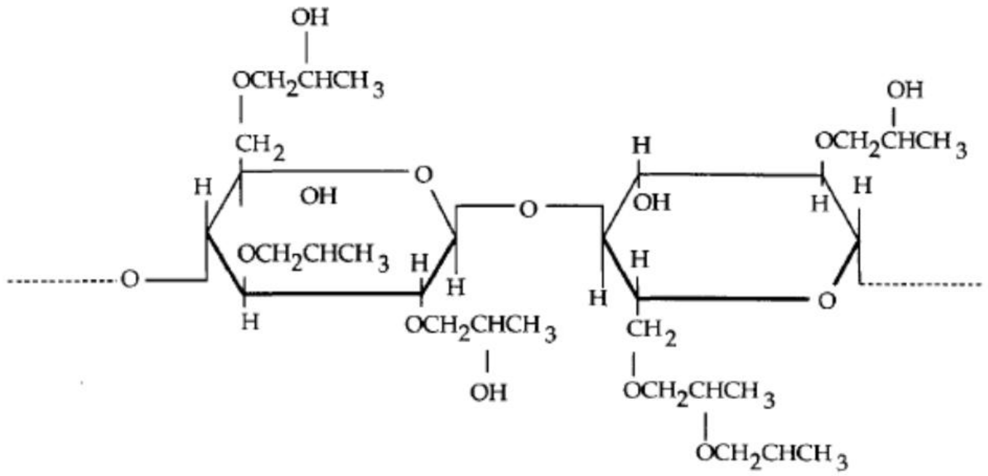


Figure 2.3: Idealized structures for Hydroxypropylcellulose (HPC) (Source: Feller, 1990)

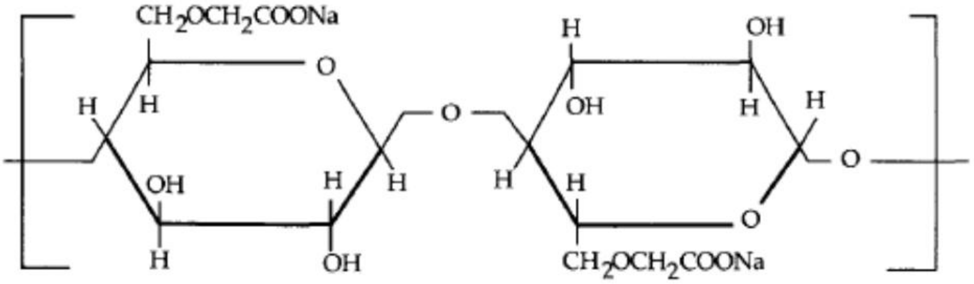


Figure 2.4: Idealized structures for Carboxymethylcellulose (CMC) (Source: Feller, 1990)

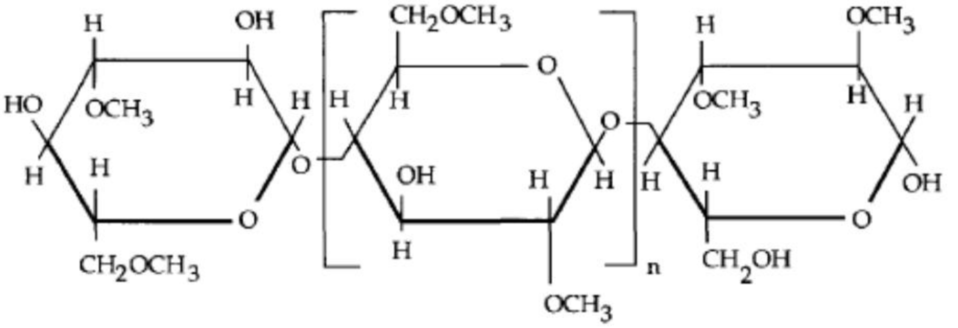


Figure 2.5: Idealized structures for Methylcellulose (MC) (Source: Feller, 1990)

Table 2.1: Types of commercial cellulose ether and their functions

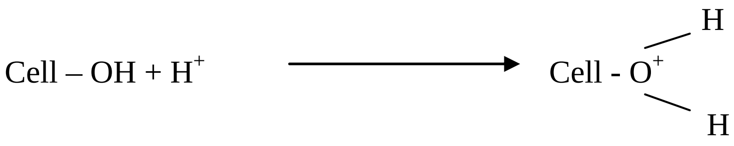
Cellulose Ether	DS range	Solubility	Etherifying Agents	Product Application
Methylcellulose	1.5-2.4	Hot H_2O	CH_3Cl	Food additives, films, cosmetics, greaseproof product
Carboxymethylcellulose	0.5-1.2	Hot H_2O	Chloroacetic acid ($Cl – CH_2$-COOH)	Food additives, fibers, coating, oil-well drilling muds, paper size, paints, detergents
Ethylcellulose	2.3-2.6	Organic solvent	C_2H_5Cl	Plastic, lacquers
Hydroxyethylcellulose	Low DS	H_2O	Ethylene oxide	Films
Hydroxypropylcellulose	1.5-2.0	H_2O	Propylenen oxide	Paints

Source: (Varshney and Naithani, 2011, Feller, 1990)

2.1.2.2 Cellulose Ester

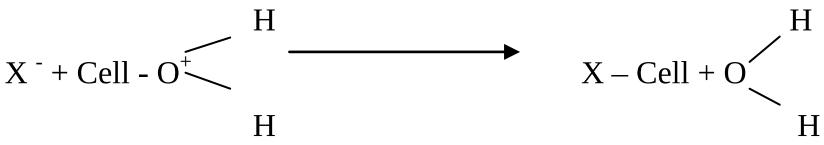
As a polyhydroxy macromolecule, cellulose readily undergoes esterification reactions (Chatterjee and Gupta, 2002). The two main purpose modifications of cellulose into cellulose ester are (1) synthesis materials that are processible into different types of useful films, such as three dimensional objects, fibers, and solutions that are suitably used for casting and coating; (2) improve the physical properties of cellulose such as the solubility parameter. The modification characteristic of these cellulose esters gave entry into a wide range of applications greatly expanded from those available to the parent polysaccharide (Edgar et al., 2001). Commercial cellulose esters are produced under heterogeneous modification reaction. Cellulose esters are generally classified into inorganic esters and organic esters (Fraser-Reid et al., 2008).

Generally, the synthesis processes of cellulose esters start in the formation of oxonium ions. The process is then followed by their nucleophilic substitution with an acid residue and also the elimination of water. Equation 2.4 and equation 2.5 show the simplified chemical reactions for the making of cellulose esters. (Fraser-Reid et al., 2008)



$$\mathrm{Cell-OH + H^{+}} \longrightarrow \mathrm{Cell-O^{+}}\begin{array}{l} \diagup \mathrm{H} \\ \diagdown \mathrm{H} \end{array}$$

Equation 2.4



$$\mathrm{X^{-} + Cell-O^{+}}\begin{array}{l} \diagup \mathrm{H} \\ \diagdown \mathrm{H} \end{array} \longrightarrow \mathrm{X-Cell + O}\begin{array}{l} \diagup \mathrm{H} \\ \diagdown \mathrm{H} \end{array}$$

Equation 2.5

The most common cellulose esters in industrial include cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB) and nitrocellulose. The chemical reactions between the cellulose and its cellulose derivatives (esters group) are shown in Figure 2.6. The important roles of cellulose esters include coating, control release, plastic, optical film, composites and lamination, membrane structure and other types of separation media applications. Table 2.2 summarizes the advantages and disadvantages of cellulose esters, and Table 2.3 shows the types of commercial cellulose esters and their functions.

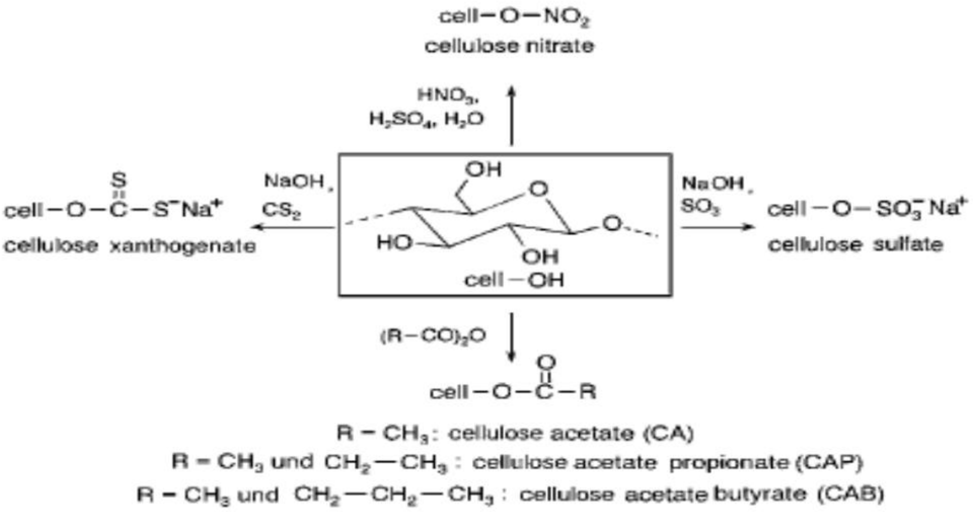


Figure 2.6: Typical technical cellulose esters. (Souce: Klemm et al., 2005)

Table 2.2: The advantages and disadvantages of cellulose esters

Advantages of cellulose esters	Disadvantages of cellulose esters
• Forms glossy molding by the thermoplastic method	• Poor solvent resistance
• Exceptional clarity (butyrates and propionate)	• Poor resistance to alkali mat
• Toughness, even at low temperatures	• Relatively low compressive strength
• Excellent colorability	• Flammable
• Non – petrochemical base	
• Wide range of processing characteristic	
• Resists stress cracking	
• Outstanding weatherability (butyrates)	
• Slow burning (except cellulose nitrate)	

(Source: Lokensgard, 2010)

Table 2.3: Types of commercial cellulose esters and their functions

Cellulose Ester	DS range	Solubility	Product Application
Nitrate	1.5-3.0	MeOh,PhNO2, ethanol-ether	Films, fibers, explosives
Acetate	1.0-3.0	Acetone	Films, fibers, coating, heat and rot resistance fabrics

(Source : Feller, 1990, Varshney and Naithani, 2011)

2.1.2.2.1 Inorganic esters

Inorganic esters are formed with nitric, sulfuric, and phosphoric acid. Cellulose nitrates are the greatest commercial product.

Cellulose nitrates are formed by treating cotton with mixtures of nitric and sulfuric acids. These cellulose derivatives were used as base films in early photography, in fine lacquers, automotive coatings. Besides, cellulose nitrate is often used in the determination of molecular weights and weight distribution of cellulose on an analytical scale (Fraser-Reid et al., 2008).

Cellulose sulfuric is synthesized by modified cellulose with sulfuric acid in the presence of an aliphatic alcohol. The reaction is depends on several variables that includes the chain length and structure of alcohol, the sulfuric acid : alcohol molar ratio, temperature and time of reaction (Chatterjee and Gupta, 2002). One of the characteristics of cellulose sulfuric is its solubility in water, especially in low degree of substitutions. Cellulose sulphate with a low degree of substitution (DS 0.2 to 0.3) are used in oil drilling, foodstuffs, cosmetic, and pharmaceuticals (Fraser-Reid et al., 2008).

Cellulose phosphate is prepared by converting cellulose with molten phosphoric acid and urea at 120˚C. Cellulose phosphate with a low degree of substitutions (DS 0.3 to 0.4) has a high water retention value. These cellulose derivatives have wide applications in textile industry for flame retardants, as thickeners and membrane used in the medical area, especially in haemodialysis (Fraser-Reid et al., 2008).

2.1.2.2.2 Organic esters

Cellulose acetate was invented by Schützenberger in 1865 (Chatterjee and Gupta, 2002) while cellulose triacetate was made by Cross and Bevan and applied the patent in 1894 (Rustemeyer, 2004). In general, cellulose esters are formed by the reaction between natural cellulose with organic acids, anhydrides, or acid chlorides. Cellulose esters of almost any organic acid can be prepared (Mark, 2004). The acetylation reaction is heterogeneous and topochemical where continuous layers of cellulose fibers respond and are solubilized in the medium, thus exposing a new surface of cellulose fiber for reactions. Cellulose must be activated before acetylation. This is because the reaction's course is determined by the rate of diffusion of the reagents into the cellulose fibers in order to achieve consistent reaction and prevent unreacted fibers in the solution (Mark, 2004). Viscosity of the solution and degree of esterification or the amount of bound acetic acids are primarily determined the properties and applications of cellulose acetate. Cellulose acetates are non-toxic, odorless, tasteless and less flammable than nitrocellulose (Balser et al., 2000).

Cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB), are the most common cellulose organic esters in industrial. These cellulose derivatives are known as the most important classical and solvent-based coating in industry (Klemm et al., 2005). Applications of cellulose acetate include textile fibers, plastic, film, LCD displays, lacquers, cigarette filter tow, and filter material in medical industries (Mark, 2004).

Cellulose acetate propionate, a mixed cellulose ester developed by the Celanese Plastic Company. This cellulose derivative is synthesized like other acetates, with the replacement of acetic anhydride with propionic acid (CH_3CH_2COOH). The characteristics of these cellulose derivatives are soluble in both organic solvent and in alcohol/water mixtures, fast solvent release rate, superior heat resistance and low moisture absorption. The application of cellulose acetate propionate, mainly in film packaging display, brush handles, steering wheels, automotive parts, toys, reverse osmosis filter membrane, etc. (Guiomar et al., 2002, Lokensgard, 2010).

Cellulose acetate butyrate is another type of mixed cellulose ester which developed in the mid 1930s by the Hercules Powder Company and Eastman Chemicals. The properties of cellulose acetate butyrate are slightly hygroscopic and practically insoluble in water and alcohol. Other than that, cellulose acetate butyrate is soluble in acetone, formic acid and in a mixture of equal volumes of methanol and methylene chloride (Europe, 2004). The synthesis reaction of cellulose acetate butyrate is almost similar to cellulose acetate except the additional of butyric acids. The cellulose reacts with a mixture of sulfuric and acetic acids, followed by acetic anhydride and butyric acid. The product made thus has acetyl groups (CH_3C0) and butyl groups ($CH_3CH_2CH_2CH$) in the repeating cellulose unit (Lokensgard, 2010).

The improvement of properties after modification includes dimensional stability, chemical and moisture resistance compares to cellulose acetate. Cellulose acetate butyrate is used in the screw driver handle, automobile parts, display sign, tubes, pipe, packaging components and others (Lokensgard, 2010).

2.1.3 Preparation of Cellulose Acetate

According to Nathan Eastman (Europe, 2004), the processes used to produce cellulose acetate can be categorized into three major groups, which include (a) solution process; (b) solvent process; and (c) heterogeneous (non-solvent or Schering) process. It is necessary to complete the acetylation of cellulose followed by hydrolyzation to the required acetyl value. The importance to complete these steps is to obtain cellulose acetate that soluble in acetone solvent. In general, the steps to produce cellulose acetate are (i) preparation of cellulose for acetylation; (ii) acetylation; (iii) hydrolysis, and (iv) recovery of cellulose acetate and solvents.

2.1.3.1 Preparation of cellulose for acetylation

The cellulose used need a dry to moisture content in the range of 4% to 7%, this is because low moisture content would lower the reactivity of the cellulose. On the other hand, too much moisture would cause a higher consumption of acetic acid and thus resulting in an extremely violent reaction (Mark, 2004).

After obtained the required moisture content, it is necessary to activate the cellulose by pre-treatment. This is because the pre-treatment process is believed to cause a partial swelling of the cellulose by splitting the hydrogen bonds, which can help to increase the accessibility of cellulose.

The greater the accessibility of cellulose, the more rapid and easier for the acetylating reagents to enter the fibers (Mark, 2004). According to Steinmann (Lewin and Pearce, 1985), pre-treatment steps are categorized into two groups: vapor phase and slurry. The vapor phase in pre-treatment involves a small amount of acetic acid based on the weight of cellulose. The cellulose with the pre-treatment reagent kept in a closed stainless steel vessel with minimum agitation from about 25˚C to 50˚C for usually 60 minutes. Different with vapour phase, the slurry pre-treatment requires a comparatively high ratio of liquid to cellulose. The cellulose is dispersing in water or in aqueous acetic acid with vigorous agitation. Then the water is replaced with acetic acid and followed by a series of continuous alternate operations to concentrate the cellulose (Lewin and Pearce, 1985). In general, acetic acid is used as a pre-treatment reagent. In some processed, small amount of sulfuric acid is also used for the pre-treatment process in order to further improve the diffusion of the acetylating reagents. The time consumed for the pre-treatment is depended upon the process and temperature, from one to several hours (Mark, 2004).

2.1.3.2 Acetylation

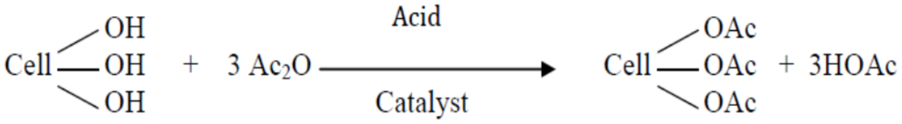
2.1.3.2.1 Acetic Acid System

Acetic acid system, or known as the solution process, is the most common acetylation processes. Acetylation in this group is obtained with acetic anhydride using glacial acetic acid as solvent. Sulfuric acid acts as the catalyst to increase the solubility of the partially esterification cellulose in acetic acid. This process can be separated into two sub category, which are a high catalysts (10-15 wt% sulfuric acid based on cellulose) and a low catalyst (< 7 wt% sulphuric acid) process (Europe, 2004). Acetylation is completed at a moderately elevated temperatures (Lewin and Pearce, 1985).

The mechanism of acetylation in the acetic acid system is started by adding the pre-treated cellulose in a mixture of acetic acid, acetic anhydrides, and sulfuric acid catalyst in a stainless steel acetylator. The stainless steel acetylator equipped with agitator and jacket for cooling. In this process, acetic anhydride will react with the moisture of cellulose to give the acetic acid a complete anhydrous reaction medium, follow by reaction between cellulose and acetic anhydride. The early phase of the acetylation consists of a heterogeneous reaction.

Viscous and clear reaction mixture is obtained at the end of acetylation. At this stage, a substantially full cellulose triacetate is dissolved in the acetic acid and excess of acetic anhydride. Excess of acetic anhydride is then killed by adding the aqueous acetic acid which acts as a stop acid. The purpose of adding stop acid kills excess acetic anhydride, desulphate the residual sulfuric linkages and provides some water in the reaction mixture so that the latter is no longer anhydrous (Lewin and Pearce, 1985).

The overall reaction in the conversion of cellulose to cellulose triacetate as in equation 2.6:



$$\mathrm{Cell}\begin{array}{l}\diagup \mathrm{OH}\\ -\mathrm{OH}\\ \diagdown \mathrm{OH}\end{array} + 3\,\mathrm{Ac_2O} \xrightarrow[\text{Catalyst}]{\text{Acid}} \mathrm{Cell}\begin{array}{l}\diagup \mathrm{OAc}\\ -\mathrm{OAc}\\ \diagdown \mathrm{OAc}\end{array} + 3\mathrm{HOAc}$$

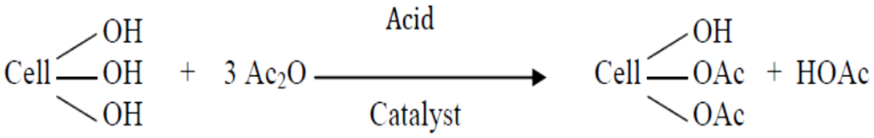
Equation 2.6

Where,

Cell = anhydroglucose ring (without hydrolxyl group)

Ac = abbreviation for acetyl, $COCH_3$

Equation 2.6 shows that 3 mol of acetic anhydride react with 1 mol of cellulose to give 1 mol of cellulose triacetate and 3 mol of acetic acid. Equation 2.7 shows the formation of a diacetate, during acetylation. The degree of substitution actually is higher than 2.4, which means that less than one acetyl group per anhydroglucose unit is hydrolyzed on an average (Lewin and Pearce, 1985).



$$\mathrm{Cell}\begin{array}{l}\diagup \mathrm{OH}\\ -\mathrm{OH}\\ \diagdown \mathrm{OH}\end{array} + 3\,\mathrm{Ac_2O} \xrightarrow[\text{Catalyst}]{\text{Acid}} \mathrm{Cell}\begin{array}{l}\diagup \mathrm{OH}\\ -\mathrm{OAc}\\ \diagdown \mathrm{OAc}\end{array} + \mathrm{HOAc}$$

Equation 2.7

2.1.3.2.2 Methylene Chloride System

Methylene chloride is substituted for all or part of acetic acid and performed as a solvent for the triacetate as it is formed (Europe, 2004). Generally, this tends to give a good filtration characteristic for the cellulose acetate flakes. Comparatively low viscosity of the reaction mixture result due to the solvent power of methylene chloride (Lewin and Pearce, 1985).

The process started with adding the pre-treated cellulose to the solution of methylene chloride, acetic anhydride and sulfuric acid catalyst. The early phases of the acetylation are heterogeneous. The reaction mixture changes from opaque to clear when acetylation is completed. Temperature is controlled by the refluxing and continuous recycling of the methylene chloride. Reaction's time is longer compared to the acetic acid system due to low level of catalyst and moderate temperature. At the end of acetylation, excess acetic anhydride is killed by additional stop acid, catalyst neutralized with basic salt such as sodium acetate, and distil methylene chloride from the reaction mixture at elevated temperatures (Lewin and Pearce, 1985).

2.1.3.2.3 Heterogeneous System

The concept of heterogeneous system is to use a swelling medium that enables the diffusion of reactants into the interior of cellulose without dissolving the acetylated cellulose. Benzene, toluene, ligroin or xylene is the suitable diluents for the heterogeneous system, especially benzene. These organic liquids are referred as the diluents or non solvent (Lewin and Pearce, 1985). The cellulose triacetate synthesized by this process is never stabilized. Therefore, its physical form is alike the original cellulose fiber (Europe, 2004).

Pre-treated cellulose is added together with pre-cooled solution of acetic anhydride (0-5˚C), diluents and perchloric acid catalyst into a mason jar. Hand stirs the reaction mixture for about 60 minutes. After that, use triethylamine to neutralize the catalyst, filter out the reaction mixture in a interred-glass funnel, and wash the fibrous cellulose triacetate with methanol, water and methanol in that order. Finally, transfers the cellulose triacetate to a dish and air-dried in the hood (Lewin and Pearce, 1985).

2.1.3.3 Hydrolysis

In order to prepare the secondary cellulose acetate with the degree of stubstitution (DS) of 2.4, the number of acetyl groups in each anhydroglucose unit (AGU), which are slightly less than 3.0 in the end of acetylation need to reduce to the desired degree of substitution (Europe, 2004). After completing the acetylation, the process is interrupted by adding water or dilutes acetic acid. Sufficient water must be added to decompose the excess acetic anhydride and to adjust the content of water in the solution to 5-10%. This is needed to make sure beside hydrolysis, no further decomposition of the molecular mass occurs. In the mean to split off the sulfuric acid bound completely, the speed of the hydrolysis depends upon the temperature, water and the amount of sulfuric acid. The reaction of hydrolysis is terminated at the desired DS by neutralizing the catalyst, preferable with sodium acetate or magnesium acetate. The proportion of free hydroxyl groups in the ester should be maintained as reproducibly precise as possible as it determines the properties and the end uses of the ester (Mark, 2004).