CHAPTER 2

BACKGROUND

2.1 Purification of Cellulose

Cotton has long been one of the most important source of cellulose for all uses. Its seed hair is not only used for textile but also for conversion into useful cellulose derivatives. There are two types of hair;-lint or stqple and linters which differ in their length. The first one has a length of over 2 cm. are used mainly in textile whereas the second one has an average length of 6-12 mm. for the first cut and of 2 mm. for the second cut. Linters are generally used for mattresses, upholstery and allied products, and especially for the preparation of pure cellulose as starting material for manufacture of various cellulose derivatives.

Several processes of purification of cellulose from natural sources have been known for over a hundred years. Among these, Watt and Burgess patented in 1853 about the pulping of wood by cooking wood under pressure with 25-27% sodium hydroxide at 160-180°C for 1-2 hours and in the presence of 2-4% sodium carbonate. According to such method known as "soda process", about 45-65% yield of pulp with high lignin content and poor bleachability is obtained (3). In 1866, Tilghman was granted a patent on his discovery concerning wood pulp known as "sulfite process" by treatment using calcium dihydrogen sulfite and sulfurdioxide and by cooking at 140°C for 8-10 hours. The sulfite process produces about 40-55 % yield of pulp containing 86% α-cellulose (3). In 1889, the soda process was modified by Dahl and was patented as "sulfate process" using sodium hydroxide, sodium carbonate and sodium monosulfide for wood cooking at 160-180°C for 3-4 hours. The product obtained is about 44-48 % yield of pulp containing 86% α-cellulose (3).

Among various commercial raw material for cellulose, the cotton-fiber contains the lowest percentage (4-12%) of noncellulosic material (4). This makes purification simpler than for most cellulosic materials. According to A.F. Martin, the sequences of step of purification of raw cotton-fiber is similar to that used in wood pulping (5). However, the exact condition employed are different because of the differences in the types and amounts of impurities which must be removed. The purification procedure is primarily designed to remove wax and coloring matter which are distributed on or in the fiber in order to destroy almost completely the contaminants which are physically dispersed in but separate from the linters (5). In general, the method of purification of cellulose consists of 2 main steps as follows:

(1) Digestion or cooking

(2) Bleaching

For digestion, the fiber are usually wetted with sodium hydroxide solution of 2-4% and heat under pressure to 135-170°C for 3 to 6 hours. Digestion factors such as time, temperature and concentration of alkali must be carefully considered and balanced to get the desired degree of cellulose purification. Under pressure treatment is necessarily carried out in the absence of air. Degradation of cellulose always occurs when it contacts with hot alkali. Severe digestion conditions are, thus, caused in loss of yield and loss of viscosity (5).

Bleaching is a process of whitening of the treated pulp or fiber. It is difficult to remove all noncellulosic material, especially from wood, by cooking without severe degradation of cellulose. The bleaching process is, therefore, applied to the treated pulp or fiber. According to R.S. Hatch, the whitening action of bleaching involves destruction of color contaminants (5). Time, temperature, pH and concentration of bleaching agent are the important factors in the bleaching operation as suggested by A.F. Martin (5). The active bleaching agent may be chlorine, hypochlorite, chlorine dioxide, peroxides, permanganate and other oxidizing agents.

For hypochlorite bleaching, it is usually conduct the process in such a way that minimize the oxidative degradation of cellulose. This is attained by bleaching at 30-35°C in alkali medium at a low fiber concentration in the solution and at a low consumption of chlorine (5). Under such mild conditions, degradation does, however, take place and produces a deterioration in the mechanical properties of cellulose. Therefore, special precuation must be taken in linter bleaching to prevent or to regulate cellulose degradation caused by oxidation.

In short, the degradation of cellulose can occur by not only conditions and techniques used in digestion but also in bleaching.

2.2 Quantitative Analysis of α-cellulose

In general, cellulose exists in three forms: α-, β- and γ- celluloses. The α-cellulose has the highest degree of polymerization. The β- and γ- forms have much lower degree of polymerization and are known as hemicellulose (6). In addition, the α-cellulose is a fraction resistant to mercerizing soda (17.5-18.5 % caustic soda solution) under controlled temperature, time and final dilution and washing conditions. The β -cellulose is a fraction represented shorter chain degradation products from the α -cellulose whereas the γ -cellulose may be derived from other constituents which are not strictly cellulose at all and it can be defined as water insoluble but alkali soluble polysaccharides that yield other hexose and pentose as well as glucose on hydrolysis (7,8). According to Kyle Ward, Jr., the α-cellulose refers to that portion of industrial cellulose pulps which is insoluble in cold sodium hydroxide of mercerizing strength (17.5 or 18%). The β -cellulose is soluble in such a solution but is precipitated on acidification, while the γ -cellulose remains in solution on acidification. The β - and γ -celluloses are not necessarily true celluloses in the sense that contain only polymers of anhydroglucose units (8).

As we know, the principal requirement for purified linters as source of cellulose for the preparation of cellulose derivatives is a high content of α -cellulose with almost complete removal of wax, coloring matter and other contaminants (5). Cellulose, from whatever sources derived, is frequently characterized by its α -cellulose content (7). In the production of the commercial important derivatives, the cellulosic raw material is usually one with high α -cellulose content as suggested by E.J. Lorand (9). It is, therefore, necessary to quantitatively determine the α -cellulose containing in the product obtained after purification.

In 1923, M.W. Bray and T.M. Andrews developed a method for determination of α -, β - and γ -celluloses (10). Such method has been improved as a standard method by ASTM (11). The α -cellulose content can be determined by either gravimetric or volumetric analysis. It is, however, found that the precision of the latter procedure is much greater than the former one (11). A number of errors are encountered in the gravimetric method which requires careful washing of α - and β -celluloses to completely free them from impurities and it is difficult for drying without decomposition as cited out by M.W. Bray and T.M. Andrews and by ASTM (10,11).

Since the volumetric analysis is considered to be more effective than the gravimetric one, only detail of the former will be described here. According to ASTM standard method, the practical procedures for volumetric analysis of α -cellulose are as follows (11):

(1) Weigh 0.3 ± 0.01 g. of the specimen in a 100 cm^3 beaker. Add 20 cm^3 of NaOH solution (17.5%), mercerate until the fibers are uniformly wet and dispersed, and let stand 10 min. from the time of addition of the NaOH solution. Then add about 33 cm^3 of water, stir the mixture thoroughly and let it stand 1 hr. After stirring once more, pour about 5 cm^3 of the unsettled mixture into a Gooch crucible. The crucible and ring are supported by a funnel fitted into the neck of a 100 cm^3

volumetric flask with a rubber stopperthrough which passes a glass tube for suction. Form a mat with gentle suction. Avoid excessive packing of the fibers, as this retards filtering. It may be necessary to refilter the first filtrate, but loss of small amounts of α -cellulose to the filtrate does not affect the results appreciably. Pour the remainder of the mixture on the mat and, before the last of the liquid has run through, wash the beaker and the mat with 35 cm^3 of water.

(2) Moisten the residue of α -cellulose with water and remove it from the crucible. Place the crucible up right in a 400 cm^3 beaker, fill it with 72% H_2SO_4 at room temperature, and rinse it after a few minutes with 50 cm^3 more of the acid. Disintegrate the α -cellulose pad in the acid, using a stirring rod. Add to the α -cellulose solution, with a pipet, 25 cm^3 of the $K_2Cr_2O_7$ solution, and heat at 140 to 150°C for 10 min.

(3) After the solution has cooled to 130°C, add 50 cm^3 of water, rinse the thermometer, etc, and cool the solution to 60°C or lower. Titrate the remaining $K_2Cr_2O_7$ with the ferrous ammonium sulfate solution.

(4) Pipet exactly half of the filtrate from the α -cellulose, after all fibers present have settled, into a 400 cm^3 beaker containing 5.0 cm^3 of $K_2Cr_2O_7$ solution.

Cautiously, while stirring constantly, pour 50 cm^3 of concentrated H_2SO_4 down to the side of the beaker containing the portion of the filtrate for analysis, then heat and titrate as describe previously for the α -cellulose solution.

(5) Calculate the percentage of α -cellulose from eqs. (1), (2) and (3)

$$A = 25\,(v_1 - r) \tag{1}$$

$$B = 2 \cdot (5 - v_2\, r) \tag{2}$$

$$\alpha\text{- cellulose, } \% = (A/(A+B))\ 100 \tag{3}$$

where:

A = volume of $K_2Cr_2O_7$ solution required to oxidize the α -cellulose.

B = volume of $K_2Cr_2O_7$ solution required to oxidize the filtrate

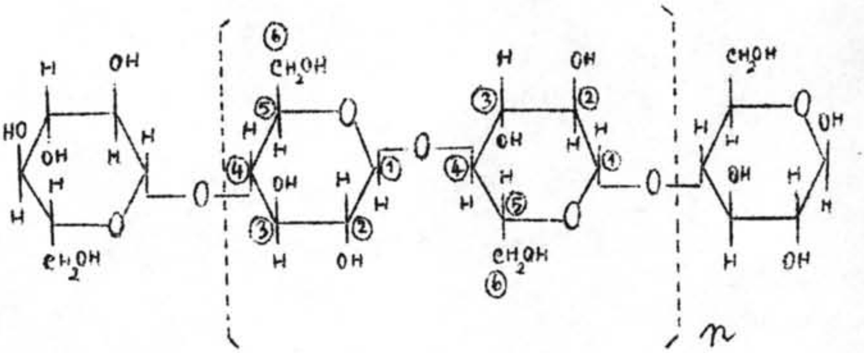
v_1 and v_2 = volume of ferrous ammonium sulfate solution required for titration of the $K_2Cr_2O_7$ remaining after oxidation of the α -cellulose and filtrate, respectively.

r = volume of $K_2Cr_2O_7$ solution equivalent to 1 cm^3 of ferrous ammonium sulfate solution (determined by titrating 5 cm^3 of $K_2Cr_2O_7$ solution in 100 cm^3 of dilute H_2SO_4)

2.3 Preparation of Sodium Carboxymethylcellulose (Na-CMC)

2.3.1 Etherification reaction of cellulose

Cellulose (I) is a natural high polymer consisting of 1,4-anhydro-β-glucose unit joined by oxygen linkage to form long and essentially linear molecular chains (6).



(I)

Structure of Cellulose (n=25-250)

There are three hydroxyl groups in each glucose unit at 2-, 3- and 6-positions. Theoretically, the chemical transformation by substitution on cellulose can occur at such positions (12). Thus, a compound with all of hydroxyl groups being substituted is said to have maximum substitution. In other words, it is possible to obtain substitution up to triesters or triethers (13). That is, a compound with all of hydroxyl groups being substituted is one with degree of subtitution (D.S.)=3.0 where the degree of substitution is conventionally designed by the average number of hydroxyl units replaced per anhydroglucose unit (14). One achievement of substitution of cellulose to its derivative involved a chemical reaction called "Etherification". Cellulose alone does not, however, react with etherifying agent (5). It must be treated with alkali to form alkali cellulose which is so far believed to be an intermediate in etherification. According to A.B. Savage, A.E. Young and R.T. Massberg, a certain etherification of alkali cellulose in which either chloroacetic acid or sodium chloroacetate used as etherifying agent is called carboxymethylation and the product is sodium carboxymethylcellulose (5). In addition, various hydroxyl groups in glucose unit of cellulose chain have different reactivities with respect to alkali (14). As pointed out by Timell and Rydholm, the substitution in cellulose chain can be first takenplace at the 6th position for its D.S. approximately up to 0.15 and the secondary hydroxyls at 2nd and 3rd positions begin to participate in reaction (15, 16, 17).

In general, carboxymethylation of cellulose is expressed by the following equation as suggested by Matao Nakamura and Koichiro Watanabe (18).

$$\text{R Cell (OH)}_3 + x\ \text{ClCH}_2\text{COONa} + x\ \text{NaOH} \rightleftharpoons \text{R Cell (OH)}_{3-x}(\text{OCH}_2\text{COONa})_x + x\ \text{NaCl} + x\ \text{H}_2\text{O} \qquad (1)$$

where x = degree of substitution

Apart from the main reaction of carboxymethylation, the sodium chloroacetate is hydrolysed to sodium glycolate

$ClCH_2\,COONa + NaOH \rightleftharpoons HOCH_2COONa + NaCl \qquad (2)$

this side reaction is induced by enhancing reaction variables which is hence adversely influence the rate of the main reaction of etherification of cellulose.

The D.S. and solubility of the product depend upon the reaction conditions used. Yehia Fahmy and Olfat Mansour found that the products with minimum D.S. of about 0.4 are water soluble and ones with D.S. lower than 0.4 are almost dilute-alkali soluble (19). From other references, Na-CMC with D.S. = 0.05-0.25 is soluble only in aqueous NaOH and ones with D.S. = 0.65-0.85 are good water soluble (5, 20). Furthermore, the higher of D.S. leads to more improvement of water solubility of the product (20).

The product with D.S. = 0.65-0.85 are found to be most application in the U.S. and ones with D.S. = 0.4-1.4 are commercially available (20). However, the product with D.S. higher than commercial grade is of interest for other specificial fields of research, especially in polymerization of new synthetic high polymers. Therefore, the attempt for preparing Na-CMC with D.S. leading to its theoretical maximum value

(D.S. = 3.0) is one of the most active field of research.

The possibilities of increasing D.S. of Na-CMC have been studied by various research groups. In 1939, E.J. Lorand published a method of preparation of cellulose ethers and he cited out about the function of alkali in cellulose (9). According to his publication, the production of highly substituted ethers is able to obtain with respect to the influence induced by the etherifying agent-cellulose ratio. Theoretically, the extent of etherification is determined by the reaction variables-reaction temperature and the relative proportions of cellulose, alkali, etherifying agent and water in the reaction mixture (14). In 1950, R.R. McLauglin and T.H.E. Herbst studied the influence of reaction variables on the D.S. and they found that the efficiency of carboxymethylation could be improved by lowering reaction temperature, decreasing excess sodium hydroxide and by increasing time (21). In 1958, Eiji Hayakawa and Yazaeman Marita tried to prepare Na-CMC by using water miscible or water immiscible organic solvent as reaction media in order to increase D.S. of the product (22). In 1965, Koichiro Watanabe and Matao Nakamura introduced a technique for preparation Na-CMC with D.S. higher than 1.0 by using multistep of etherification (23). According to their report, they obtained products with D.S. = 1.4 by two steps of etherification and with D.S. = 1.74 by three steps of etherification. In 1966, Yehia Fahmy and Olfat Mansour reported that the addition of inert solvent into reacting solution eliminated dough formation and increased the D.S. of the product (24).

Although none of those results produces the product with D.S. closed to its theoretical maximum value, the technique of increasing D.S. must be encountered the physical parameters involved in the system as well as nature of the reaction medium used.

In short, D.S. of product can be increased if the influence of reaction variables on the D.S. is in the state of optimization.

2.3.2 Determination of degree of substitution of sodium carboxymethylcellulose

In ASTM, there are two methods known as "acid wash" and "nonaqueous titration" for determining D.S. of Na-CMC (25). The first method involves the conversion of water soluble Na-CMC to insoluble acid form. After purification by washing, drying, a known weighed sample is reconverted to the sodium salt with a measured excess of sodium hydroxide. The D.S. can then be calculated. This method is, however, good for crude and purified grades of Na-CMC with D.S. up to 0.85 whereas D.S. above 0.85 may obtain **slightly** low results with estimated precision of ±.03 of degree of etherification units. The second method involves a measurement based upon a nonaqueous acid base titration. The sample is refluxed with glacial acetic acid, and the resulting sodium acetate is titrated with a standard solution of perchloric acid in dioxane, to a potentiometric end point. Impurities containing alkaline sodium will also be titrated under these condition without interference of sodium chloride. This method is good for purified grades of Na-CMC of all D.S.'s. It is not appreciable to the crude grades. According to statistical analysis, test results indicate the precision of this method listed below

Approximate D.S.	Precision (95% Confidence level)
0.40	± 0.010
0.80	± 0.012
1.35	± 0.038

The other simple, convenient, and more practical method was introduced by Matao Nakamura and Koichiro Watanabe in internal report of Nakamura's Laboratory, Institute of Industrial Science, the University of Tokyo, Tokyo, Japan. This method requires common chemicals and simplified techniques with reliable result and it is also good for either crude or purified grades of Na-CMC with various D.S..

The D.S. of Na-CMC can be determined by 2 steps as follows:

a) Determination of moisture content

In order to obtain the exact weight of an etherification product used for calculating its D.S., the moisture content must be first determined. The Na-CMC sample of known weight is simply vacuum dried in a temperature controlled incubator. After a certain period, weigh the sample and then find weight loss on drying of the sample. The moisture content can thus be calculated by using the following equation:

$$\text{percentage of moisture} = \left(\frac{A}{B}\right) \times 100 \qquad (1)$$

where A = mass loss on drying

B = grams of sample used.

b) Determination of degree of substitution

In etherification of cellulose, the chemical reaction may be expressed in the following equation as suggested by Matao Nakamura and Koichiro Watanabe (17).

$$\text{R Cell (OH)}_3 + x\ \text{ClCH}_2\text{COONa} + x\ \text{NaOH} \rightleftharpoons \text{R Cell (OH)}_{3-x}(\text{OCH}_2\text{COONa})_x + x\ \text{NaCl} + x\ \text{H}_2\text{O}$$

where x = degree of substitution

The quantity of sodium presented in the etherification product can be calculated as follows:

$$\% \text{ Na} = \frac{(23x) \cdot 100}{162 + 80x}$$

$$\text{Then } x = \frac{162 \; (\%\text{Na})}{2300 - 80(\%\text{Na})} \qquad (2)$$

where

RCell(OH)_3 is taken as the formula of the anhydroglucose unit $(C_6H_7O_2(OH)_3)$. Its formula weight is 162.

x is degree of substitution (D.S.) which is the average number of hydroxyl group substituted per anhydroglucose unit.

$\text{R Cell (OH)}_{3-x}(\text{OCH}_2\text{COONa})_x$ is the etherification product having molecular weight 162 + 80x