

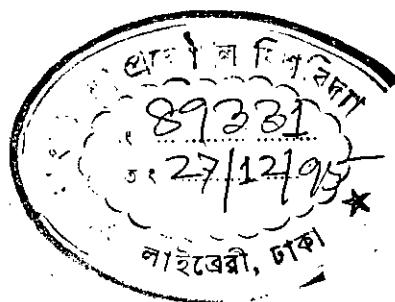
OPTIMIZATION OF THE PROCESS  
PARAMETERS FOR THE PRODUCTION OF  
SODIUM CARBOXYMETHYL CELLULOSE  
(SCMC)

A Thesis

Submitted to the Department of Chemical Engineering in partial  
fulfillment of the requirements for the degree of Master of  
Science in Engineering (Chemical).

By

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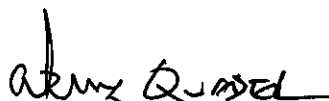


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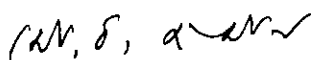
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## ABSTRACT

The present work deals with the study of the process parameters such as alkali concentration for steeping, reaction time, maturing time and reaction temperature for the preparation of sodium carboxymethyl cellulose (SCMC) for obtaining the optimum conditions for commercial application.

Experiments were carried out both in aqueous and ethanolic media. On the basis of the experiments carried out using glass wares, a stainless steel stirred cylindrical reactor was used to study the process using a cellulose mass of 50 gm in each batch.

Alkalization or steeping was carried out at different alkali concentrations and the suitable concentration to obtain stoichiometric amount of consumption of alkali was found to be 18%. Temperature in the range 25-30°C and reaction time for 2 hours were found to be optimum for steeping operation. Maturing time after steeping was established at 12-16 hours. The most suitable conditions for carboxymethylation were : reaction temperature = 40 to 45°C; reaction time = 8 hours; and maturing time = 18 to 20 hours.

Optimization of the use of reactants was obtained by recycling the reactants and alcohol. The use of make-up reactants decreased with the increase of the number of batches in a cycle.

Alcohol recovery was also improved to 87%.

Not all SCMCs produced were soluble in water. Degree of Substitution (DS) varied in the range of 0.69-0.99. Viscosities of 1% and 2% solutions were in the ranges of 7.16-262 centipoise and 35.0 - 2110 centipoise respectively. Water solubility, DS values and solution viscosities of the products indicate that the SCMCs obtained were of commercial quality.

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## CHAPTER - ONE

### INTRODUCTION



Production of commercial grade Sodium Carboxymethyl Cellulose (SCMC) is important for its wide range of applications in Bangladesh specially in textile and pharmaceutical sectors. The properties and effectiveness of SCMC depend on the production processes and the process parameters. The parameters include: alkali concentration for preparing alkali-cellulose, carboxymethylation residence time, maturing time and temperature. Economics of SCMC production depends on the recovery of excess reactants and the recovery of reaction media when it is other than water.

This experimental work examined the following for the preparation of SCMC in the context of commercial production on small scale :

- i) conditions for alkali-cellulose and carboxymethylation reactions;
- ii) recycling of reactants for achieving their consumption to stoichiometric levels; and
- iii) recovery of reaction media, i.e. alcohol.

Experiments were carried out using batch process as well as recycle schemes. Batch processes provided information related to alkali concentration for alkalization, Na-MCA concentration for

carboxymethylation, reaction temperature, reaction time, and maturing time for recycle experiments.

Recycling of reactants indicate that consumption of reactants approaches stoichiometric level.

SCMC products showed values of DS in the range 0.692-0.99, while 1% solution viscosities were in the range 7.16-262 cp. These meet the requirements of commercial grade SCMC.

## CHAPTER - TWO

### LITERATURE REVIEW

#### 2.1 HISTORICAL BACKGROUND

Sodium carboxymethyl cellulose (SCMC) or cellulose gum, formerly called sodium cellulose glycolate, is an anionic cellulose ether. It may be manufactured by the reaction of alkali cellulose with sodium monochloroacetate.

Production of sodium carboxymethyl cellulose (SCMC) was originally developed by Jansen [41] in Germany during World War I. Its widespread use as a detergent promoter started only during World War II. Commercial production of SCMC in the United States began in 1943. A wide range of applications and uses has resulted in a spectacular growth in production from the year 1947 onward. A sudden increase in any one of its potential areas of application such as laundry starch replacement, soil conditioner, textile sizing, paper coating, latex paint stabilizer or pharmaceutical would certainly stretch the production capacity to its limits. Relative costs of SCMC and equivalent products appear to be the reason for its selective use. The greater effectiveness of SCMC is still not attractive enough to cause its widespread use because of its higher price.

## 2.2 PROPERTIES OF SCMC

Sodium carboxymethyl cellulose is a white powder when dry. It browns upon heating to 180°-225°C and chars upon heating to 210° - 250°C. The polyelectrolyte structure of SCMC influences viscosity and stability in solution. Maximum viscosity and best stability occur in the pH range 7-9, Figure 2.2.1. At  $\text{pH} \leq 4$ , formation of the less soluble free acid form results in significant increases in viscosity and eventually insolubility at  $\text{pH} \leq 2$ . At  $\text{pH} > 10$ , a slight decrease in viscosity occurs. The viscosity of SCMC solutions is dependent on temperature, decreasing as the temperature increases. Under normal conditions, the effect is reversible. The viscosity can also be controlled by choice of equipment, solvent or polymer composition. Bulk

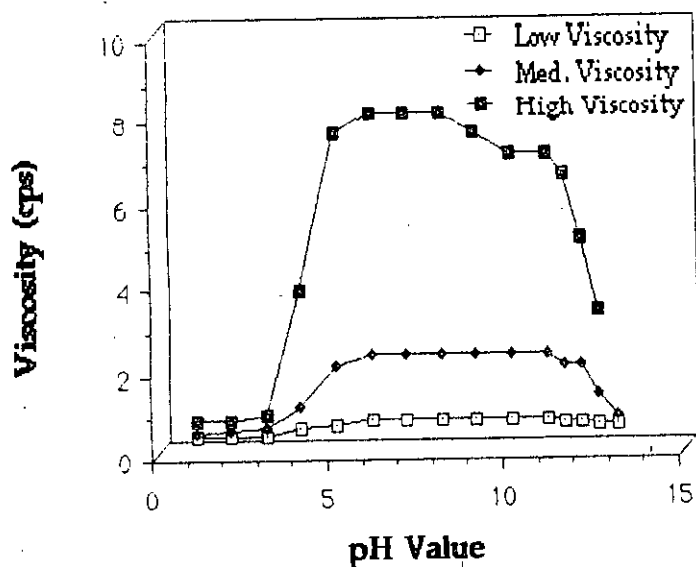


Figure 2.2.1. Carboxymethyl cellulose: variation of solution viscosity with pH (Brown & Houghton). Viscosities in 1% solution in water at 25 degrees Celsius.

densities of SCMC ranges from 0.4-0.8 g/ml. It is odorless and tasteless. It is soluble in hot and cold water.

Various degrees of etherification for SCMC have been commercialized. SCMC is available in purified, technical and semirefined grades as well as the free acid form. Cellulose ethers contain substituent groups that differ greatly in molecular weight. The Degree of Substitution (DS) defines the number of substituted ring sites. It is a very useful property of SCMC. There are three hydroxyl groups on each anhydroglucose ring of the cellulose polymer that are available for reaction. So, the maximum value of DS may be 3.0. The commercial products have a Degree of Substitution (DS) ranging from 0.38 to 1.4, the most widely available products have a DS in the range 0.65 to 0.85. Solubility of SCMC in water is greatly dependent on its DS. Cellulose retains its fiber structure and does not go into solution when the DS is below 0.4. Solubility increases with the increase in DS value.

SCMC is highly moisture absorbent and may gain its own weight of water at high humidity. The rheological properties of SCMC solutions depend upon concentration, rate of shear and uniformity of substitution. At very low shear rates, solutions approach Newtonian flow. Solutions of medium and high viscosity types with a DS of 0.9-1.2 and other special substitutions show time-independent, shear thinning pseudoplasticity. The medium and high viscosity types with a DS of 0.4-0.7 generally exhibit time-

dependent shear thinning thixotropy. Figure 2.2.2 shows the relation of solution viscosity to concentration for SCMC. SCMC is a weak acid ( $K_{\text{ionization}} = 3 \times 10^{-5}$ ). It can react with metal ions such as the alkaline earth elements and heavy metal ions to

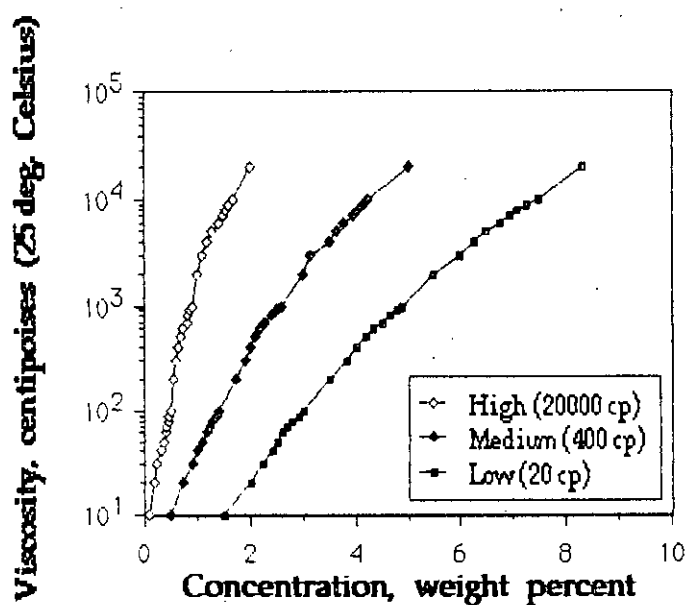


Figure 2.2.2: Sodium carboxymethyl cellulose: viscosity-concentration chart (Hercules Powder Co.). Viscosities in 2% solution in water at 25°C are shown in parentheses on the curves.



form precipitates. This characteristic can be modified by hydroxyethyl substitution on the SCMC structure. This mixed cellulose ether retains some of the useful properties such as the solubility while gaining lower sensitivity to precipitation by salt solutions and acids. Since SCMC is a polyelectrolyte, metathesis reactions with other cations can occur. Monovalent cations form soluble salts, divalent cations are borderline depending upon the grade of SCMC and the mixing technique used and the trivalent cations form insoluble precipitates.

Table 2.2.1 lists the properties and characteristics of SCMC commonly encountered [33].

Table 2.2.1 : Typical Properties of Sodium Carboxymethyl Cellulose

Property	Value
Polymer as shipped	
Sodium carboxymethyl cellulose, dry basis, %	99.50
Moisture content, maximum %	8.00
Browning temperature, °C	227.00
Charring temperature, °C	252.00
Bulk density, g/mL	0.75
Biological oxygen demand	
0.7 DS, high viscosity, ppm	11,000
0.7 DS, low viscosity, ppm	17,300
Solutions	
Sp gr, 2% soln, 25°C	1.0068
Refractive index, 2% soln, 25°C	1.3355
pH, 2% soln	7.00
Surface tension, 1% soln. mN/m (=dyn/cm) at 25°C	71.00
Bulking value in soln, cm <sup>3</sup> /gm	0.544
Films	
Sp gr, g/mL	1.59
Refractive index	1.515

## 2.3 USES OF SCMC

Sodium carboxymethyl cellulose (SCMC) has a variety of industrial uses. Being a partially carboxylated derivative it is used mainly for surface treatment of papers because of good film forming and other useful properties. Apparently, the lower DS products are preferred for the wet end. The factors determining the efficiency of SCMC and the deflocculating activity may be reversed in the presence of alum, particularly at low pH. The use of SCMC at the wet end is valuable for the purpose of accelerating the beating process. It was found that the addition of 3 percent SCMC showed a reduction of beating time by 40 to 50 percent.

SCMC is used in toweling and other high wet-strength grades where it makes the system negatively charged, resulting in improved resin retention and thus leading to increased dry and wet strength. For this purpose, a 2 percent of SCMC solution with a viscosity of 100 cp or more is satisfactory.

SCMC is physiologically inert and is employed as a protective coating for textiles and paper. It is also used as a sizing material. It is used as a stabilizer for icecream and other emulsions and as an additive to impart strength to sausage casings and other films. SCMC functions as an antiredeposition agent to inhibit resoiling of fabrics by the soil removed during laundering. SCMC of low DS is used in washing thereby giving them a negative charge and preventing soil particles from

redepositing. It is very effective in washing of cotton clothing.

The textile industry uses it for thickening dyestuff printing pastes and for warp-sizing formulations to improve weaving efficiency. Material of higher DS values is used as a water soluble thickener and dispersant.

The purified SCMC products are used in many types of food and pharmaceutical products where thickening, rheology control, emulsion stabilization and water-loss control are desired. SCMC is not metabolized and can be used in low-caloric food products.

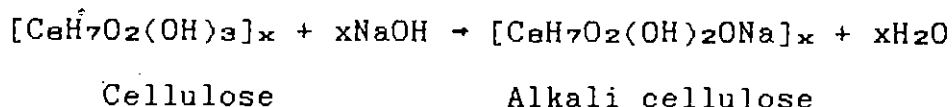
Control of water loss to soil formation is important in drilling fluids. They are used in the drilling industry to prevent reduction in oil flow from the formation and to inhibit swelling of certain types of clay which reduces the diameter of the drill hole.

Other potential uses include cosmetics, in adhesives such as wallpaper paste and as a suspending agent and binder in ceramics and enamels.

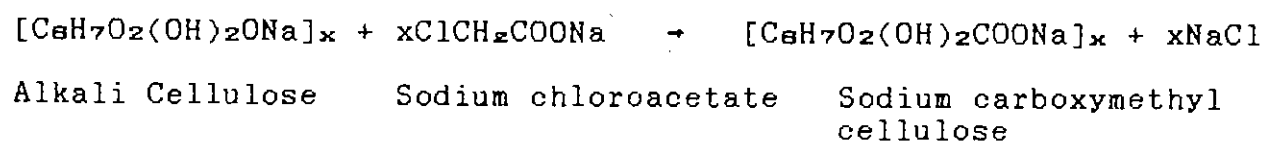
## 2.4 CHEMICAL REACTIONS FOR THE PREPARATION OF SCMC

SCMC may be prepared by treating alkali cellulose directly with sodium chloroacetate. The actual production may involve a number of separate steps consisting of preparation of alkali cellulose and sodium chloroacetate followed by the final reaction step.

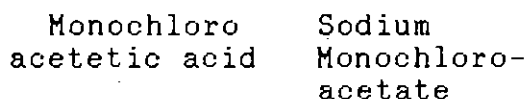
Alkali cellulose is obtained at first by reacting cellulose with sodium hydroxide. The reaction involved is :



This alkali cellulose is then treated with sodium chloroacetate to obtain sodium carboxymethyl cellulose (SCMC). Reaction involved is :



The sodium chloroacetate is added either as an aqueous solution or as free monochloroacetic acid. When the free acid is used, sufficient additional NaOH must be added to neutralize it. Here sodium monochloroacetate is formed by the reaction of monochloroacetic acid with sodium hydroxide and it is given below:



During these reactions, a side reaction occurs simultaneously. Sodium chloroacetate is converted to sodium glycolate by reacting with sodium hydroxide.



Like the preparation of other cellulose ethers, at higher concentration of sodium hydroxide the DS is increased and the extent of side reactions is decreased. The cellulose retains its fiber structure unless the dS exceeds 0.4 when a dough is obtained. Viscosity reduction can be achieved by oxidation with air and by use of chemical oxidants. Sufficient liquid media must be present to ensure adequate swelling so that the etherification is uniform. Water or an inert organic liquid may be used as a media as required.

If an alcohol is used as a medium, a side reaction takes place between alcohol and sodium hydroxide producing sodium alcoholate. The reaction is written as :



Formation of sodium alcoholate leads to consumption of alkali and alcohol resulting in the increase of production cost and decrease in the purity of commercial grade products.

## 2.5 STANDARDS AND SPECIFICATIONS

Specifications for SCMC/CMC are listed in Food Chemicals Codex II, the USP XIX and in publications of the FAO/WHO [33]. The European Economic Community (EEC) product number of SCMC is E 461 and the specification reference is FAS/IV/19. SCMC is also classified with substances that are "generally recognized as safe" (GRAS) under title 21, part 182.1745 of the code of Federal Regulations [33].

Technical grade product contains NaCl and sodium glycolate and purity ranges from 36.5 to 62 percent by weight. Purified (cellulose gum) product has a purity of 99%. Commercial grades have DS in the range of 0.3 to 1.2 (theoretically a completely substituted product would have a DS of 3.0). Commonly available products have a DS of 0.7 (actually 0.65-0.85). Typical viscosities for these grades are :

<u>Grade</u>	<u>Solution conc., wt%</u>	<u>Solution viscosity, cp at 25°C</u>
Low viscosity	2	25 - 50
Medium viscosity	2	300 - 600
High viscosity	1	1,300-2,200

SCMC is soluble in hot and cold water producing a viscous solutions at 1 to 6% concentrations. Its solubility increases with the increase of DS. It is odorless and tasteless. It is available in fibrous or granular powder form.

## 2.6 TEST METHODS

Procedures for the analysis of SCMC are described in ASTM Monograph D1439-65 [5]. Further information is available from the publications of its manufacturers, e.g. Hercules, Inc. which includes assays in formulations [33]. Additional tests are listed in USP XIX and in the US Food Chemicals Codex II. The test procedures appear in the following order :

- a. Moisture
- b. Degree of Etherification/Degree of Substitution
  - Method A-Acid Wash
  - Method B-Nonaqueous Titration
- c. Viscosity
- d. Purity
- e. Sodium Glycolate
- f. Sodium Chloride
- g. Density.

## 2.7 REACTION PARAMETERS

SCMC may be prepared either in alcoholic media or in aqueous media. Alcoholic media requires the recovery of alcohol with minimum loss. Enough solvent/medium (water or alcohol) must be present to ensure first wetting followed by adequate swelling so that the etherification is uniform. The sodium chloroacetate or free monochloroacetic acid is then added. If the acid is used, sufficient additional sodium hydroxide must be present in the alkali cellulose to neutralize it. While adding sodium chloroacetate or free monochloroacetic acid, the medium may be water or an alcohol consistent with the preparation of alkali cellulose. At higher sodium hydroxide concentrations as in the preparation of other cellulose ethers, the degree of substitution (DS) is increased and the extent of side reactions is minimized. The DS and the extent of reaction depend also on the residence time, maturing time and the reaction temperature. The reaction temperature may be kept at room temperature or it may be conducted at higher temperature such as 40-50°C or higher. So, the reaction parameters include : alkali concentration for preparing alkali cellulose, residence time, maturing time and reaction temperature.

Following the report of Majid and Ismat [41], it appears that DS of SCMC slowly rises from 0.54 to a maximum of 0.7 for the change of alkali concentration from 15% to 20%. After this, the DS decreases with the increase in alkali concentration,



Figure 2.7.1.

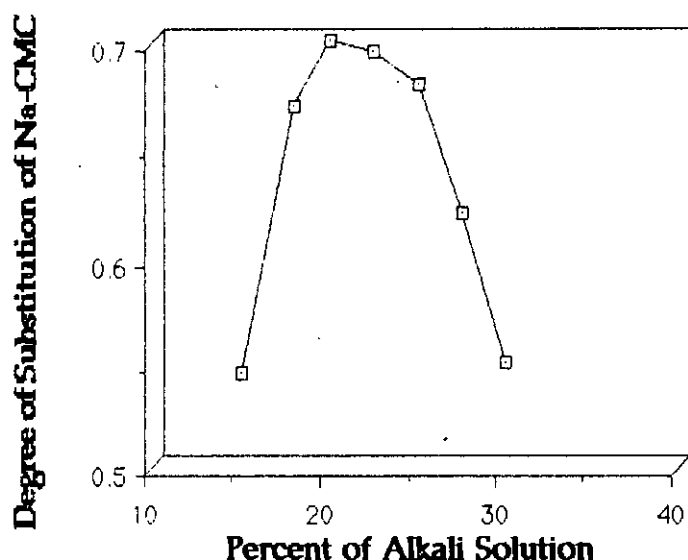


Figure 2.7.1. Variation of degree of substitution of Na-CMC with strength of alkali solution.

The reaction conditions for this observation were as follows :

- Steeping of rayon waste in aqueous ethanolic solution (1:1, v/v) for 2 hours at 28-30°.
- treatment with 80% MCA for 5 hours at 50°C.

The same author treated rayon waste with 20% aqueous alcoholic NaOH (1:1) for 2 hours. Then the alkali cellulose was carboxymethylated with 80% MCA for 5 hours. The reaction

temperature was varied to show the effect on the DS of SCMC, Figure 2.7.2.

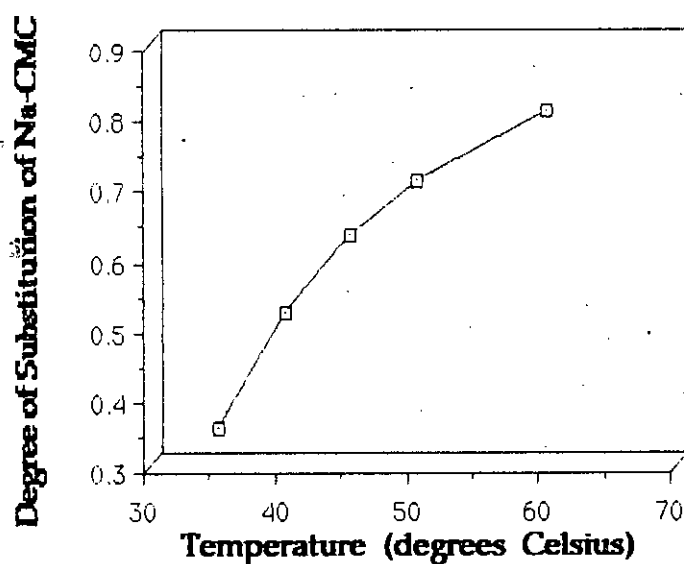


Figure 2.7.2. Variation of degree of substitution of Na-CMC with the temperature of reaction

It was observed that initially the DS increased sharply with the increase in temperature. After 55°C, the slope of the curve declined with upward trend.

To show the reaction time effect on SCMC, the alkali concentration, steeping time, reaction temperature were kept constant and the carboxymethylation time was varied [41]. The

effect was shown graphically. The observation was that it was not worthwhile to continue the reaction beyond 5 hours, Figure 2.7.3.

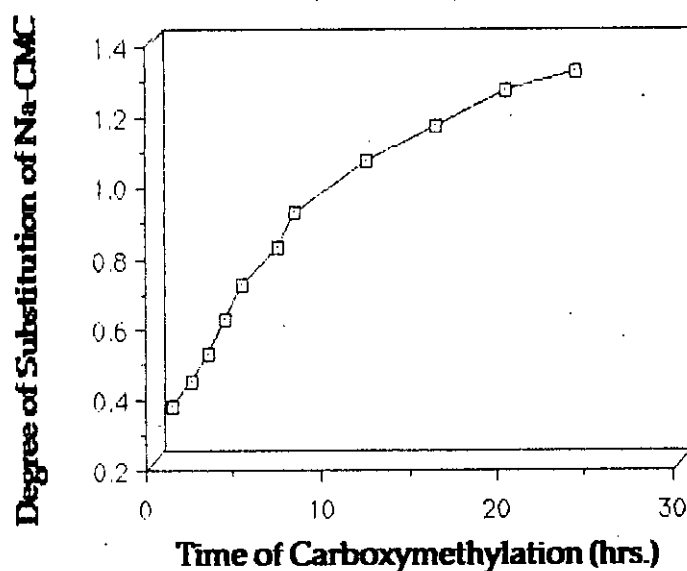


Figure 2.7.3. Variation of degree of substitution of Na-CMC with the time of reaction.

There is another factor which affects the quality and has influence on the production process. This involves the nature of the starting material. Different types of cellulose can be used for the production of SCMC. The same process parameters or the same process treatment cannot be used for all the celluloses. The product quality is also raw material dependent. Water content of various initial materials is to be controlled. Generally, the allowable moisture content of cellulose is about 5% by weight.

## 2.8 PRODUCTION METHODS

The basic principle for the preparation of sodium carboxymethyl cellulose (SCMC) is to treat alkali cellulose with sodium chloroacetate. Alkali cellulose is first prepared by reacting cellulose with a caustic soda solution. Then this alkali cellulose is treated with either free monochloroacetic acid or sodium chloroacetate.

Enough water or an inert organic liquid such as ethanol or propanol may be used to ensure first wetting followed by adequate swelling which is necessary for uniform etherification.

The alkali cellulose may be prepared batchwise by methods such as steeping and shredder mixing. Processes for continuous production of alkali cellulose are also used.

If free monochloroacetic acid is used, enough additional sodium hydroxide must be added to neutralize the acid. This sodium hydroxide neutralizes the free acid by producing sodium chloroacetate. Reactions have been carried out in sigma-bladed shredders. An alternative method of preparation is the slurry process in which the product is obtained as a slurry. It is neutralized at the end and by-product salts are removed by washing with 70-80% methanol if a higher purity product is desired.

In one process it is prepared by spraying powdered cellulose first with a caustic soda solution and then with chloroacetic

acid. Manufacturers often produce SCMC by a batch process in which alkali cellulose "crumbs" are reacted with dry sodium chloroacetate in a kneader. Another manufacturing method employing a continuous process uses cotton linters in continuous sheet form which is treated with the necessary reactants. The final SCMC sheet is ground to have a powdered product.

Most of the equipment used in CMC production use Type 316 stainless steel as materials of construction [19]. The dilution tank for chloroacetic acid is made of Hastelloy C.

## 2.9 DIFFICULTIES IN THE COMMERCIAL PRODUCTION OF SCMC

Several factors are to be considered. The production of SCMC has to be cost effective. At the same time, the product has to meet the purposes for which it is to be used. All the qualities and grades of product are not required for all the applications and uses.

SCMC can be produced either in aqueous media or an inert organic solvent such as ethanol or propanol is used as a diluent. When alcohol is used as the reaction media, the cost of the SCMC is largely dependent on the recovery of alcohol. In this case, the loss of the alcohol has to be minimum. Since solubility of SCMC in water is very high, in order to avoid the loss of

product, it is washed with additional alcohol. This alcohol is to be recovered with the least possible loss. Use of propanol or higher alcohols lead to higher substitution [41].

Another factor that affects the quality as well as the cost of SCMC is the concentration of alkali solution in the reaction media. It was shown that as the alkali concentration increases, DS of SCMC increases leading to the increase in the water solubility of the product [41]. It has been proved by different workers that if the stoichiometrically required amount of alkali is used, the effectiveness of the reaction is not good. So, excess alkali concentration is used. This excess alkali would require excess amount of monochloroacetic acid and the neutralization requirement would increase the cost of production. That is why in the production process, the excess alkali is to be discarded or removed at the end of the alkalization of the cellulose. This can be done by simple decantation or by centrifugation and it makes the process more complicated. But the recovery of the excess alkali makes the process more cost effective.

The solubility of SCMC is a major factor to characterize the commercial product. The solubility is dependent on the DS of the product. It depends on the reaction temperature. The DS of commercial SCMC varies in the range of 0.68-0.85. To select and maintain appropriate reaction temperature is sometimes difficult.

The reaction temperature range may be 25-100°C. The temperature at which the reaction is to be carried out is chosen on the basis of the end uses of SCMC.

The effectiveness of the reaction and the product quality are often dependent on the starting cellulosic material. The water content of the starting material is also to be maintained at a certain level. Correct selection of the raw material is a prerequisite for producing the desired quality product to meet specific end uses at a minimum cost.

Time is another important criteriaon which affects the quality of the product. Residence time for reaction and maturing time (aging) are to be carefully determined. Otherwise, the product quality such as DS, DP, viscosity, solubility may vary widely from the desired specification.

## 2.10 RECENT DEVELOPMENTS IN THE PRODUCTION OF SCMC

Askahi [3] prepared SCMC with excellent liquid absorbability by controlled carboxymethylation of cellulose. This SCMC [9004-32-4] absorbed 20 times its weight of H<sub>2</sub>O at 37°C.

Pavlov and Petkov [51] produced SCMC with beechwood cellulose as cellulose source. The cellulose was first treated

with chloroacetic acid for 30 minutes. The acid-treated material was then treated for 90 minutes with aqueous NaOH which led to simultaneous swelling and carboxymethylation. The maximum DS of the SCMC was attained at 30-40% moisture in the initial cellulose.

SCMC was prepared by Isserils and Gorodnov [25] by mercerization of cellulose with aqueous NaOH. After removing excess alkali, O-alkylated cellulose was treated with Na-MCA in the presence of a modifying additive. Consumption of MCA was reduced and water solubility of SCMC was increased by using  $\text{Na}_2\text{SO}_3$ .

Toshihiko and Haruo [69] prepared SCMC by acid hydrolysis of wood pulp. The product had DS in the range 0.2 to 1.0 and apparent density 400-800 g/l. It was found to be a soluble additive for tablets. Preparation of this CMC involved these steps :

- 2200 ml water was absorbed by 1650g wood pulp, the pulp was degraded.
- 1% HCl solution was added to it and the slurry was heated for 30 minutes at 90-95° and then the HCl solution was removed.
- To this pulp 10 litre of water was added following by NaOH.



- The material was then dehydrated.
- The hydrolyzed pulp was then treated with 300g Na-MCA and 140g NaOH. The reaction product was treated with dilute  $\text{H}_2\text{SO}_4$ , washed, dried and pulverized.

One method of CMC production consists of these steps [26] :

- Mercerization of cellulose
- Carboxymethylation
- ripening
- drying
- grinding.

Purity of CMC and its particle size distribution are improved by carrying out carboxymethylation in the presence of an aqueous solution of 0.1-0.5% Na-alkylbenzene sulfonate and 0.001-0.005% aqueous solution of Co-salt.

Isserils et al [27] statistically evaluated the temperature, aqueous NaOH concentration and pressing ratio in 2-step mercerization of cellulose. The analysis gave regression equations for optimization of the dp and DS of SCMC. A maximum DS obtained was 0.868. The temperatures in both steps were 40°C, aqueous NaOH concentration in the 1st and 2nd step 261.1 and 135 g/l respectively. The pressing ratio was 3.5 in the 1st step. A maximum dp of 684 was attained at following conditions: temperature 50.3°C at 1st step and 22.7°C at 2nd step, NaOH

concentration 350 g/l and 1980 g/l respectively and pressing ratio in the 1st step 2.5.

Chen [15] prepared CMC from cellulose, NaOH and chloroacetic acid. The Na content in CMC was controlled by adjusting the amounts of NaOH and MCA. The reaction time was 2-4 hours.

Pelzer [52] prepared cellulose ether with low, uniform viscosity and good storage stability by preparing alkali cellulose in the presence of aqueous NaClO<sub>2</sub> and etherifying it. In this method, 37% NaOH was used and etherification temperature was < 100°C. A 1.8% aqueous solution of the formed product had viscosity of 25 mpa-s.

SCMC with good distribution of DS and transmittance was prepared by Sasaki et al [62]. In this method, linter pulp was kneaded with a propanol-water mixture and NaOH at 25°C for 90 minutes. This material was heated with a propanol-water mixture and MCA neutralized with 50% NaOH solution at 30-70°C was used. The reaction product (SCMC) exhibited DS 0.67, viscosity 8800 pa-s and transparency at 470 nm for 1% aqueous solution.

One method of SCMC preparation involved [2] the causticizing of cellulose with aqueous NaOH in the presence of ethanol. MCA was added to this to complete the carboxymethylation. The temperature was kept first at < 35°C and then it was raised to

70°C. The purified product showed clear 1% solution which had a viscosity of 4000-10,000 mpa-s.

Pribadi and Tulus [54] showed that the use of ethanol in alkalization prior to carboxymethylation rendered the cellulose less active. Ethanol causes a decrease of DS and purity in spite of the improved homogeneity of the Na-cellulose. The temperature of both alkalization and carboxymethylation as well as the aging time affected the properties of the product. High purity SCMC could be obtained by washing and soaking in ethanol.

Rahman and Shakila [57] produced SCMC under various conditions by using agricultural waste as the raw material. Cellulose was isolated from straws of rice and wheat. The products were easily purified and soluble in water. The DS was increased by multistage carboxymethylation. 80% ethanol was good enough for SCMC with low DS. 95% ethanol was the most suitable for highly substituted SCMC.

SCMC with DS 0.45-0.75 and good salt-water dispersibility was prepared by Omiya [49]. Cellulose was treated with alkali anhydroglucose units in aqueous iso-Propanol and carboxymethylating agent. The alkali content of the alkali cellulose was lowered with  $\text{ClCH}_2\text{COOPr}$ -iso-Propanol and iso-Propyl esters. Alkali cellulose was prepared by mixing powdered cellulose with iso-Propanol, 98% NaOH, and water at 15-20°C for 1

hour.  $\text{ClCH}_2\text{COOPr}$ -iso-Propanol, isopropyl acetate and iso-Propanol were added at 20-30°C over 30 minutes and mixed at 70°C for 1 hour to produce SCMC. The product had a DS 0.56, transparency 600 mm and viscosity of 1% aqueous solution 8,456 Pa-s.

Yoshimura [75] produced transparent SCMC. Pulverized pulp was stirred in a mixture of water, 70-84% iso-Propanol and aqueous NaOH at 15-30°C for 60 minutes. Then 55% solution of MCA in iso-Propanol and iso-Propanol were added and the mixture was stirred at 70°C to give transparent SCMC.

SCMC used in drilling fluids, toothpastes etc. was prepared [49] by stirring powdered linter pulp (5% water, dp 2300) with a mixture of iso-Propanol, NaOH (98% pure) and water at 12-20°C for 120 minutes. The produced Na-cellulose was mixed with water, treated with MCA (98.5% pure) in iso-Propanol and heated at 70°C for 120 minutes.

Klose et al [35] produced quality SCMC without expensive pulp alkalization. Cellulose having 20-35% water was sprayed with 38% NaOH and mixed for 5 minutes. It was thereafter sprayed with MCA, NaOH and water and mixed for 5 minutes. The mass was heated at 50°C for 6 hours. This process gave SCMC with DS 0.6 and solubility 87.7 percent.

SCMC was produced by Yang Qingli [74] by alkalization of

pretreated fibers with 17.5-22% aqueous NaOH solution for 50-60 minutes at  $< 40^{\circ}\text{C}$ . The Na-cellulose was then etherified with 10-13% chloroacetic acid for 45-50 minutes at  $74-78^{\circ}\text{C}$ .

Klose [36] produced SCMC with good quality and high space time yield. Alkali cellulose and carboxymethylating agents were added at a constant ratio to a continuous high shear kneader operating at low temperature with short residence time (resulting in low conversions). Alkali cellulose was mixed with MCA at  $25^{\circ}\text{C}$  for 86 seconds and the mixture was heated at  $50^{\circ}\text{C}$  for 5 hours. The resulting SCMC had water content of 10%, DS 0.97, viscosity of a 3% solution 92 mpa-s and solubility 100 percent.

Commercial SCMC was manufactured by Halaburda [20] by treatment of cellulose with MCA and  $\text{Na}_2\text{CO}_3$ . The MCA- $\text{Na}_2\text{CO}_3$  mixture was used in a ratio of 2:0.5-0.9 and reaction was conducted at  $20-60^{\circ}\text{C}$  for 1-6 hours. The product was aged at  $20-50^{\circ}\text{C}$  for 6-18 hours.

Spottke et al [68] mixed beechwood sulfite pulp with 39% NaOH and 90% MCA in mole ratio of 1:3, 5:1.7. 2.1% NaOCl was added as a 12% solution to the NaOH just before the mixing. Conventional procedure was followed to produce SCMC of DS 0.92, viscosity of a 3% solution 28.6 mpa-s and solubility 98.7% percent.

Printing pastes containing carboxymethylated starch-cellulose were prepared by Kako [31]. Sweet potato starch-cellulose was stirred in methanol containing NaOH. Reaction time was 60 minutes and temperature 30°C. This cellulose was treated with MCA at 40-65°C to give the product with DS 1.53 and NaCl content 0.35%.

Rahman and Shakila [59] produced SCMC from alpha cellulose and rice hulls. Reaction was carried out both in aqueous and aqueous ethanolic media. Single stage product had low DS, but multistage SCMC gave high DS. After 5th stage of carboxymethylation, SCMC was obtained with DS 2.8.

Majid and Ismat [41] studied carboxymethylation of regenerated cellulose (rayon) waste under various reaction conditions. The DS and dp of the products were determined. The optimum conditions for the preparation of SCMC were steeping the rayon in about 7 times its wt. in 20% aqueous alcoholic NaOH for 2 hours. Then heating the mixture with 2.75 times its weight of 80% MCA at 50°C for 5 hours. The DS and dp of the product were 0.7 and 235 respectively.

Cai Yipeng [10] reported that alkalization and etherification were two major factors for the preparation of cellulose ethers like SCMC. Suitable alkalization conditions were: NaOH-water-ethanol ratio 2:3:5 and temperature 35°C. Proper

regulation of the reactants ratio and the etherification temperature was essential for obtaining products with desirable DS.

Sasaki Mesao [64] improved the production of SCMC by increasing the DS and lowering the decomposition of agent and cellulose. These were achieved by: (a) mixing a cellulose material with an aqueous organic solution of the stoichiometrically equivalent salt of MCA with NaOH and (b) adding gradually 2-5.55 mol NaOH per glucose unit to activate the etherification reaction.

Ragheb [56] investigated the dependence of the properties of SCMC on the purity of the starting material and on the concentration of etherifying agents. SCMC was prepared from jute waste fibers. The DS of the SCMC increased with the increase in the degree of purity of the starting cellulose and also with the increase in the concentration of the etherifying agents (MCA and NaOH). The solubility of the SCMC was governed not only by DS and purity of the starting material but also by the concentration of the etherifying agents used. The presence of lignin and rosin are undesirable in cellulose. The product showed non-Newtonian pseudoplastic behaviour, although few samples exhibited thixotropic behaviour. The apparent viscosity was dependent on the degree of purity of the cellulosic samples, DS and duration of storing before measurement.

The DS of SCMC prepared [70] from bagasse-cotton linter mixture pulp, was greatly dependent on the chemical composition and microstructure of cellulose and alkalization conditions. SCMC had DS 0.73-0.75 and viscosity 900-1000 mpa-s under the following conditions: bagasse-cotton linter ratio (30-40):(60-70), cellulose-NaOH ratio 1:(0.58-0.63), cellulose-MCA ratio 1:(0.65-0.68) and cellulose-ethanol ratio 1:(2-2.2).

Bonder [7] streamlined the manufacture of SCMC by mixing cellulose with aqueous NaOH and MCA or NaMCA in the presence of C<sub>2-4</sub> aliphatic alcohol at -10°-50°C for 30-180 seconds followed by ripening at 70-80°C for 30-120 minutes.

Isserils [29] improved friability, solubility and antiresorbability of SCMC by mercerization of cellulose followed by alkalization in the presence of Na<sub>2</sub>SO<sub>4</sub>. He prepared SCMC by carboxymethylation of alkali cellulose in the presence or absence of organic solvents such as ethanol. The amount of water in the reaction system affected significantly both the effectiveness of the reaction and the uniformity of the product. The course of the etherification reaction was also affected by the structure of the alkali cellulose.

SCMC with average DS  $\geq 0.6$  and enzyme resistance (ER)  $\geq 10\%$  was prepared [23] from regenerated cellulose in water containing organic solvents. 200 g Rayon was added to a mixture of 108.5 g



MCA, iso-Propanol and water at 25°C over 10 minutes. The solution was stirred for 90 minutes at 25°C and 60 minutes at 70°C. It was then neutralized with acetic acid to give SCMC with DS 0.75, ER 32% and good printability on polyester fabric.

Baishuan [67] prepared SCMC by etherification of paper pulp with aqueous NaOH ethanolic solution. The viscosity of the product was dependent on reaction temperature, reaction time and NaOH concentration.

Hebeish [21] used agricultural wastes to prepare SCMC. DS and rheological properties of SCMC were dependent on the purity of cellulose and its source. Higher degree of purity was accompanied by higher DS and lower apparent viscosity. Thixotropic behaviour of the product solution was observed. Raw cotton stalk was treated with MCA and NaOH. The yield and DS were increased and apparent viscosity was decreased with the increase in the concentration of etherifying agents. Conditions appropriate for aqueous carboxymethylation were developed. In this process, 250 g cellulose, 250 g NaOH were mixed in 300 ml water and shredded for 90 minutes. 250 g MCA was added to it and the material was shredded for another 90 minutes. The product was aged for 3 days to attain the desired SCMC.

Duran [17] manufactured SCMC from pineapple peels, rice husks and sawdust by alkali extraction. The substrates were

extracted with 2% NaOH aqueous solution. The cellulosic material was then bleached with 2.5% NaClO solution for 4 hours. The material was soaked in aqueous NaOH solution and then treated with MCA in ethanol at 40-45°C for 6 hours under constant stirring. The yield was > 61% having DS 0.91-1.25 and purity > 94%. The SCMC had a water absorbidity proportional to the DS.

Olabu [48] derived empirical equations for the DS of CMC and carboxymethylation efficiency. These could be used to find the optimal composition of the system for obtaining the desired DS and efficiency.

## 2.11 WORKS ON THE PRODUCTION OF SCMC IN BANGLADESH

SCMC has a range of industrial applications in Bangladesh including textile and pharmaceutical sectors. A number of works on the production of SCMC using locally available cellulose materials have been carried out [39, 40, 41, 57]. Main emphasis was to produce SCMC and to improve its quality in terms of DS, dp, solubility etc. by considering media, alkali concentration, reaction time and temperature, maturing time etc. But the economics of production process received hardly any attention.

Mahmud [39] enhanced the DS of SCMC by repetitive carboxymethylation of cellulose. He used fibrous cotton and wood

pulp as cellulose source. Detailed production procedure was not disclosed. He showed that the enhancement of DS was dependent on the source of cellulose.

Rahman, Shakila and Ismat [57] carboxymethylated agricultural wastes such as straws of rice and wheat to prepare SCMC. Steeping of cellulose was carried out both in aqueous and aqueous-alcoholic media. They found that the DS of SCMC increased with the increase in the number of stages of carboxymethylation. Preparation details followed by them are outlined :

1. Aqueous medium

Cellulose = 2 g

Conditions of steeping:

NaOH taken = 10 ml of 70% aqueous solution,

Temperature = 28 - 30°C.

Time : 2 hours.

Conditions of carboxymethylation :

MCA = 4 ml of 80% solution,

Temperature = 30-45°C

Time : 6 hours.

The DS of the product was in the range 0.68-0.86.

2. Aqueous ethanolic medium :

Cellulose = 2 g

Condition of steeping :

NaOH solution taken = 14 ml of aqueous ethanolic solution,

Temperature = 28-30°C

Time : 2 hours.

Condition of carboxymethylation :

MCA = 14 ml of 80% ethanolic solution,

Temperature = 30-45°C

Time : 6 hours.

The product was soluble in water, but insoluble in 80% ethanol.

The DS of the product was in the range of 1.02-1.18.

Rahman, Shakila and Neger [58] prepared SCMC from rice husk. They showed that multistage carboxymethylation increased the DS value of the produced SCMC. The reaction conditions were similar to those used earlier [57]. After the fifth stage of carboxymethylation, DS values of SCMC was greater than 2.

Mahtabuddin, Rahima et al [40] carboxymethylated water hyacinth cellulose to produce SCMC. Reactions were carried out in absolute alcohol-water, rectified spirit-water and water only media. Experiments were also carried out with different concentrations of NaOH. Variation of time and temperature for

carboxymethylation was also studied. They showed that the SCMC could be used as a good detergent aid. The optimum conditions for the reaction were : use of locally available rectified spirit adjusted to 10% water content, temperature of 40°C and reaction time of 2 hours.

Majid, Ismat et al [41] carboxymethylated regenerated cellulose waste (Rayon waste) under various reaction conditions. They studied the effects of the reaction conditions on the DS and dp of the produced SCMC. To study the effect of alkali concentration, the reaction conditions followed were :

- Steeping the rayon waste for 2 hours in 30 ml of aqueous ethanolic solution (1:1 v/v) with varying NaOH concentration, Temperature 28-30°C.
- Treating it with 7.5 ml of 80% MCA  
Time = 5 hours  
Temperature = 50°C

The results showed that the DS of the product increased with the increase in alkali concentration upto 20%. The maximum DS of SCMC was found to be 0.7. The DS decreased with further increase in the alkali concentration. The dp decreased with the increase in the alkali concentration.

Keeping the alkali concentration at 20% and performing carboxymethylation at the previous conditions with the variations in the molar ratio of cellulose to alkali, the result obtained

was : the DS initially rose to 0.7 till cellulose-alkali ratio of 1:5 and then dropped for further rise in the molar ratio.

Keeping other conditions same, the reaction temperature was varied to study the effect. The result showed that the DS of SCMC initially increased sharply with the increase in the temperature. But after 60°C the slope of the curve declined. The explanation presented was the permanent loss of viscosity at higher temperature. Variation of DS of SCMC with the reaction time was also studied by them. In this case, the carboxymethylation reaction time was varied by keeping the other conditions unchanged. The reaction temperature was 50°C. It was observed that the DS continued to rise steadily with the passage of time. But the slope of the DS curve seemed to decline after 5 hours. It was concluded that continuation of carboxymethylation beyond 5 hours is not worthwhile. So, the optimum conditions proposed were:

alkali concentration - 20%

cellulose-alkali ratio - 1:5

Cellulose-MCA ratio = 1:1.75

reaction temperature - 50°C

reaction time - 5 hours

alkali-ethanol ratio = 1:5.

## 2.12 COMMERCIAL PRODUCTION OF SCMC

Published literature provides limited details concerning commercial production to appreciate the technological problems and solutions therefor.

Commercial products have Degree of Substitution (DS) in the range 0.65-0.85 with purity of about 68%. For such a product consumption of raw materials expected are [19, 55]:

Basis: 1 mole of cellulose

NaOH : 1.680-1.887 moles

MCA : 0.803-0.904 moles.

But how these consumption rates of alkali and acid are achieved are not mentioned. For alcoholic media, if used, the loss of alcohol is expected to be not over 5%.

The available laboratory works indicate that excess reactants (over the stoichiometric requirement) are necessary to cause required swelling during alkali cellulose preparation and carboxymethylation reaction. For commercial production, the recovery of the excess reactants with little loss is desirable. If possible, recycling of the excess reactants would achieve the same result. But how much of these undesirable reaction products such as sodium glycolate, sodium chloride, sodium alcoholate etc. could be tolerated in the process and product are not stated in

the literature. However, by washing the product, the presence of byproducts such as sodium chloride and sodium glycolate may be reduced at the expense of solvent to improve the product quality and purity.



## CHAPTER - THREE

### STATEMENT OF THE OBJECTIVES

Literature reveals that different workers produced sodium carboxymethyl cellulose (SCMC) by following different procedures. Limited information is available on the industrial production of SCMC. Laboratory works at home and abroad clearly show that the use of stoichiometric amount of the reactants could not yield the desired grades of SCMC and sometimes no product at all; while industrial productions consume the stoichiometric quantity of reactants for a product having the degree of substitution (DS) in the range of 0.65-0.8. But how this is achieved is not discussed. Minimization of the consumption of reactants could be achieved by recovering the excess amount of reactants and recycling these. Parameters other than the quantity of reactants to be used for the production of SCMC such as the concentration of alkali, temperature at which the reactions take place, reaction time and maturing time are of considerable importance for determining the most desired processing conditions.

This work has made an effort to investigate the production process of SCMC for its commercial application. The following were the objectives to develop a process for the industrial production of SCMC on small scale :

- i) to minimize the consumption of the reactants;
- ii) to optimize the temperature of the reaction, specially the

carboxymethylation temperature;

- iii) to maximize the recovery of the solvent i.e. the media of the reaction and use it time and again;
- iv) to ascertain the reaction time to obtain the desired quality product; and
- v) to find the maturing time of the product to improve the quality.

In order to achieve these objectives, a number of experiments were carried out using glass wares using small samples to appraise the production process. This was followed by experimentation using a stirred stainless steel reactor.

Sources of cellulose were : cotton linter and microcrystalline cellulose obtained from jute fibre.

Product quality was tested by following ASTM D1439-65[5] method by observing its solubility in water, viscosity of 1-2% solution (by weight) and by measurement of DS.

## CHAPTER - FOUR

### EXPERIMENTAL SET-UP AND PROCEDURE

#### 4.1 EXPERIMENTAL EQUIPMENT

The present work on the production of sodium carboxymethyl cellulose (SCMC) was carried out in two stages. In order to appraise the production of SCMC, preliminary experiments were carried out using glass wares. Conical flasks, beakers, round-bottom flasks, etc. of different capacities ranging from 50 ml to 500 ml were used as per requirements. A motorized stirrer of propeller type was used to stir the reactants.

On the basis of experience gained, a stainless steel cylindrical reactor of 1650 ml capacity (Inside diameter 10.16 cm, Length 20.32 cm) with a motorized anchor type stirrer was used. The reactor was kept inside a water bath for maintaining the desired operating temperature. The arrangement is shown in Figures 4.1.1 to 4.1.4. During the recycling of alkali-alcohol solution, dissolution of make-up alkali was carried out either in a 500 ml conical glass flask or in a stainless steel cylindrical vessel (inside diameter 7.62 cm, length 17.78 cm) with constant stirring and cooling.

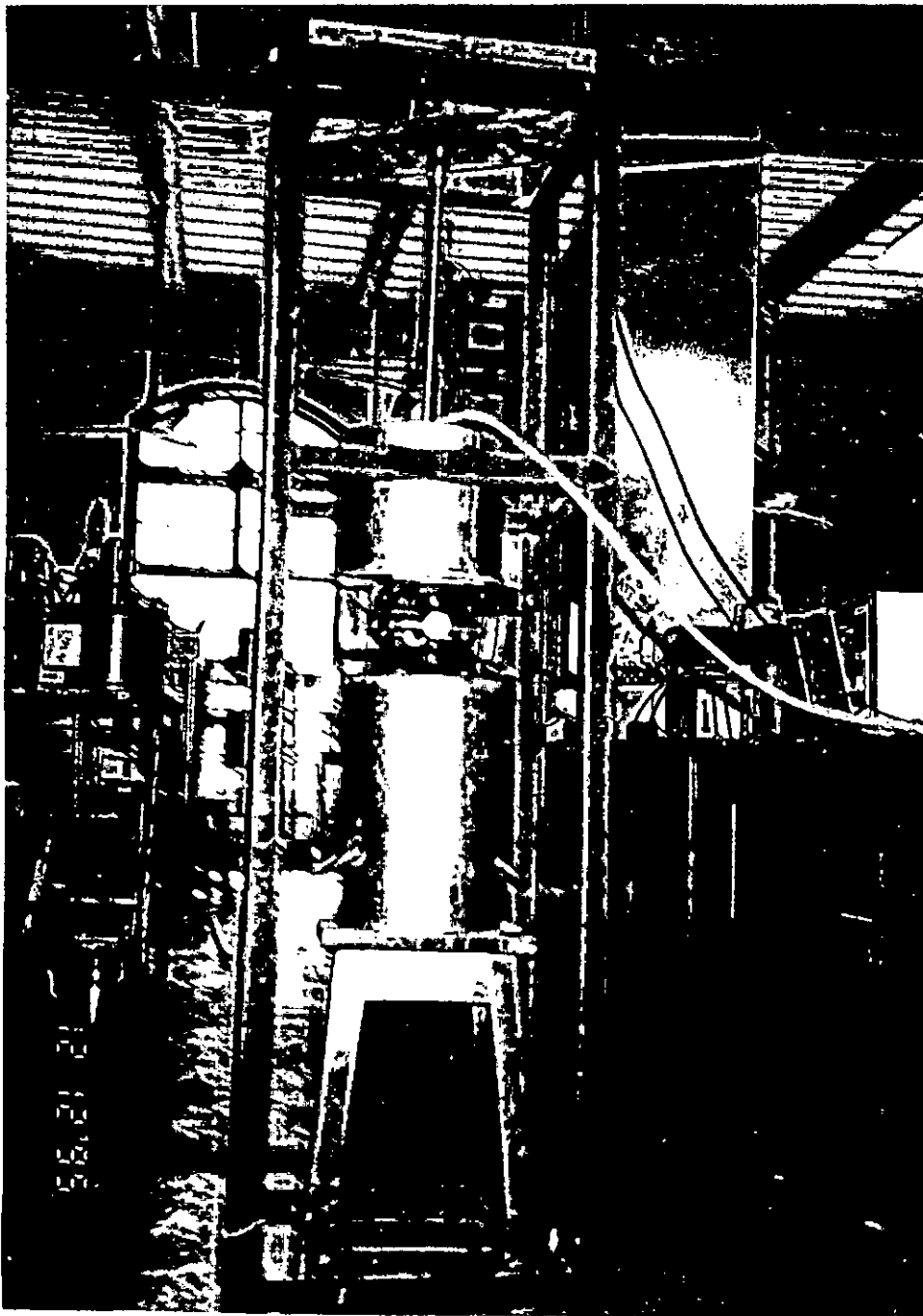


FIGURE 4.1.1      PHOTOGRAPH OF EXPERIMENTAL SET-UP-A

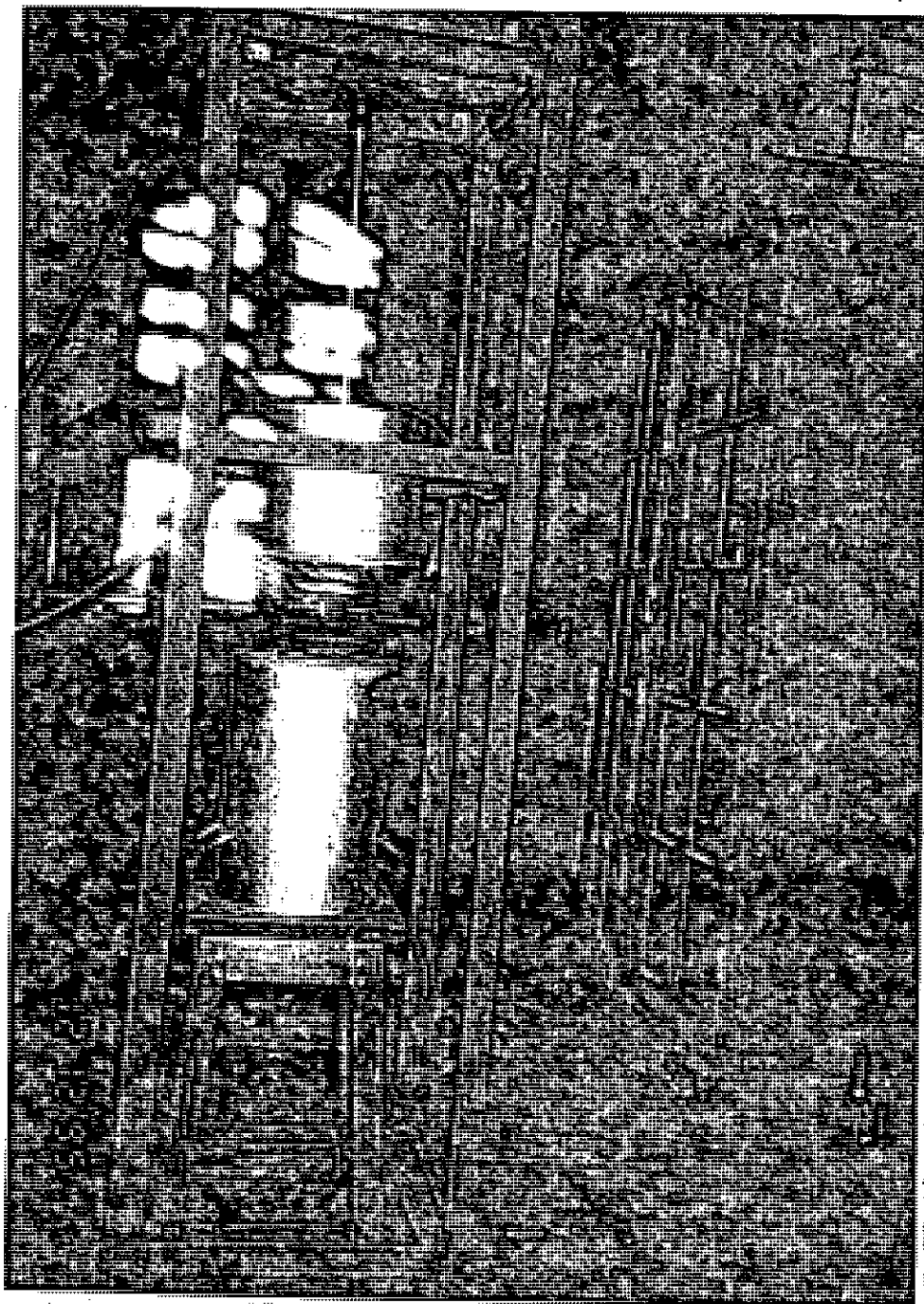


FIGURE 4.1.2: PHOTOGRAPH OF EXPERIMENTAL SET-UP-B

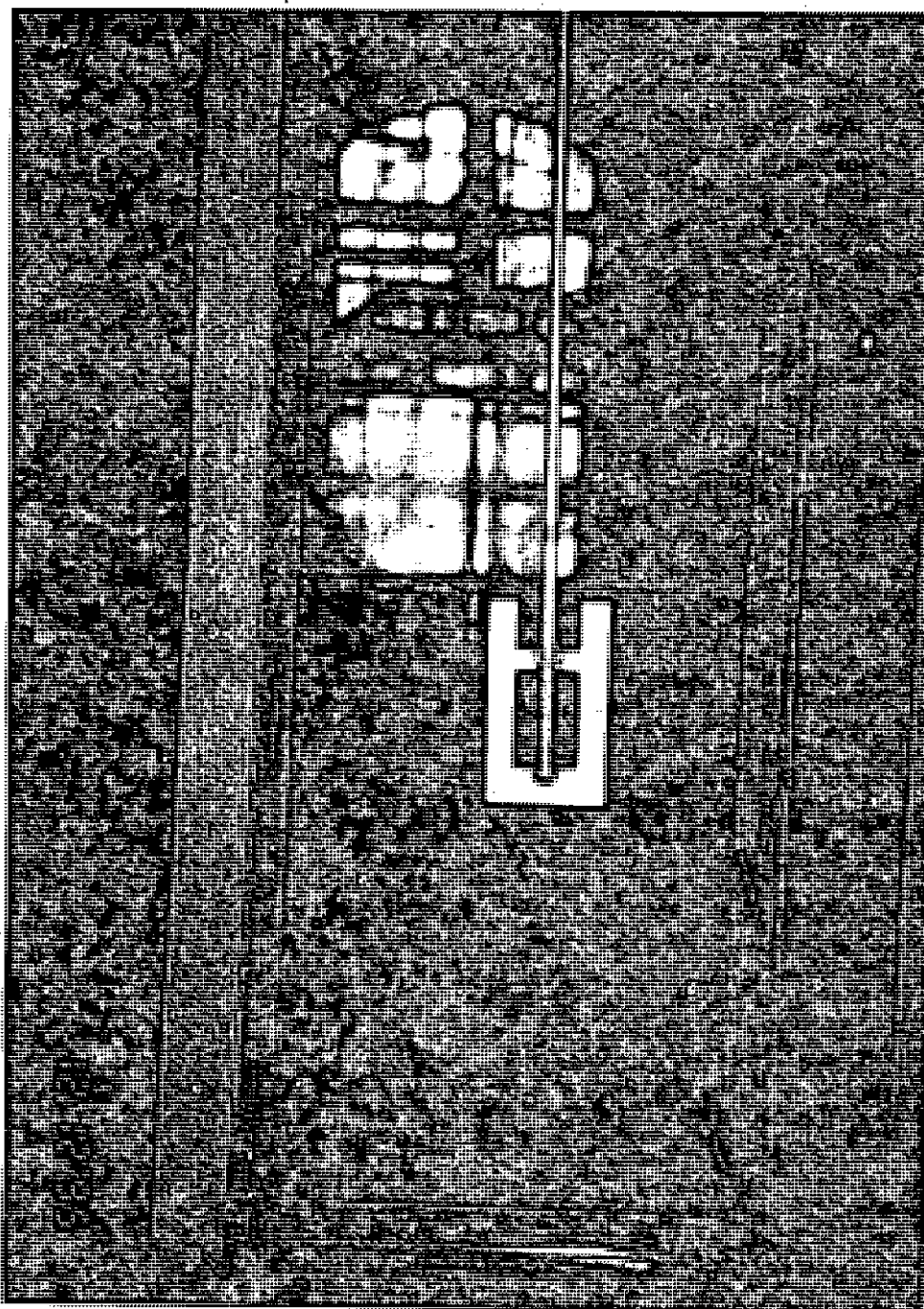


FIGURE 4.1.3 PHOTOGRAPH OF THE AGITATOR

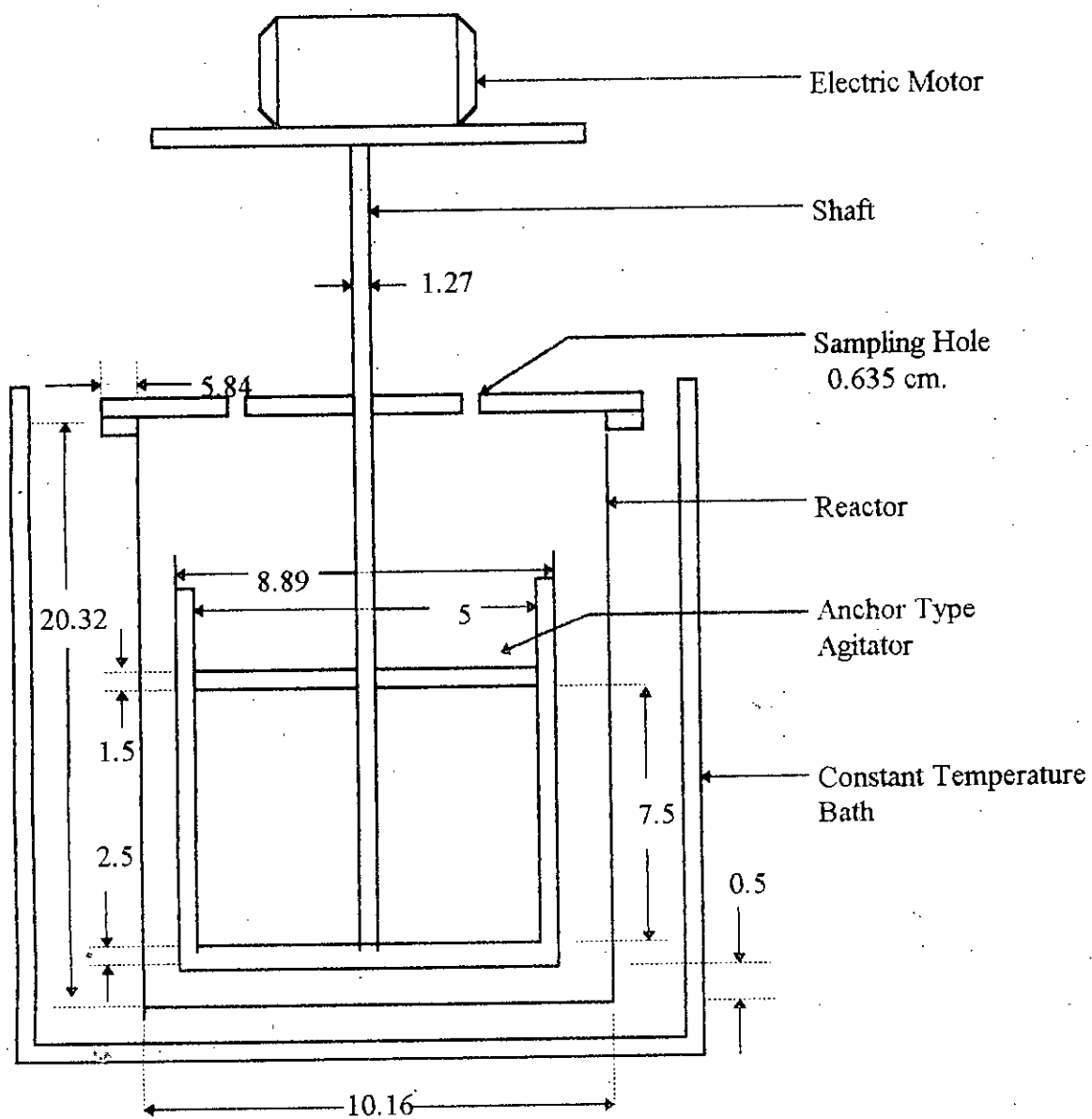


Figure 4.1.4. Diagram of the Reactor. (All dimensions in cm. Not upto scale)

## 4.2 EXPERIMENTAL PROCEDURE

The following steps were involved in the preparation of SCMC throughout the work :

- i) cleaning, washing and drying of cotton linters
- ii) determination of moisture content
- iii) preparation of alkali solution
- iv) steeping of cellulose in alkali solution
- v) carboxymethylation
- vi) maturing
- vii) neutralization
- viii) washing of the product
- ix) recovery of alcohol
- x) drying of product
- xi) grinding
- xii) testing the product

The procedures for the above mentioned steps are described below:

### 4.2.1 CLEANING, WASHING AND DRYING OF COTTON LINTERS

Cotton linters obtained from the mills were first cleaned, washed with water and dried first in the air and then oven dried at 105°C. The fresh cotton linters were then cut into small pieces with scissors to be used in the experiments. Microcrystalline cellulose being already a powdered material was only dried at 105°C before use.



#### 4.2.2 DETERMINATION OF MOISTURE CONTENT

Literature indicates that product quality and purity of SCMC are somewhat dependent on the moisture content of the starting cellulose. So, the moisture content of the cellulose used to produce SCMC in the present work was determined for both cotton linters and microcrystalline cellulose obtained from jute fibre.

A given amount of the cellulose was dried at 105°C. Drying was stopped when two successive weights of the sample became constant.

#### 4.2.3 PREPARATION OF ALKALI SOLUTION

To use an alkali solution of desired concentration, it was required to dissolve solid sodium hydroxide (NaOH) in ethanol. NaOH pellets were stirred continuously in alcohol until no more solid NaOH was observed. Since the dissolution evolves heat, an ice-water system surrounding the reactor or dissolving unit was used to cool the system and to avoid the evaporation of alcohol.

#### 4.2.4 STEEPING OF CELLULOSE

Production of SCMC from cellulose consists of mainly two stages. The 1st stage is steeping i.e. alkalization of cellulose which was conducted by stirring cotton linter or microcrystalline cellulose in alcoholic sodium hydroxide solution at room temperature (25-35°C) for approximately two hours. Na-cellulose

was formed in this reaction.

Weight increment of cellulose due to alkalization was determined by two methods. One of them was by washing, drying and weighing the cellulose after alkalization. The difference between the weights before and after steeping gave the increment of weight.

The second method was by titrating the remaining ethanolic sodium hydroxide solution after one hour and two hours of steeping. Thereby the amount of sodium hydroxide consumed could be determined from the normalities of the solution before and after the reaction from which the increment of weight of cellulose could be determined. Sodium hydroxide solution was titrated with potassium hydrogen phthalate using phenolphthalein as an indicator.

#### 4.2.5 CARBOXYMETHYLATION OF Na-CELLULOSE

Carboxymethylation is the second stage to prepare SCMC in which sodium-cellulose produced in the steeping stage was reacted with monochloroacetic acid (MCA) in presence of sufficient amount of sodium hydroxide to neutralize the acid. The reaction was carried out by stirring Na-cellulose with MCA and NaOH at 25-60°C for 2-10 hours. Sometimes steeping and carboxymethylation were carried out simultaneously. Here the required amounts of cellulose, NaOH and MCA were mixed and stirred continuously for a certain period of time at room temperature. Carboxymethylation

was always carried out in alkaline condition.

#### 4.2.6 MATURING

Literature reveals and experience has shown that complete reaction of the reactants to form SCMC does not occur only through the reaction period; but improved quality product is obtained by aging or maturing the product after both alkalization and carboxymethylation. Maturing of the product was done by keeping it in the solution without stirring. It was done at room temperature for 14-30 hours.

#### 4.2.7 NEUTRALIZATION

Carboxymethylation is carried out using excess alkali (more than that required to neutralize monochloroacetic acid). This excess alkali is neutralized with acetic acid after maturing the product.

#### 4.2.8 WASHING

After neutralizing the product, it was washed with sufficient amount of ethanol and sometimes with water to remove impurities and side products of reaction.

#### 4.2.9 RECOVERY OF ALCOHOL

When alcohol was used as the reaction media and washing

agent, it was required to recover the alcohol with least loss and reuse it to make the production process cost-effective. The alcohol was recovered in different steps such as from the alkali solution decanted from sodium-cellulose after steeping, from sodium-MCA solution discarded from the final product after carboxymethylation, from the filtrate obtained after washing and filtering the product and from the final product itself where alcohol was absorbed by the product and could not be decanted as such.

During the recycling experiments, alcohols from alkali solution and from sodium-MCA solution were recovered after the last batch of the cycle.

Alcohol recovery throughout the work was done by distillation of the solution at 76-79°C.

#### 4.2.10 DRYING OF PRODUCT

After the recovery of alcohol from the product, it was dried first on water bath and then oven-dried at 105°C.

#### 4.2.11 GRINDING OF PRODUCT

Product obtained after drying remains unaltered apparently in the shape of starting cellulose. But it is convenient to use SCMC in powder form. A grinder was used for this purpose.

#### 4.2.12 TESTING THE PRODUCT

Quality of product was determined by measuring some properties. Tests were conducted to determine solubility, viscosity and degree of substitution (DS) of the product.

Solubility was measured by preparing 1 percent and 2 percent solutions in water and determining the percent product went to solution.

Viscosity at particular temperature was determined by preparing 1 percent and 2 percent solutions of the product and determining the viscosities by Saybolt Viscometer.

Degree of substitution of the product was determined by following the procedures described in ASTM Monograph [5]. The acid wash method was followed in this work.

#### 4.2.13 RECYCLING OF REACTANTS

When recycling and reuse of the reactants were done, the above mentioned steps of procedure were also followed. In this case, reactions were carried out in four-batch cycles. Alkali solution and Na-MCA solution decanted from one batch were used in the next batch of the cycle. Make-up alkali and MCA were added for the later batch and this procedure was continued until the cycle was completed. The process is shown in Figure 4.2.13-1.



## CHAPTER - FIVE

### EXPERIMENTAL RESULTS

#### 5.1 EXPERIMENTAL RAW MATERIALS, REACTANTS AND REACTION MEDIA

Sources of cellulose used in this work included cotton linter and microcrystalline cellulose. Moisture content of the celluloses are shown in Table 5.1.1. The experiments were carried out using freshly oven-dried celluloses. The materials were dried at 105°C.

TABLE 5.1.1 : MOISTURE CONTENT OF CELLULOSE

Cellulose Type	Moisture Content %
Microcrystalline Cellulose	10
Cotton linter	9

Reactants used for the experiments were : NaOH and Monochloroacetic acid. Reagent grade reactants were used. Acetic acid used for neutralization after carboxymethylation was of reagent grade.

Both water and ethanol were used as reaction media. Technically pure ethanol having 95% alcohol content was used.

## 5.2 APPRAISAL OF PRODUCTION PROCESS

Experiments were first carried out to study that the alkalization reaction i.e. the reaction between alkali and cellulose actually occurred. This was determined from the consumption of alkali and weight increment of cellulose. Experiments were carried out both in glass wares and stainless steel cylindrical reactor.

Experiments were done using two methods such as direct washing, drying and weighing; and titration. Experimental data are presented in Tables 4.2.4-1 and 4.2.4-2 and results are shown in Table 5.2.1.

TABLE 5.2.1: WEIGHT INCREMENT OF CELLULOSE DUE TO ALKALIZATION

Cellulose Type	Method used	% Increment of weight
Microcrystalline Cellulose	Weight measurement	12.4
	Titration	13.36
Cotton linter	Weight measurement	5-11



### 5.3 EXPERIMENTS FOR ESTIMATING PARAMETERS

Process parameters such as alkali concentration during steeping, reaction time, maturing time and temperature for both steeping and carboxymethylation were selected through a number of experiments. These experimental data are presented in Tables 4.2-A, 4.2-B, 4.2-C.1 and 4.2-C.2 and results are shown in Table 5.3.1.

TABLE 5.3.1 : PROCESS PARAMETERS FOR THE PRODUCTION OF SCMC

Alkali concentration during steeping, %	Time, hours				Temperature, °C			
	Reaction		Aging		Reaction		Aging	
	Alkalization	Carboxymethylation	Alkalization	Carboxymethylation	Alkalization	Carboxymethylation	Alkalization	Carboxymethylation
18	2	8	12-16	> 16	25-30	40-45	Room Temp.	Room Temp.

## 5.4 CYCLIC EXPERIMENTS

Optimum use of reactants and reaction media was determined by maximizing the recovery of these materials and recycling the same through two cyclic experiments. Experimental data are listed in Tables 4.2.13-1 and 4.2.13-2 and results are presented in Table 5.4.1.

TABLE 5.4.1 : OPTIMIZATION OF THE USE OF REACTANTS AND MEDIA  
CELLULOSE : COTTON LINTER, 50 gm  
MEDIA : ETHANOL

			Cycle							
			1				2			
			Batch 1	Batch 2	Batch 3	Batch 4	Batch 1	Batch 2	Batch 3	Batch 4
Make-up NaOH used, gm			62.1	36.6	35.45	35.37	62.1	36.93	35.72	35.5
Make-up MCA used, gm			51	43.26	39.36	34.56	51	40	40	39.41
Alcohol Recovered	Per batch	ml	514	865	910	1060	862	1005	1035	1005
		%	71.0	87.0	86.2	75.4	80.0	81.7	82.1	75.0
	Through out the cycle	%	80.1				80			
Acetic Acid required, ml			1.5	1.5	1.0	1.0	1.5	0.5	0.0	0.0
Alkalization	Time, hour		2				2			
	Temp. °C		25-30				25-30			
Carboxymethylation	Time, hour		8				8			
	Temp. °C		40-45				40-45			
Aging	Time, hour		> 16				> 16			
	Temp. °C		Room Temperature				Room Temperature			

## 5.5 MEASUREMENT OF PROPERTIES

Properties such as solubility in water, DS and viscosity; percent recovery of alcohol from some processes; and quantity of final products obtained are shown in Table 5.5.1. Solubility of SCMC in water was estimated by observing the swelling and suspension-sedimentation of the solution. Since determination of DS is a very lengthy and laborious process, Appendix - 5.5, the DS of only three soluble products were determined. Viscosities for 1% and 2% solutions of seven products were determined with Saybolt Viscometer. Saybolt universal viscosities were converted to centistokes. Viscosities were determined at room temperature (21-24°C).

TABLE 5.5.1 : ALCOHOL RECOVERY AND PROPERTIES OF SCMC

Expt No.	Cellulose		SCMC Product Obtained (gm)	Recovery of alcohol, %	Properties of SCMC product			
	Type	Quantity used (gm)			Solubility in water	D.S.	Solution Viscosity (cp)	
							1%	2%
5 Table 4.2-C.1	Microcrystal. Cell.	20	36.5	-	Soluble	-	19.5	34.6
5 Table 4.2-C.2	Cotton linter	50	94.5	81.5	Soluble	0.992	194.0	1417.0
4 Table 4.2.13-1			99.4	75.4	Soluble	0.692	262.0	2110.6
1 Table 4.2.13-2			91.5	80.0	Partially Soluble	-	7.16	-
2 Table 4.2.13-2			84.5	81.7	Partially Soluble	-	51.0	77.0
3 Table 4.2.13-2			82.84	82.1	Soluble	-	36.0	69.4
4 Table 4.2.13-2			91.56	75.0	Soluble	0.77	59.9	242.4

## CHAPTER - SIX

### DISCUSSIONS

This work deals with the study of process parameters for the production of sodium carboxymethyl cellulose (SCMC), for establishing optimum conditions for commercial application on small scale. Experiments were carried out using two types of cellulose sources, namely, cotton linters and microcrystalline cellulose. Cotton linters are waste product of hosiery industries and microcrystalline cellulose is a purified cellulose obtained from jute fibre.

The moisture contents of the cotton linter and microcrystalline cellulose were found to lie in the range of 9-10% by weight Table 5.1.1. The values are consistent with those reported in the literature.

One of the important steps in SCMC preparation is the completion of alkalization of cellulose which is indicated by the weight increment of cellulose after the alkalization step. The results obtained from the direct washing, drying and weighing of alkali-cellulose after alkalization showed the weight increments were in the range of 5-12.4%, Table 4.2.4-1. These are close to the stoichiometric value (13.5%). Here the alkali absorption was maximum when microcrystalline cellulose was treated in alcoholic media at temperatures 30-38°C for 3 hours. Results obtained by following titration method showed that after two hours of

alkalization, the weight increment was 13.36% which was close to the stoichiometric value Tables 5.2.1 and 4.2.4-2. Weight increment in this case after one hour and two hours showed that the reaction actually continued with time.

The products obtained by reacting cotton linter in aqueous media at room temperature (30-35°C) for 2-4 hours were insoluble in water, Table 4.2-A. Since solubility in water is one of the main properties of SCMC, this was used as a criterion to determine whether the desired product has been obtained or not.

Simultaneous alkalization and carboxymethylation of the cellulose yielded products which were also insoluble in water, Table 4.2-B. These experiments were carried out with stoichiometric amount of sodium hydroxide and monochloroacetic acid at room temperature; reaction time varied from 5 to 8 hours and the products were matured for 18-30 hours.

Swelling and solubility of SCMC in water were found to improve when

- i) alkalization was carried out at room temperature (25-30°C),
- ii) aged after alkalization for at least 12 hours,
- iii) carboxymethylation was carried out at elevated temperature in the range 40-45°C; and
- iv) the product aged for 14-30 hours.

Some products swelled partially and were partially soluble in water. Some product swelled but did not go into solution

completely while some products swelled immediately depending on the process conditions mentioned above. Alcohol could be recovered partially and recovery was in the range 78-87% of the alcohol used.

After studying the process conditions such as temperature, reaction time and aging or maturing time, optimization of the use of reactants and media were done by recycling the reactants and alcohol from different steps of reaction, Figure 4.2.13-1. Results from two four-batch cycles indicate that recovered reactants such as NaOH and Na-MCA and alcohol from one batch could be used in the next batch of the cycle, Table 5.4.1. The consumption of reactants in each successive batch thereby decreased gradually. The recovery of reactants and alcohol were possible more efficiently for cycle 2 than for cycle 1. From the product properties from these cycles, it was observed that product quality such as solubility and viscosity improved from the beginning to the end of the cycle and requirement of reactants decreased gradually, Tables 5.5.1 and 5.4.1. The reason behind the improved qualities of product may be the increase of alcoholic media leading to uniformity of reactions. Another reason may be that recycling of reactants led to the availability of excess reactants for both alkalization and carboxymethylation which are essential for obtaining a quality SCMC. Use of stoichiometric quantity of reactants does not produce the desired SCMC.

Extent of recycling and purge from individual stage have not been, however, established. This would require the knowledge of the amount of by-products such as sodium glycolate, sodium chloride, and sodium alcoholate would be tolerated in the recycle streams. In actual production process, alcohol will be recovered in two stages. All recycle streams containing alcohol will be treated together, while drying stage 1 would recover alcohol from the final product.

One of the soluble SCMC's was washed with alcohol of different concentrations, Table 4.2.12-1. The result reveals that the SCMC lost weight upon washing and the maximum weight loss occurred with 60% alcohol. Washing was conducted with alcohol and not with water alone, because SCMC dissolves in water and thereby the product loss would occur. The weight loss of SCMC indicates that the product contains side products which were washed out with the alcoholic solution.

A number of experiments including two involving of recycling of reactants failed. The reason was probably the formation of sodium alcoholate when the alkaline alcoholic solutions were being prepared or kept for some hours after the dissolution of sodium hydroxide in alcohol. The media became slimy, thick and dark yellowish instead of usual clear and thin solution. The products obtained were superficially slimy upon soaking in water and did not go into solution at all.

Properties such as solubility, solution viscosity and degree

of substitution (DS) were determined for a number of soluble SCMC products, Table 5.5.1. DS varied in the range of 0.69-0.99 and it was determined using ASTM method D1439-65[5]. Viscosities of 2% and 1% solutions were determined at room temperature (21-24°C) which were in the range of 7.16 cs to 2110 cp. It was observed that product from microcrystalline cellulose was more soluble having the least viscosities. During the preparation of 2% and 1% solutions of SCMC, 1% solution showed sediment at a rate quicker than that of 2% solution. Viscosity was measured using the Saybolt Viscometer. The solutions were filtered through a net to remove any dissolved/fibre materials remaining in the solution before measuring viscosity.

Comparison of the optimum parameters of present work with those obtained by Majid [41], listed below, show that they are close and in some cases identical.

<u>Optimum Parameter</u>	<u>Work of Majid</u>	<u>Present Work</u>
alkali concentration	20%	18%
cellulose-alkali ratio	1:5	1:5
cellulose-MCA ratio	1:1.75	1:1.74
reaction temperature	50°C	40-45°C
reaction time	5 hours	8 hours
alkali-ethanol ratio	1:5	1:6
DS	0.7	0.69-0.99

However, the net consumption of reactants in cyclic schemes of the present work was found to decrease as the number of batches in a cycle increased.



## CHAPTER - SEVEN

### CONCLUSIONS

The following conclusions are drawn from this work dealing with the optimization of the process parameters for the commercial preparation of SCMC on small scale :

- i) Steeping of cellulose is to be carried out at room temperature in a solution containing about 18% NaOH by weight and two hours of steeping time would be sufficient,
- ii) Aging after alkalization/steeping would be required for at least 12 hours,
- iii) Carboxymethylation temperature would be in the range of 40-45°C for 8 hours,
- iv) Aging after carboxymethylation is required for at least 16-30 hours to complete the reaction,
- v) Quality product cannot be produced by using stoichiometric amount of reactants such as NaOH and MCA,
- vi) Minimization of the use of reactants and alcohol would be obtained by recycling and reusing the reactants and alcohol.
- vii) Quantity of make-up reactants and alcohol decreases and quality of product improves with the increase in the number of batch in a cycle which approaches the use of reactants to the stoichiometric levels.

## CHAPTER - EIGHT

### RECOMMENDATIONS FOR FUTURE WORK

The following works may be carried out in future dealing with the production process of SCMC :

- i) Recycling of the reactants to achieve stoichiometric level of consumption of reactants.
- ii) Recovery of alcohol to be achieved upto 95%.
- iii) Investigation on how the side products of reactions affect the production parameters and how much of these side products can be tolerated in recyclic process for maximizing the use of reactants for obtaining a commercial grade SCMC.

## NOMENCLATURE

cs	Centistoke
dp	Degree of Polymerization
DS	Degree of substitution
MCA	Monochloroacetic Acid
Na-Cellulose	Sodium Cellulose
NaMCA	Sodium Monochloro Acetate
NaOH	Sodium Hydroxide
SCMC	Sodium Carboxymethyl Cellulose.

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# APPENDIX

## APPENDIX - 4.0 EXPERIMENTAL DATA

TABLE 4.2.2-1: MOISTURE CONTENT OF THE CELLULOSE

Cellulose		Drying Temperature, °C	Weight of dry cellulose, gm	Moisture, gm	% Moisture content
Type	Amount, gm.				
Cotton linter	5.45	105	5.00 25.94	0.45	9
Microcrystal	28.50	105		2.56	10

TABLE 4.2.4-1: WEIGHT INCREMENT OF CELLULOSE DUE TO ALKALIZATION - I  
METHOD : DIRECT WASHING, DRYING AND WEIGHING  
MEDIA : AQUEOUS

Media	Cellulose		Amount of Alkali Solution, ml	Concentration of Alkali Solution, %	Reaction		Drying Temp. °C	Weight of Na-Cellulose	% Weight Increase
	Type	Amount gm			Time, hour	Temp. °C			
Aqueous	Cotton linter	10	200	30	2	25-30	100	11.1	11
		10	200	30	2	25-30	110	10.5	5
		10	150	30	2½	30-35	105	10.74	7.4
Alcoholic	Microcrystal line cellulose	50	233	18	3	35-38	105	56.2	12.4

TABLE 4.2.4-2: WEIGHT INCREMENT OF CELLULOSE DUE TO ALKALIZATION - II  
METHOD : TITRATION  
MEDIA : ALCOHOLIC  
CELLULOSE: MICROCRYSTALLINE CELLULOSE  
INDICATOR: PHENOLPHTHALENE  
REAGENT : POTASSIUM HYDROGEN PHTHALATE.

Cellulose, gm	Reaction		Amount of NaOH Solution, ml	Strength of remaining NaOH Solution, (N)	Amount of Remaining NaOH in Solution, gm	Consumption of NaOH, gm	% weight increment
	Time hour	Temp., °C					
50	-	35	235	3.12	29.4	-	-
50	1	35-38	235	2.3	21.62	7.78	8.94
50	2	35-38	235	1.828	17.1832	12.2168	13.36

TABLE 4.2-A: PRODUCTION OF SCMC IN AQUEOUS MEDIA  
CELLULOSE : COTTON LINTER

a. ALKALIZATION

Amount of cellulose, gm	NaOH, gm	Water, ml	Time, hour	Temperature, °C	Na-cellulose, Produced, gm
10	60	200	2	25-30	10.5
10	22.5	150	2½	30-35	10.74

b. CARBOXYMETHYLATION

Na-cellulose, gm	NaOH, gm	MCA, gm	Water, ml	Time,	Temperature, °C	Aging, hours	Solubility of product in water
5.25	15	10	50	2	30	16	Insoluble
5.00	1.2	3	60	4	30-32	16	Insoluble
5.00	2.0	3	60	2	30-35	16	Insoluble

TABLE 4.2-B: SIMULTANEOUS ALKALIZATION AND CARBOXYMETHYLATION OF CELLULOSE  
 MEDIA : ETHANOL  
 CELLULOSE: MICROCRYSTALLINE CELLULOSE

Amount of	Cellulose, gm	10	50	50
	NaOH, gm	7	25	25
	Alcohol, ml	50	250	190
	NCA, gm	7	25	25
Reaction	Time, hour	5	8	8
	Temp., °C	35-38	35-38	35-40
Aging, hour		18	30	30
Amount of Product, gm		24.6	86.0	87.5
Alcohol Recovered, ml		-	60	10
Solubility in water		Insoluble	Insoluble	Insoluble



TABLE 4.2.-C.1: PREPARATION OF SCMC IN ALCOHOLIC MEDIA - I  
CELLULOSE: MICROCRYSTALLINE CELLULOSE

Experiment No.			1	2	3	4	5
Alkalization	Amount of	Cellulose, gm	50	50	50	50	20
		NaOH, gm	25	32.5	35	35	18
		Alcohol, ml	170	180	195	195	100
	Reaction	Time, hour	5	5	4	3	2
		Temp., °C	35-40	30	30-35	25-30	25-30
	Aging, hours		16	18	16	-	16
Alkali solution decanted, ml		-	40	-	-	50	
Carboxymethylation	Alcohol added, ml		-	50	-	50	50
	Amount of MCA, gm		25	30	45	45	23
	Reaction	Time, hour	3	2	3.5	3	8
		Temp., °C	35-38	30-33	30-35	25-30	40-45
	Aging, hour		18	2	20	20	25
Neutralization	Acetic Acid, ml		-	-	5	2	1.0
Alcohol Recovered, ml			30	-	-	-	-
Product obtained, gm			82.0	106.0	99.2	-	36.5
Product condition			Parti-ally solu-ble	Parti-ally solu-ble	Insolu-ble	Insolu-ble	Soluble

TABLE 4.2-C.2: PREPARATION OF SCMC IN ALCOHOLIC MEDIA - II  
CELLULOSE: COTTON LINTER

Experiment No.			1		2		3			4			5			
Alkaliza- tion	Amount of	Cellu- lose, gm	50	50			50			50			-			
		NaOH, gm	35	35			35			62			62			
		Alco- hol, ml	295	295			295			345			345			
	Reaction	Time, hour	3	3			3			3			3			
		Temp., °C	25-30	25-30			25-28			25-28			25-28			
	Aging, hours		-	18			18			18			18			
Alkali solution decanted, ml		-	-			-			145			150				
Carboxy- methyla- tion	Alcohol added, ml		50	53			50			145			200			
	Amount of MCA, gm		45	45			45			45			45			
	Reaction	Time, hour	3	2	2	3	2	2	2	1	1	4	3	1	6	3
		Temp., °C	25-30	25-30	40-45	50-55	25-28	40-45	50-55	60	25-28	40-45	50-55	25-28	40-45	50-55
	Aging, hours		18	16			16			16			16			
	Neutrali- zation		Acetic Acid, ml		2.5	2.4			1.25			2.2			2.0	
Alcohol added for washing, ml			-	-			400			600			500			
Alcohol Recovered , ml from	Product		-	-						146			175		145	
	Filtrate		-	-						419			600		560	
Product obtained, gm			-				87.1			99			104		116	
Solubility in water			Insoluble			Soluble			Insoluble			Soluble		Soluble		

TABLE 4.2.12-1: WEIGHT LOSS OF SCMC DUE TO WASHING WITH ALCOHOL

Amount of SCMC, gm	5	5	5	5	5	5
Concentration of Alcohol, %	95	90	80	70	60	50
Amount of Alcohol, %	100	100	100	100	100	100
Washing Time, hour	1	1	1	1	1	1
Drying Temperature, °C	105	105	105	105	105	105
Amount of dry SCMC, gm	4.75	4.54	3.85	3.67	3.51	3.83
Weight loss	0.25	0.46	1.15	1.33	1.49	1.17
% weight loss	5.00	9.20	23	26.60	29.8	23.4

TABLE 4.2.13-1: PREPARATION OF SCMC BY RECYCLING OF REACTANTS AND MEDIA

CYCLE - 1

Operation	Parameters	Batch 1	Batch 2	Batch 3	Batch 4
Steeping	Make-up Alcohol, ml	345	165	110	140
	Recycled Alkali-Alcohol, ml	-	180	235	205
	NaOH, gm	62.1	36.6	35.45	35.37
	Time, hour	2	2	2	2
	Temp. °C	25-28	25-28	25-28	25-28
Aging	Time, hour	18	18	16	16
	Temp., °C	room temp.	room temp.	room temp.	room temp.
Washing	Alcohol used, ml	170	150	100	-
	Alcoholic solution record, ml	184	255	210	125
Carboxy-methylation	MCA, gm	51	43.26	39.36	34.56
	Make up Alcohol, ml	60	-	-	-
	Recycled alcohol-NaMCA, ml	-	135	406	560
	Time, hour	7	8	8	7
	Temp. °C	40-45	40-45	40-45	40-45
Aging	Time, hour	16	18	16	16
	Temp., °C	room temp.	room temp.	room temp.	room temp.
Washing	Alcohol used, ml	150	500	150	500
	Alcoholic solution Recovered, ml	150	406	560	-
Neutralization	Acetic Acid, ml	1.5	1.5	1.0	1.0
Washing	Alcohol used, ml	-	-	-	-
	Alcohol Recovered, ml	-	-	-	-
Drying I	Temperature, °C	76-79	76-79	76-79	76-79
	Alcohol Recovered, ml	75	205	140	185
Drying II	Temperature, °C	105	105	105	105
Product Collection	Quantity of product, gm.	97.5	84.9	86.35	99.4

TABLE 4.2.13-2: PREPARATION OF SCMC BY RECYCLING OF REACTANTS AND MEDIA

CYCLE - 2

Operation	Parameters	Batch 1	Batch 2	Batch 3	Batch 4
Steeping	Make-up Alcohol, ml	345	137	100	93
	Recycled Alkali-Alcohol, ml	-	208	250	252
	NaOH, gm	62.1	36.93	35.72	35.5
	Time, hour	2	2	2	2
	Temp. °C	25-28	25-28	25-28	25-28
Aging	Time, hour	12	12	13	14
	Temperature, °C	room temp.	room temp.	room temp.	room temp.
Washing	Alcohol used, ml	70	130	130	150
	Alcoholic solution Record, ml	212	250	260	265
Carboxy-methylation	MCA, gm	51	40	40	39.41
	Make up Alcohol, ml	160	-	-	-
	Recycled Alcohol-NaMCA, ml	-	305	380	395
	Time, hour	9	8	8	8
	Temp. °C	40-45	40-45	40-45	40-45
Aging	Time, hour	16	16	16	16
	Temperature, °C	room temp.	room temp.	room temp.	room temp.
Washing	Alcohol used, ml	250	200	150	200
	Alcoholic Solution Recovered, ml	310	380	400	-
Neutralization	Acetic Acid, ml	1.5	0.5	0.0	0.0
Washing	Alcohol used, ml	250	250	250	250
	Alcohol Recovered, ml	175	200	205	640
Drying I	Temperature, °C	76-79	76-79	76-79	76-79
	Alcohol Recovered, ml	165	175	170	100
Drying II	Temperature °C	105	105	105	105
Product Collection	Quantity of product, gm.	91.5	84.5	82.84	91.56

## APPENDIX - 5.5 ASTM MONOGRAPH



AMERICAN NATIONAL  
STANDARD

ANSI/ASTM D 1439 - 72 (Reapproved 1978)

### Standard Methods of Testing SODIUM CARBOXYMETHYLCELLULOSE<sup>1</sup>

This Standard is issued under the fixed designation D 1439; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

#### 1. Scope

1.1 These methods cover the testing of sodium carboxymethylcellulose.

1.2 The test procedures appear in the following order:

	Sections
Moisture .....	3 to 6
Degree of Etherification:	
Method A—Acid Wash .....	8, 9 to 14
Method B—Nonaqueous Titration ..	8, 15 to 20
Viscosity .....	21 to 26
Purity .....	27 to 33
Sodium Glycolate .....	34 to 41
Sodium Chloride .....	42 to 48
Density .....	49 to 53

#### 2. Reagents

2.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>2</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled water.

#### MOISTURE

##### 3. Scope

3.1 This method covers the determination of the volatile content of sodium carboxymethylcellulose.

3.2 The results of this test are used for calculating the total solids in the sample; and, by common usage, all materials volatile at this test temperature are designated as moisture.

##### 4. Apparatus

4.1 *Oven*—Gravity convection oven, ca-

pable of maintaining a temperature of  $105 \pm 3^\circ\text{C}$ .

4.2 *Weighing Bottles*, low-form, 50-mm inside diameter by 30-mm height, or equivalent.

4.3 *Analytical Balance*.

##### 5. Procedure

5.1 Weigh 3 to 5 g of the sample to the nearest 0.001 g in a tared and covered weighing bottle.

5.2 Place the bottle in an oven at  $105^\circ\text{C}$  for 2 h with the cover removed. Cool the bottle in a desiccator, replace the cover, and weigh.

5.3 Replace the sample in the oven for 30 min, cool, and reweigh.

5.4 Continue this procedure to a mass loss of not more than 5 mg for 30 min drying time.

##### 6. Calculation

6.1 Calculate the percentage of moisture as follows:

$$\text{Moisture, percent} = (A/B) \times 100$$

where:

$A$  = mass loss on heating; and

$B$  = grams of sample used.

##### 7. Precision

7.1 Statistical analysis of interlaboratory test results on samples containing 2 to 10 percent moisture indicates a precision of  $\pm 0.2$

<sup>1</sup>These methods are under the jurisdiction of ASTM Committee D-23 on Cellulose and Cellulose Derivatives.

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<sup>2</sup>"Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."



percent absolute at the 95 percent confidence level.

## DEGREE OF ETHERIFICATION

### 8. Scope

8.1 These methods cover the determination of the degree of etherification (D.E.) of sodium carboxymethylcellulose.

8.2 Two methods are included as follows:

8.2.1 *Method A (Acid Wash)*, for crude and purified grades of sodium carboxymethylcellulose with degrees of etherification up to 0.85. Above 0.85 degree of etherification, slightly low results may be obtained.

8.2.2 *Method B (Nonaqueous Titration)*, for purified grades of sodium carboxymethylcellulose of all degrees of etherification. It is not applicable to the crude grades.

#### *Method A—Acid Wash*

### 9. Summary of Method

9.1 The water-soluble sodium carboxymethylcellulose is converted to the insoluble acid form, purified by washing, dried, and then a weighed sample is reconverted to the sodium salt with a measured excess of sodium hydroxide.

### 10. Apparatus

10.1 *Stirrer*, air-driven.

10.2 *Buchner Funnel*, 75-mm, fitted with a 70-mm fine-texture, heavy-duty filter paper. A 60-mm medium-porosity, fritted glass funnel may also be used.

10.3 *Drying Oven*, maintained at 105 C.

### 11. Reagents

11.1 *Diphenylamine Reagent*—Dissolve 0.5 g of diphenylamine in 120 ml of sulfuric acid ( $H_2SO_4$ , 9+2). The reagent should be essentially water-white. It will give a deep blue coloration with traces of nitrate or other oxidizing agents.

11.2 *Ethyl Alcohol (95 volume percent)*—Denatured ethyl alcohol conforming to either Formula 2B, 3A, or 30 of the U. S. Bureau of Internal Revenue.

11.3 *Ethyl Alcohol (80 percent by volume)*—Dilute 840 ml of Formula 2B, 3A, or 30 denatured alcohol to 1 liter with water.

11.4 *Hydrochloric Acid, Standard (HCl, 0.3 to 0.5 N)*.

11.5 *Methanol*, anhydrous.

11.6 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid ( $HNO_3$ ).

11.7 *Sodium Hydroxide, Standard Solution (0.3 to 0.5 N)*—Prepare and standardize a 0.3 to 0.5 N solution of sodium hydroxide (NaOH).

11.8 *Sulfuric Acid (9+2)*—Carefully mix 9 volumes  $H_2SO_4$  with 2 volumes of water.

### 12. Procedure

12.1 Weigh approximately 4 g of the sample into a 250-ml beaker and add 75 ml of ethyl alcohol (95 percent). Stir the mixture with an air-driven stirrer until a good slurry is obtained. Add 5 ml of  $HNO_3$ , while agitating, and continue agitation for 1 to 2 min. Heat the slurry and boil for 5 min. (**Caution:** Note 1.) Remove the heat and continue agitation for 10 to 15 min.

**NOTE 1: Caution**—Care should be exercised to avoid fire.

12.2 Decant the supernatant liquid through the filter and transfer the precipitate to the filter with 50 to 100 ml of ethyl alcohol (95 percent). Wash the precipitate with ethyl alcohol (80 percent) that has been heated to 60 C, until all of the acid has been removed.

12.3 Test for the removal of acid and salts (ash) by mixing a drop of the acid carboxymethylcellulose slurry from the filter with a drop of diphenylamine reagent on a white spot plate. A blue color indicates the presence of nitrate and the necessity for further washing. If the first drop of reagent does not produce a blue color, further drops should be added until an excess of reagent is known to be present, noting the color after each drop. Four to six washings will usually suffice to give a negative test for nitrate.

12.4 Finally, wash the precipitate with a small amount of anhydrous methanol and draw air through it until the alcohol is completely removed. Transfer the precipitate to a glass or aluminum weighing dish provided with a cover. Heat the uncovered dish on a steam bath until the odor of alcohol can no longer be detected (in order to avoid fires due to methanol fumes in the oven), then dry the dish and contents, uncovered for 3 h at 105 C. Place the cover on the dish and cool to room temperature in a desiccator.

12.5 The sulfate ash content of the sample at this point should be less than 0.5 percent



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when determined on 0.5 g of the sample by the procedure given in Section 6 of ASTM Methods D 1347, Testing Methylcellulose.<sup>3</sup> If the ash content is greater than 0.5 percent, the sample should be rewashed with ethyl alcohol (80 percent). If necessary, the procedure described in 12.1 to 12.4 should be repeated.

12.6 Weigh, to the nearest 0.01 g, about 1 to 1.5 g of the dried acid carboxymethylcellulose (depending on the normality of the acid and base to be used) into a 500-ml Erlenmeyer flask. Add 100 ml of water and 25.00 ml of 0.3 to 0.5 *N* NaOH solution, while stirring. Heat the solution to boiling, and boil for 15 to 30 min.

12.7 Titrate the excess NaOH, while the solution is hot, with the 0.3 to 0.5 *N* HCl to a phenolphthalein end point.

### 13. Calculation

13.1 Calculate the degree of etherification as follows:

$$A = (BC - DE)/F$$

$$\text{Degree of etherification} = 0.162A/(1 - 0.0584)$$

where:

- A* = milliequivalents of acid consumed per gram of sample,
- B* = milliliters of NaOH solution added,
- C* = normality of the NaOH solution,
- D* = milliliters of HCl required for titration of the excess NaOH,
- E* = normality of the HCl,
- F* = grams of acid carboxymethylcellulose used,
- 162 = gram molecular mass of the anhydroglucose unit of cellulose, and
- 58 = net increase in molecular mass of anhydroglucose unit for each carboxymethyl group substituted.

### 14. Precision

14.1 The precision of this method is estimated to be  $\pm 0.03$  D.E. units.

#### Method B—Nonaqueous Titration

### 15. Summary of Method

15.1 This measurement is 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 conditions. Sodium chloride does not interfere.

### 16. Apparatus

16.1 *pH Meter*, equipped with a standard glass electrode and a calomel electrode modified as follows:

16.1.1 Discard the aqueous potassium chloride solution, then rinse and fill with the calomel electrode solution as described in 17.2.

16.1.2 Add a few crystals of potassium chloride and silver chloride or silver oxide to the electrode.

16.2 *Buret*, micro, 10-ml capacity.

### 17. Reagents

17.1 *Acetic Acid*, glacial.

17.2 *Calomel Electrode Solution*—Add 2 g of potassium chloride (KCl) and 2 g of silver chloride (AgCl) or silver oxide (Ag<sub>2</sub>O) to 100 ml of methanol and shake thoroughly to saturate. Use the supernatant liquid.

17.3 *1,4-Dioxane*.<sup>4</sup>

17.4 *Perchloric Acid (0.1 N)*—Add 9 ml of concentrated perchloric acid (HClO<sub>4</sub>, 70 percent) to 1 liter of dioxane, with stirring (Caution, Note 2). Store in an amber glass bottle. Any slight discoloration that appears on standing may be disregarded.

NOTE 2: **Caution**—The solution of perchloric acid in dioxane should never be heated or allowed to evaporate.

17.4.1 Standardize the solution as follows: Dry potassium acid phthalate for 2 h at 120°C. Weigh 2.5 g to the nearest 0.0001 g into a 250-ml volumetric flask. Add glacial acetic acid, shake to dissolve, and then make up to volume and mix thoroughly. Pipet 10 ml into a 100-ml beaker and add 50 ml of acetic acid. Place on a magnetic stirrer and insert the electrodes of the pH meter. Add nearly the required amount of HClO<sub>4</sub> from a buret, then decrease the increments to 0.05 ml as the end point is approached. Record the milliliters of

<sup>3</sup> Annual Book of ASTM Standards, Parts 21 and 28.

<sup>4</sup> 1,4-Dioxane available as Eastman Kodak Catalog No. 2144 or Mateson, Coleman, and Bell Catalog No. CB 368 has been found satisfactory for this purpose.

