Studies of Kinetics with Partly Carboxymethylated Pulp in terms of Chemical Upgradation

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Keywords : Carboxymethylation, Bursting Strength, Carboxyl Content, kinetic model

The Carboxymethylation of a Cotton and Imported Pulp was conducted in presence of Monochloroacetic acid. The change in a Hydroxyl value was observed as a function of a time during carboxymethylation. Cotton Pulp has higher initial hydroxyl value than that of imported Pulp, hence the rate of carboxymethylation was also higher for cotton pulp than that of imported Pulp. Imported Pulp observed to exhibit Paper Characteristics, Hence imported Pulp is more suitable for Papermaking. Evolution of Characteristics shows the improvement in Tearing Strength for the Paper Sheet made from reacted Pulp but shows decrease in bursting strength and Bursting Factor as Compared to the paper made from Unreacted Pulp. Effect of addition of Acid, Alkali and Alum on the Physical Properties of the Paper Sheet made from the imported Pulp and Cotton Pulp was tested and improvement is observed in a apparent Density, Molten Bursting Strength, Tearing Strength and Opacity. Specially with addition of alkali to the Pulp gives better performance. Kinetics study observed that Monochloroacetic acid was the Limiting Reactant for the Product Carboxymethylcellulose (CMC). The first order kinetics expression based on calculation of fractional conversion (XA), Carboxymethylation as a function of a time and has been presented in graphs. The plot was linear and passing through the origin confirming first order characteristics of Carboxymethylation reaction. The first order Carboxymethylation rate constants for Cotton Pulp and imported Pulp and has been reported 0.20 and 0.19 hr^{-1} respectively. The Chemical Structure and Composition of the Product obtained by reaction of Cellulose with Chloroacetic acid is supported by above different Characteristics. IR absorption bands and Spectroscopic Characterization of Carboxymethylated samples are investigated and presented by table and graphs.

INTRODUCTION

The hydroxyl group of cellulose play an important role in the pronounced affinity of cellulose for waste. And in the bonding of cellulose fibre in the formation of paper. Several investigation among them Jayme, and Froundjian (1), Bletzinger (2), Aiken (3), and Harrison (4) have studied cellulosic pulps 1 which varying amounts of these hydroxyl group have been substituted with hydrophobic group such as the methxyl or acetyl groups. These investigator found that at low degree of substitution (D.S.). The affinity of water of these substituted celluloses was increased, due perhaps to an opening up of the cellulosic structure making more cellulosic hydroxyl groups available for bonding and for the adsorption of water. Most of the work discussed in the literature deals with soluble CMC of high D.S. (Gretter than 0.3) Daul, Rein Hart and Reid (5,6,7,8) CM derivative of cellulose are well known for their commercial application (13,14) lot of work has been done on the carboxymethylation of cellulosic product like cotton. Some of the work is also reported from paper pulp. The area in which the systematic study of carboxymethylation of paper pulp has not been reported so far. Hence it was thought to under take the study of carboxymethylation of the paper pulp. And the study of the resultant product. The goal of this study was to develop a method for the preparation of low D.S. (CMC), partly carboxymethylated retaining the fibrous nature of the pulp and without excessive degradation. The paper making behavior of these pulp was observed and Physical strength properties of hand sheet formed from these pulp were determined.

The Carboxymethylation of cellulose differs from acetylation and Cynoethylation in one respect. Carboxymethyl group is hydrophilic while acetyl and Cynoethyl group are hydrophobic. If hydrophilic group instead of Hydrophobic groups are substituted for the cellulose hydroxyls, the resulting pulp should have properties that differ from the Properties of both the original pulp and one modified with hydrophobic group, Carboxymethylation of pulp fibre at low substitution under the certain condition produced improvement in the strength properties of paper sheet made from them. Carboxymethylation carried out with diamethyl sulphoxide as the medium were markedly superior, while aqueous alkali was inferior to isopropanol solution. (15) C.M.C. is usually prepared commercially and in the laboratory by successively soaking a cellulose pulp in aqueous solution of strong caustic and Sodium monochloroaacetate. Paper making properties at low degree of substitution of Carboxymethylcelluloses have been described (16) A theory to explain these changes in properties on the basis of the increased hydrophilic nature of the C.M.C. pulps is presented (16) most of the work discussed in the literature deals with soluble C.M.C. of high degree of substitution (greater than 0.3) Daul Reinhart and Reid (17-20), However, have studied C. M. C. products from a degree of substitution of 1.8 dawn to a degree of substitution of 0.015 hand sheet from he low degree of substitution pulps had higher strength properties than hand sheet of original rag pulp and achieved these strength with less beating.

Natural Sources of Cellulose

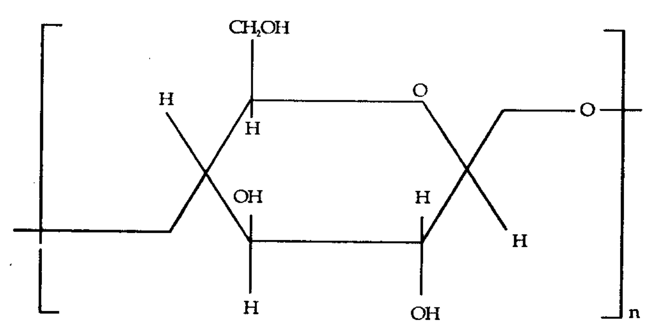
Cellulose plastics are polymers, which have the cellulose as their major constituents. These are prepared by reacting cellulose from natural sources with various chemicals. The following are some of the important cellulosic polymers commercially produced. Cellulose nitrate, Cellulose Acetate, Regenerated Cellulose, Cellulose acetate-butyrate Cellulose propionate, Ethyl Cellulose, Methyl Cellulose, Carboxymethyl Cellulose, Hydroxyl ethyl Cellulose, hydroxylpropyl Cellulose and Blended Product with Resin Cellulose is the main constituent of the cell walls of plants. Some of these sources in nature have cellulose in more fibrous form than others. These materials are the sources of Cellulose for the manufacture of cellulose plastics.

Some of the natural sources having high content of the cellulose in them are listed in bellow table :

Materials	Cellulose %
Jute	70
Straw	50
Bamboo	50
Wood	50
Flax	90
Hemp	90
Cotton	90
Cotton Linters	95

All the natural cellulose materials, except material like cotton, flax have in them a binder, which is a lignin, to hold the fibrous cellulose together. In addition, the natural material have polysaccharides, small amounts of minerals and proteins usually two sources of cellulose are utilized for the preparation of the cellulose plastics. They are Cotton linters and Wood Pulp. Cotton linters are the shorts fibres over the cottonseeds left after the removal of cotton fluffs. Cotton linters have higher cellulose content than long fibre used in textiles Cellulose from the natural sources in fact has three forms, the alpha-form. The Beta - form and gamma-form when cellulose is digested in aqueous sodium hydroxide solution of less than 4% strength, the beta and gamma varieties are removed from it. The fibre which remain are of the alpha - cellulose (a term given to pure cellulose of high molecular weight) Variety of molecular weight ranging from 100,000 to 500,000. Cellulose has the empirical formula $C_6 H_{10} O_5$ corresponding to a glucose anhydride unit

The structure of Cellulose as a polymer, may be represented as



The 'n' may range between 600 & 3000

Material and Methods

Experimental Methodology

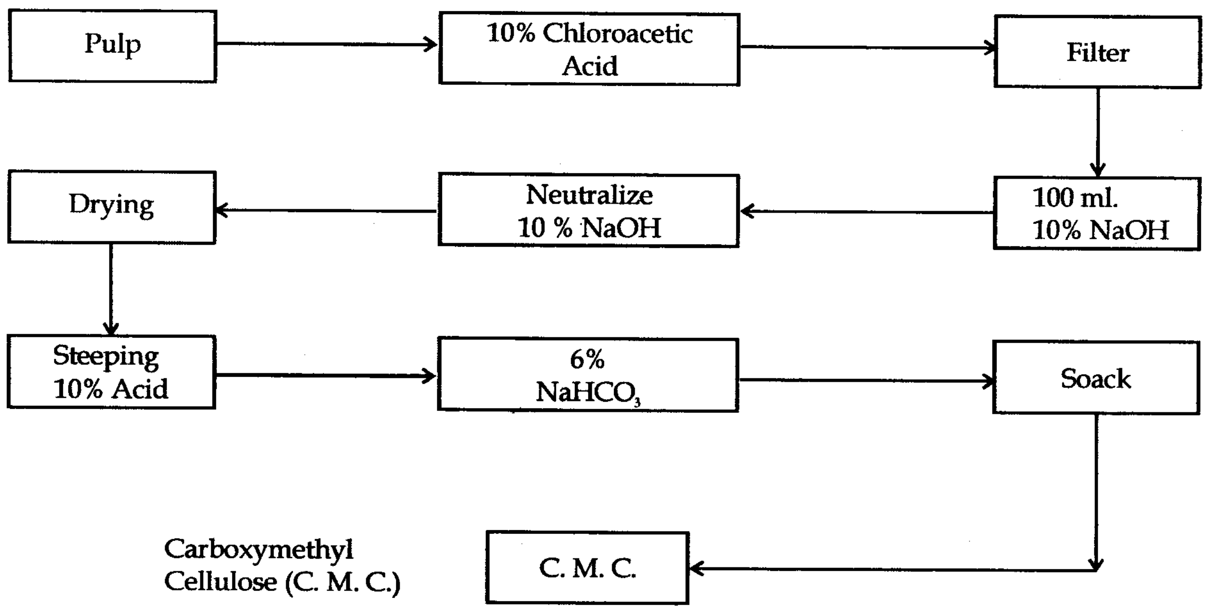
Chemical : Acetic Anhydride, DMF, Dry pulp sample, Distill water, butanol Alcoholic NaOH Chloro acetic Acid, Aqueous Acetic Acid, 10% $NaHCO_3$

Laboratories Process

In 12.5 gram pulp add 20 ml 10% Chloroacetic Acid for 30 minute filter it and then neutralized in 200 ml 10% NaOH. After drying 30 minute Steeping in 10% Acetic acid with water. Adding 6% $NaHCO_3$. Soack for 24 hours for getting C.M.C.

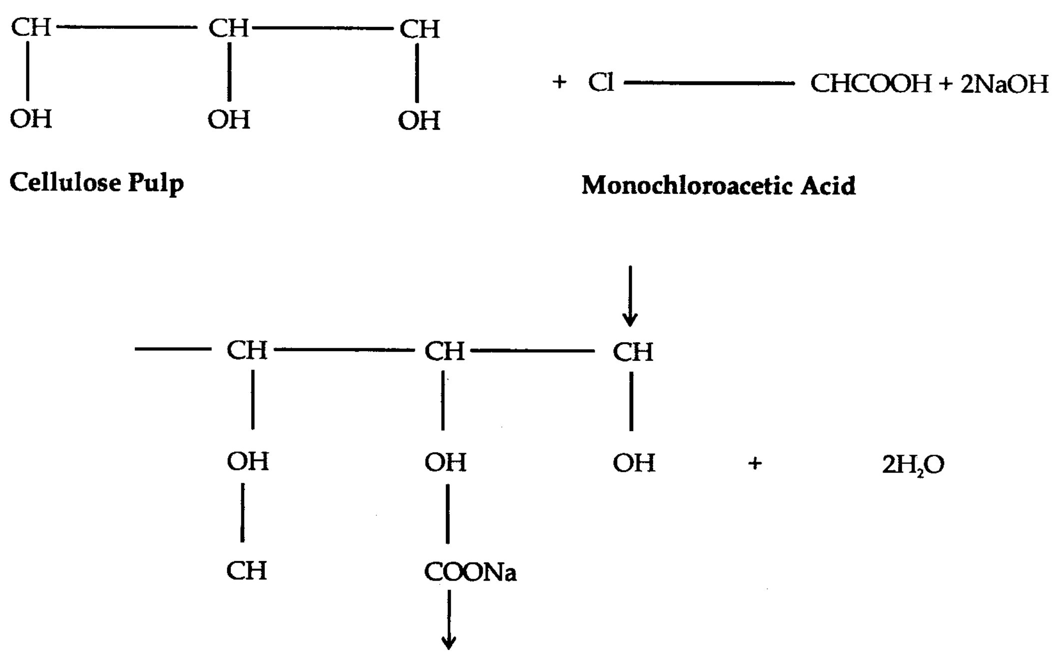
Paper making Properties of CMC Pulp

Chemically modified paper is tested for different parameter. Different parameter of paper is tested the Standard test procedure of TAPPI Standard Table 1.



Flow Diagram for C. M. C. upgradation Techniques

Chemical Reaction



Carboxymethyl Cellulose (C.M.C.)

Table 1. Paper Making Property of CMC Pulp

Parameter	Tappi No.	Parameter	Tappi No
Bursting strength	T-403	Tear factor	T-220
Tearing strength	T-414	Moisture	T-412
Tensile strength	T-404	Bulk density	T-21 OS-74
Rosin in paper	T-408 OS-74	Processing of Pulp	T-200 OS-70
Consistency	T-240 OS-75	Basis weight	T-412
Sheet Making	T-206 OS-71	Apparent density	T-21 OS-74

Table 1. Hydroxyl value of CMC Pulp vs Reaction Time

Time (Hrs)	Imported Pulp	Cotton Pulp
0.0	42.05	64.51
1.0	41.90	64.35
1.5	41.50	63.92
3.5	41.00	63.48
5.5	40.57	63.00
7.5	40.39	62.80

Hydroxyl value Determination

Hydroxyl value of Carboxymethylated pulp with respect to specific time should be investigated during the synthesis and recorded in a tabulated forms for Imported Pulp and Cotton Pulp.

Kinetics of Carboxymethylation

Development of Kinetics Model is important for synthesis of Carboxymethylation. To study the different parameter like Excess reactant, Limiting reactant, (CAO-CA), NAO, conversion, and Equilibrium Constant for deciding the Order of reaction. The main aim of the research is to study the Hydroxyl value (OH−) for different span of time which is a key role for acetylation for different types of pulps.

Cellulose + Chloroaceticacid = Carboxymethyl Cellulose (CMC)

Feed : 12.5 gram (6.25 ml) of pulp + 0.222 gram of Chloroacetic acid (200 ml) Sodium Hydroxide (200 ml) Acetic acid (25 ml) Water (100 ml) Sodium bi carbonate (50 ml)

Total Volume of Reactant = 631.25 ml. (0.631 liter)

Product : Carboxymethyl Cellulose (CMC)

As per Stiochiometry Calculation Excess Reactant (631.25 ml, 0.631 liter)

Limiting Reactant (Chloroacetic acid) : 0.222 gram : or 0.00234 gram mole

$$CA0 = NAO / V = 0.00234/0.631$$

$$= 0.003722 \text{ Gram Mole/Liter}$$

Amount of Chloroacetic acid reacted as per run :

$$\frac{(\text{Difference Delta} - OH) * 94.5}{56100}$$

$$= (CAO - CA)$$

$$\text{Conversion } (XA) = \frac{(CAO - CA)}{CAO}$$

$$\text{Equilibrium Constant } (K) = 1/t\,(-\ln CA / CAO)$$

RESULTS AND DISCUSSION

There is a Considerable reduction in Hydroxyl Value with time is Observed using Imported Pulp and Cotton Pulp. Paper making Properties depends on the Degree of

K can be calculated and represented Tables No 02 and Table No. 03

Substitution no adverse effect on the properties is obtained for Chemical Modification of the pulp. Rather paper made from the reacted pulp shows a better Properties such as Apparent Density, Molten Bursting Strength, Tearing Strength, than the Unreacted Pulp. As compared to cotton pulp, Imported Pulp observed to Exhibit Paper Characteristics. Hence Imported Pulp is more Suitable for Papermaking. Evolution of Characteristics shows the improvement in Tearing Strength for the Paper Sheet made from reacted Pulp (Imported Factor as Compared to the paper made from Unreacted Pulp, Effect of addition of Acid. Alkali and Alum on the Physical Properties of the Paper Sheet made from the Imported Pulp and Cotton Pulp was tested and improvement is observed in a Apparent Density, Molten Bursting Strength, Tearing Strength, and Opacity as Compared to Cotton Pulp, Specially with the addition of alkali to the Pulp.

Kinetics study Process that Monochloroacetic acid was

Table 2. Estimation of Carboxymethylation Reaction Parameter
Sample : Imported Pulp

Time (t)	CAO-CA	XA	-In(1-XA)	K(1/hr)
0.0	0.0	0.0	0.0	0.0
1.0	0.0002527	0.0678	0.07020	0.07020
1.5	0.0009266	0.2489	0.2862	0.1908
3.5	0.001769	0.4752	0.6447	0.1842
5.5	0.002469	0.6633	1.088	0.1979
7.5	0.002796	0.7514	1.391	0.1855

Table 3. Estimation of Carboxymethylation Reaction Parameter
Sample : Cotton Pulp

Time (t)	CAO-CA	XA	-In(1-XA)	K(1/hr)
0.0	0.0	0.0	0.0	0.0
1.0	0.0002527	0.0724	0.07515	0.07515
1.5	0.0009266	0.2670	0.3106	0.2071
3.5	0.001769	0.4661	0.6275	0.1793
5.5	0.002469	0.6835	1.1631	0.2115
7.5	0.002796	0.7740	1.4872	0.1982

Table 4. Characteristics of Carboxymethylated Pulp-I

Parameter –	Cotton Pulp		Imported Pulp	
Rosin : 1.5% and	with		with	
Alum : 4.0 %	without		without	
Tearing Strength	60	120	150	210
Bursting Strength	0.20	0.18	0.50	0.40
Bursting Factor	2.66	2.10	5.79	4.39

Table 5. Characteristics of Carboxymethylated Pulp-II

Parameter	Reaction	Cotton Pulp	Imported Pulp
Alum: 0.002%	Unreacted	Reacted	Reacted
Apparent Density	9.10	9.33	9.93
Molten B. Strength	34.0	34.9	68.9
Tearing Strength	8.78	9.88	13.98
Opacity	87.5	81.9	78.30

Table 6. Effect of Alkali, Acid and Alum

Parameter	Alkali	*	Acid	*	Alum	*
Alum : 0.001%	Cotton pulp	I. Pulp	Cotton pulp	I. Pulp	Cotton pulp	I.Pulp
Apparent Density	9.58	10.43	8.71	9.13	9.14	9.20
Molten B. Strength	48.2	77.9	37.5	38.8	40.6	40.90
Tearing Strength	12.32	16.68	9.59	9.60	9.82	9.78
Opacity	74.4	75.3	80.9	81.1	81.0	81.2

* I. Pulp -Improted Pulp

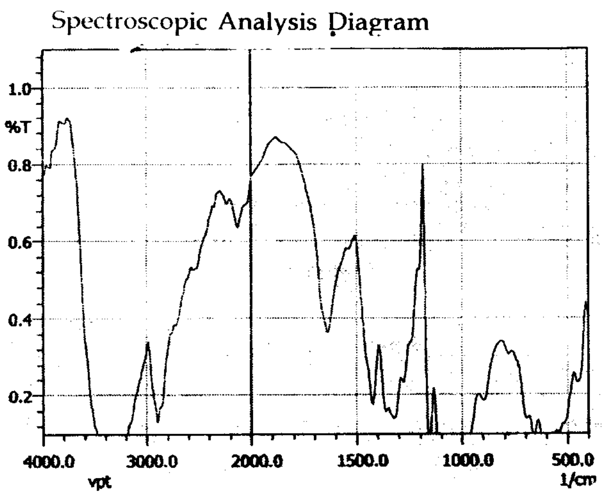


Figure 1. Bagasse Pulp Carboxymethylated

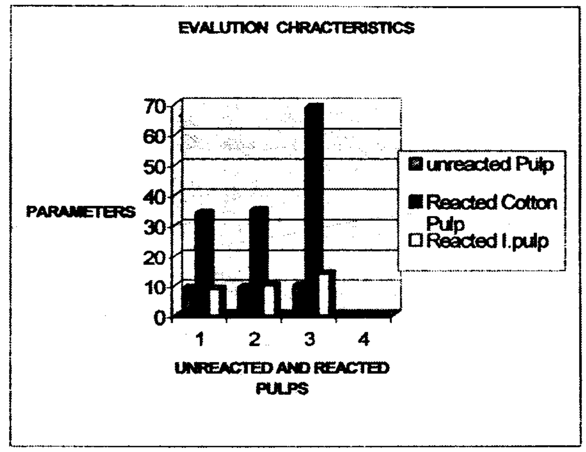


Figure 3.

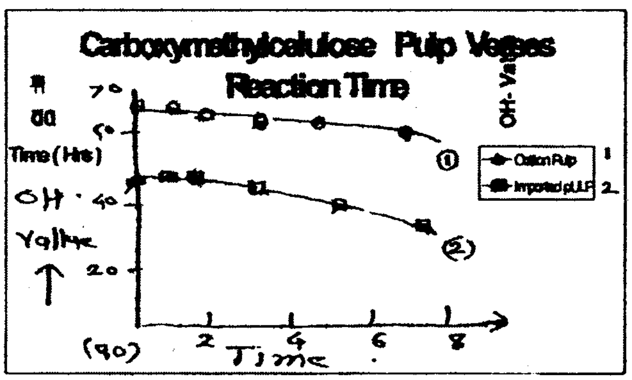


Figure 2. OH - Value verses Time in Hours.

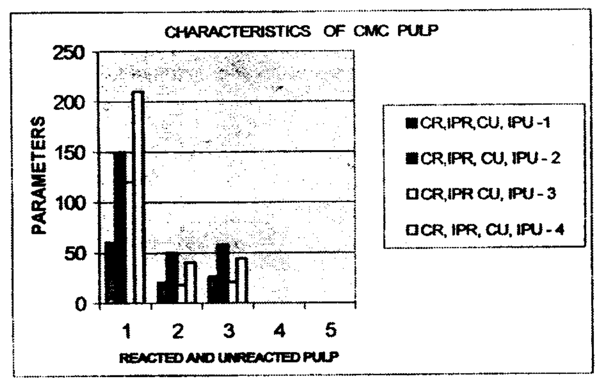


Figure 4. Reacted and Unreacted Pulp

the Limiting Reactant for the Product Carboxymethylcellulose (CMC) and Conversion data - In (1-XA) with respect to time (T) represents Straight-line relation ship with empirical equation Imported Pulp : Y = 0.188X. Cotton Pulp : Y = 0.198 X

Equilibrium Constant (K) = 1/t (-In CA/CAO)

The Carboxymethylation of a Cotton and Imported Pulp was conducted using Monochloroacetic acid. The change in Hydroxyl value as a function of a time during carboxymethylation have been presented in Table 1. Cotton Pulp has higher initial hydroxyl value than that of imported Pulp, Hence the rate of Carboxymethylation on was also higher for cotton pulp than that of imported Pulp. The first order kinetics expression based on calculation of fractional Carboxymethylation as a function of a time and has been presented in graph no. 8,9. The plot was linear and passing through the Origin confirming first order characteristics of Carboxymethylation reaction. The first order Carboxymethylation rate constants for Cotton Pulp and Imported Pulp. Has been 0.20 and 0.19 hr^{-1}s respectively.

The Carboxymethylation and Acetylation although were first order in nature. Later is rapid and requires 2-3 hours has less that previous reaction. While all the chemical modification described previously were casing increasing hydrophobic by way of replacement of Hydroxyl group with acetyl/ Cynoethyl groups Carboxymethylation imported Hydrophilic to paper by partial substitution of hydroxyl groups. kinetics of Carboxymethylation reaction has already been described and discussed. The reaction was found to follow first order kinetics. The goal of Carboxymethylation was to develop a method for the Preparation of low Degree of Substitution Carboxymethylation Cellulose Pulp, retaining the fibrous nature of the pulps and without exercise degradation. Further the Paper making behavior of these Pulps was observed and Physical strength properties on hand sheets formed frame these Pulp were determined

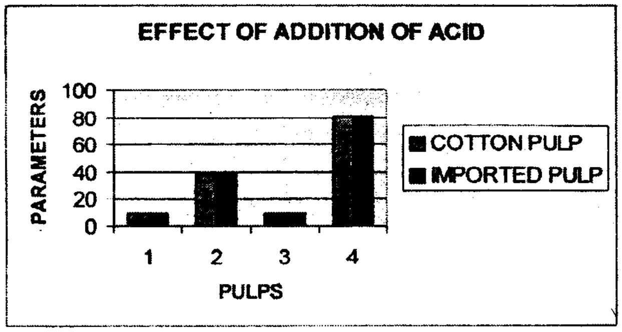


Figure 5. Effect of Addition of Acid

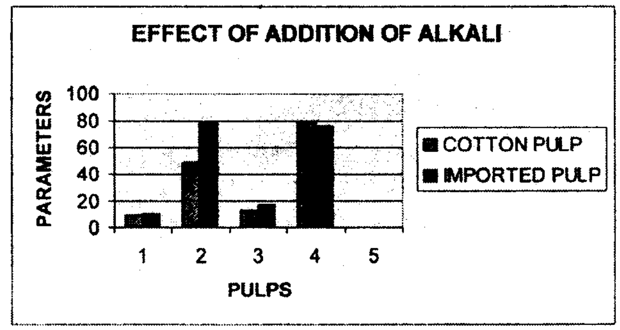


Figure 7. Effect of Addition of Alkali

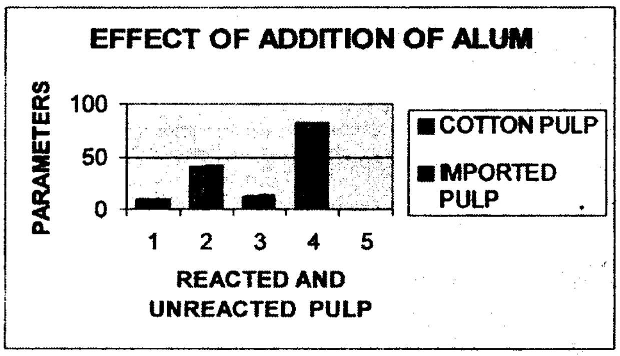


Figure 6. Effect of Addition of Alum

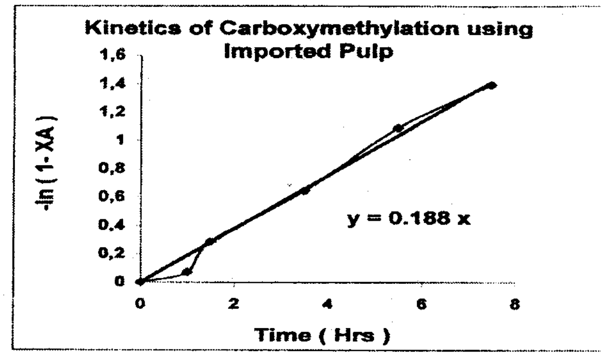


Figure 8. Kinetics of Carboxymethylation using Imported Pulp

Carboxymethyl group is Hydrophilic group. The Carboxymethylated pulp should have Properties that from both the Original Pulp and acetylated and Cynoethylated Pulps. The starting material for this study was cotton pulp and Imported Pulp with initial hydroxyl value of 64.5 and 42.05 respectively.

The table No. 3,4 describes paper characteristics of original and Carboxymethylated Pulp. An effort was made to restrict the reaction to low degree of Substitution. Carboxymethylation causes greater hydration of the fibre surfaces. The substituted groups participate in inter fibre bonding (Substituted hydrophobic group does not enter into normal inter fibre bonding).

The Degree of Substitution however is restricted in practice to a low value for reason of Solubility. Alkali and Water insolubility are required in the reaction and Paper making systems.

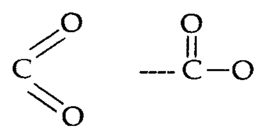
Improved the paper Properties (Tearing Strength, Bursting Factor and Bursting Strength) resulted from carboxymethylation of Cotton and Imported Pulp. Further treatment with alkali, acid and alum exhibited same trend. The result with Alkali treatment were superior than those obtained with acid and alum. The result have been shown in the form of bar charts No.

The explanation for improvement with Carboxymethylation can be presented as follows, the carboxymethyl group is more hydrophilic than the hydroxyl group. It has replaced and substitution probably disrupts the fibre structure making it less uniform and more accessible to water due to this the amount of water absorbed by the Pulp, the degree of Swelling of fibre and the Consequent plasticity of the fibre gets enhanced. The internal fibrillation in Carboxymethyl cellulose fibres and more soluble character of the interior of the fibres bring about and increase in bonding between cellulose chains within the fibre. The bonding within the fibre would create a more uniform structure, filling in some of the wids in the fibre and creating a stronger cellulosic fibre.

The chemical structure and composition of the product obtained by reaction of cellulose with chloroacetic acid is supported by above different characteristics IR absorption bands, the spectroscopic characterization of carboxymethylated samples as represented as graph no 01 bagasse pulp carboxymethylated.

Spectroscopic characterization

Table 7. The Spectroscopic Characterization of Carboxymethylated Cellulose samples is as follows:

Groups/Vibrations	IR absorption (cm^{-1})
* O -- H stretching of alcoholic groups and acidic groups	3600--3100
* O - H deformation and	1410, 1355, 1315
* C - O stretching	1260,
* O - H deformation of acidic group	950
* C - H Stretching of -- CH_2, CH group	2980-2820
* C-H deformation	1445, 1335
* C = O,  Groups (H - bonding and Salt)	1680 -- 1600
* Structure Modification Change in a position of Substituent	
* C - O Cyclic ether linkage	1105
* C - O of ---- COOH group	1250

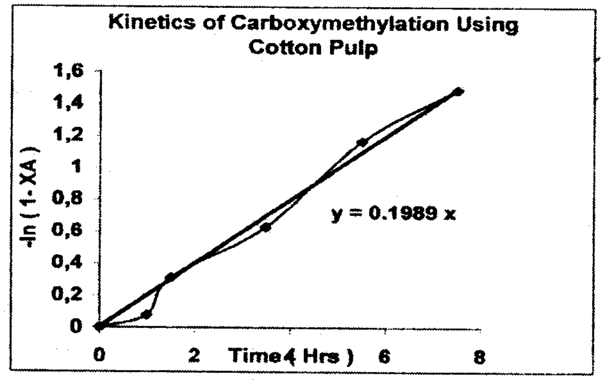


Figure 9. Kinetics of Carboxymethylation Using Cotton Pulp

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