Studies on Kinetics and Spectroscopic Characterisation of Acetylated Pulps

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ABSTRACT

Acetylation is expected to reduce the hydrogen bond density between -OH groups, increase water-repelling characteristics and enhance paper- making characteristics. The experimental acetylation procedure using DMF solvent and related calculation has been described. The reaction was monitored by determination of hydroxyl value at regular reaction intervals. The observation showing effect of acetylation on paper making properties have been reported. Kinetics of acetylation has also been reported by using integral method of analysis. The empirical observations were strengthened by IR spectrophotometer analysis using Shimadzu IR-800. The acetylation reaction was carried out at room temperature at 30 ^{0}C at a time. The time for the reaction varied between 5 to 8 hours, which depends on hydroxyl value of acetylated pulp. The acetyl content of acetylated bagasse, bamboo and waste paper pulp were estimated and found to contain 5.26 %, 4.96 % and 5.11 % respectively.

Characterization of acetylated pulp was conducted and hydroxyl values were determined at regular interval. Considerable reduction in hydroxyl value with time was observed using bagasse pulp, bamboo pulp and wastepaper pulp. As per hydroxyl value obtained, bagasse pulp acetylation equilibrium was established after 8 hours and low hydroxyl value was found. In case of bamboo pulp highest hydroxyl value, equilibrium established after 6 hours., and had waste paper pulp observed intermediate hydroxyl value and equilibrium established after 7 hours. The first order rate constant, for bagasse pulp, bamboo pulp and waste paper pulp were 0.177 0.188 and 0.196 hr^{-1} respectively.

The changes in properties of paper after acetylation were visualized. The acetylation did not bring any change in weight per unit area of pulp as indicated by GMS value. Acetylated waste paper pulp and bagasse pulp did not exhibit change in burst factor, at 80 GSM. . Acetylated bamboo pulp exhibited 33 % increase in burst factor. The effect of acetylation on tear force, tear factor and tearing strength of pulp was found to be remarkable. At lower degree of acetylation, the enhancement in tear factor was very high. With further acetylation, the tear factor increases was small and at further increase in degree of acetylation, tear strength decreased. The folding endurance of acetylated bamboo pulp was found to be excellent (almost 100 % increase), The acetylated product was characterized by IR Spectroscopy to conform the acetylation of cellulose pulp. In this case, the **- OH** group of bagase pulp was expected to convert to

— O C CH $_3$ group

Key words: Degree of acetylation, kinetics, spectra, folding endurance and acetyl content

INTRODUCTION

Jayme (1) and Frouundjian (4), Bletzinger (5) and Aiken (6) demonstrated that slight methylation of pulp appreciably increased the paper strength. Walecka (7) showed that substitution by hydrophilic groups greatly magnifies the increase in sheet strength. Higgins and co workers (12-15) found that the strength of paper from beaten acetylated pulps is also increased only at low substitution and that beyond this point decreased sharply. Mckerzise and Higging (16-19) obtained similar result on eucalyptus pulp. An introduction of hydrophobic groups like few acetyl into the cellulose molecule is a physical distortion of the fiber structure. The fiber structure opens up and prevents the hydrogen bonding between the cellulose hydroxyls in the vicinity of the acetyl group. This facilitates moisture sorption and swellings.

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 products. Some of the natural sources having high content of the cellulose are listed in the table:

TABLE: 1.1 Natural Sources of Cellulose

SR NO	MATERIAL	CELLULOSE (%)
1	Jute	70
2	Straw and bamboo	50
3	Bamboo	50
4	Wood and flax	50
5	Hemp and Cotton	90
6	Cotton Linters	95

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Cellulose has the empirical formula $(C_6 H_{10} O_5)_n$ corresponding to a glucose anhydride unit. Cellulose is a straight chain polymer of anhydroglucoses, in which glucose units are linked by β-1-4 linkages (20-23).

EXPERIMENTAL METHODOLOGY

Acetylation of cellulose fibers

Acetylation of cellulose with acetic anhydride yield cellulose tri-acetate empirical formula $C_6H_7O_5(CH_3COO)_3$

In the present work acetylation of cellulose was carried out with acetic anhydride as a acetylating agent and dimethyl formamide (DMF) as a solvent

Chemicals used: The chemicals used in the acetylation of pulp were 1N alcoholic KOH, 1N oxalic acid, acetic anhydride, dimethyl formamide, 10% sulfuric acid, acetic acid and butanol. All chemicals were standard and readily available, 99 % AR Grade materials were used. (Quligen, Bombay India)

Cellulose Materials for acetylation

Bagasse pulp, bamboo pulp and wastepaper pulp were used as cellulose materials. These were supplied by Nepa Ltd., Nepanager, Vindhya Paper Mill, Duskheda, and Bhusaval

Procedure for Acetylation of Cellulose pulp

Cellulose pulp (50 g), diamethyl formamide (350 g), acetylating reagent consisting of equal quantities of glacial acetic acid and acetic anhydride (20 g) were placed in three necked 1000 ml round bottom flask fitted with agitator. The reaction was carried out at room temperature (30^0C). for 7 hours. At this stage the cellulose product was viscous liquid containing small quantity of suspended cellulose triacetate formed. Then it was diluted with equal parts of conc. Acetic acid, containg small quantity of 10 % sulphuric acid. as a result of which the precipitate of triaceatate formed during the acetylation gots hydrolyzed to the soluble secondary acetate and completion of reaction is indicated by disappearance of fibers completely. It took about 15 to 20 hours at room temperature. At this stage, acetylated pulps, (Bagasse pulp, Bamboo pulp and Waste paper pulp) were prepared using various reaction time (0, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0,4.5 hrs) and analysis was performed with mass taken out from the reaction mixture to determine its hydroxyl value.

This clear viscous liquid was poured into a plastic bucket containing 10 liter of water, to stop further hydration and to precipitate secondary cellulose acetate. It was then centrifuged; washed with water and dried in a dryer at 60 to 80 ^{O} C. The final product is dried cellulose acetate flakes and the yield was approximately 35 gm.

In case of acetic anhydride as acetylating agent, the active part is acetic acid, which acts as acetylating agent and the water is by product. Hence acetylation with acetic anhydride is irreversible, while with acetic acid it is reversible reaction. Acetic anhydride was thus preferred for acetylation of cellulose pulp.

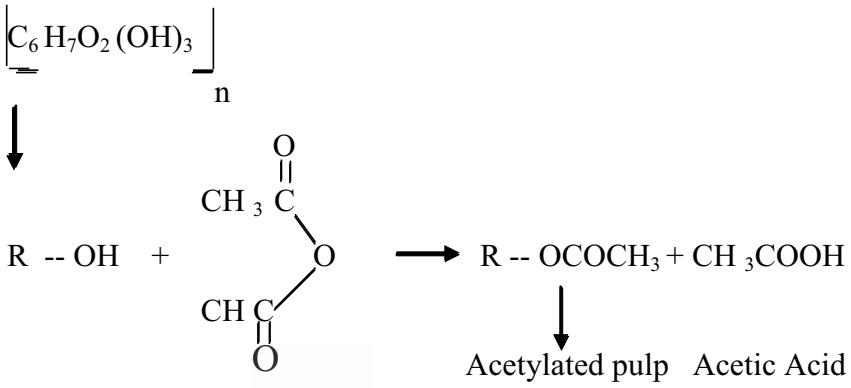
Characterization of Acetylated Pulp

The procedure described below to determine hydroxyl value; sheet making and testing of the paper sheets made from acetylated pulp was common for all pulps. The result of the experiments are tabulated in table No: 1.5 to 1.7

Method of Determination of Hydroxy Value (11)

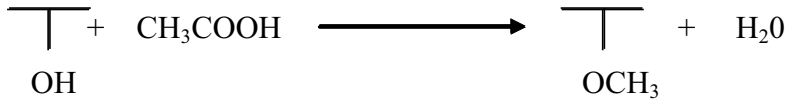
0.2 g of the pulp was placed in a round flask and add 10 ml of acetylation reagent (i part of acetic anhydride+7 parts of diamethy1 formamide) was added to the pulp with the help of piptte. Reflux condenser was attached to the flask and mixture was refluxed for 2 hrs. Distilled water (2ml) was added through a reflux condenser and the reaction mixture was then further refluxed for 30 min. Butanol (30 ml) was added through the condenser and

Chemical Reaction:



R = Remainder of cellulose molecule

The side reaction could be



(Intial and Final Reading Calculation)

TABLE: 1.2 (A) Amount of KOH required for time, t=0, and t=4.5h

Blank Reading For all samples	Volume of KOH required. Back Reading in (ml)		Hydroxyl Value (mg of KOH per g of sample)	
(28.7 ml)	t=0,	t=4.5 h	t=0,	t=4.5 h
Bagasse pulp	22.50	22.80	760	720
Bamboo pulp	21.40	21.80	885	841
Waste Paper pulp	22.00	22.30	820	778

TABLE: 1.3 Hydroxyl values for acetylated cellulose from different cellulose pulps at different time interval

SR NO	Time in Hours	Hydroxyl value of acetylated cellulose sample (mg of KOH per g of sample)		
		Bagasse Pulp	Bamboo Pulp	Waste Paper Pulp
1	0.0	760	885	820
2	1.0	754	877	813
3	1.5	749	871	808
4	2.0	742	866	799
5	2.5	735	861	792
6	3.0	729	856	786
7	3.5	725	850	782
8	4.0	722	845	780
9	4.5	720	841	778

TABLE: 1.2 (B)% Acetyl content of different cellulose pulps

Sr NO	Sample	Acetyl (%)
1	Bagasse	5.26
2	Bamboo	4.96
3	Waste paper	5.11

TABLE: 1.4 % Degree of acetylation for different cellulose pulps at different time interval

Sr No	Time (Hr)	% Degree of Acetylation of Cellulose sample		
		Bagasse Pulp	Bamboo Pulp	Waste paper Pulp
0	0.0	0.0	0.0	0.0
1	1.0	0.789	0.9032	0.8533
2	1.5	1.44	1.58	1.46
3	2.0	2.36	2.14	2.55
4	2.5	3.28	2.70	3.41
5	3.0	4.07	3.27	4.14
6	3.5	4.60	3.95	4.63
7	4.0	4.99	4.51	4.87
8	4.5	5.26	4.96	5.11

the total contents were titrated against (0.87 N) potassium hydroxide using phenolphthalein as indicator. A blank experiment was carried out under same reaction conditions. Volume of 0.87 potassium hydroxide required to neutralize acetyl reagent and pulp sample was determined and the hydroxyl value was calculated using empirical equation as given below.

Hydroxyl Value **(OH)** =

$$\frac{(B-S) \times N \times 56.1}{W}$$

Where,

B=Volume of KOH solution in ml (Blank)

S=Volume of 0.87 N KOH Solution in ml

N=Normality of Potassium Hydroxide (0.87 N)

W=Weight of Pulp Sample in g (0.4 g)

56.1=Molecular Weight of Potassium Hydroxide.

Hydroxy1 value is calculated for period between 0 and 4.5 hr in table no:1.2 (A). And remaining values of the result of the experiment of different samples like bagasse pulp, bamboo pulp and waste paper pulp for every half hr are tabulated in table No :1.3

Method of determination of acetyl content (10)

Dried cellulose acetate (1.9 g) was dissolved in 150 ml of mixed solvent of acetone and diamethyl sulfoxide (4:1in volume ratio). Then 1 N sodium hydroxide aqueous solution (30 ml) was added .The mixture was allowed to stand at 25^{o} C. to saponify. Then phenolphthalein solution was added as an indicator and the excess sodium hydroxide was titrated with 1N sulphur--ic acid till pink colour disappeared. Blank experiment was carried out under identical condition except sample.

$$\text{Acetylation (\%)} = \frac{6.005 \times (B\ A)}{W}$$

Where,

A = ml of 1N H_2SO_4 used for sample titration.

B = ml of 1N H_2SO_4 used for Blank titration.

W = Weight of sample in g

6.005 Calculation factor for acetyl content

The result of the experiment of different samples like bagasse pulp, bamboo pulp and waste paper pulp were tabulated in table No: 1.2 (B), and Fig: 1.2. % Degree of acetylation was calculated from the hydroxyl value obtained for period between 0 to 4 hr for every half hr. in table no:1.4

$$\text{\% Degree of Acetylation} = \frac{(X - Y) \times 100}{X}$$

X = Initial hydroxyl value

Y = Final hydroxyl value

Procedure for papermaking

The 50-g of acetylated pulp obtained from above given method and was first disintegrated at 2.5 % consistency and it was suspended in water. The slurry was tested for freeness as per TAPPI

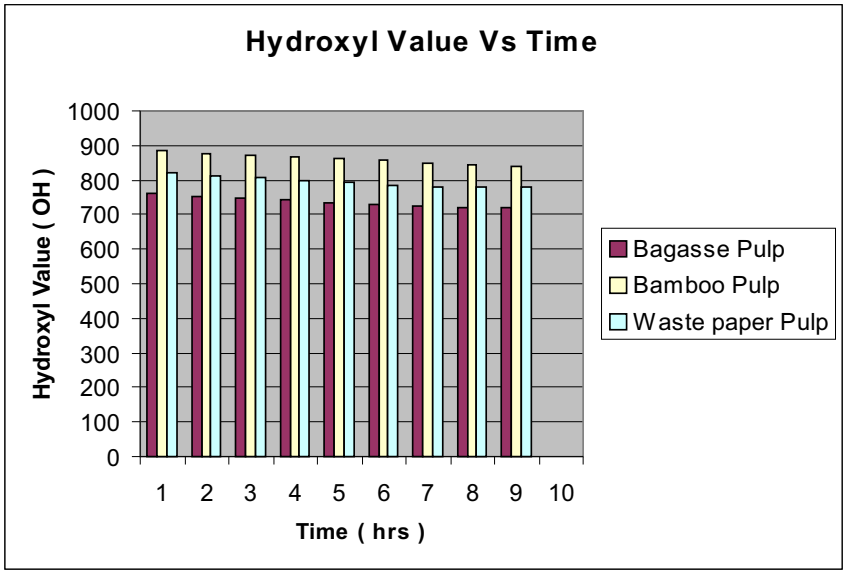


Fig: 1.1 Hydroxyl value (mg of KOH per g of pulp) of acetylated pulps Versus reactions time in hours .Bar chart of hydroxyl value for bagasse pulp, bamboo pulp and waste paper pulp.

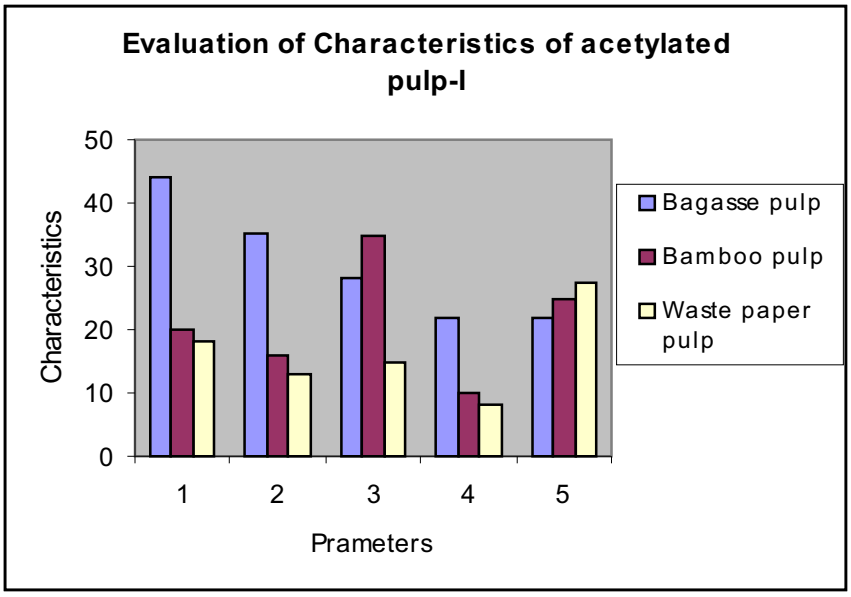


Fig: 1.2 Evaluation of characteristics like 1) Tear factor 2) Tear force, 3) Freeness 4) Tearing strength, and 5) Burst factor for bagasse pulp, bamboo pulp and waste paper pulp

Standards (T-227, OS-58). The sizing material, rosin 1.5 % and and alum 4.0 % on the oven dry weight basis of pulp were added to the slurry. Each time solution was disintegrated for 5 min. 100ml of sample was taken out from this slurry and poured in sheet making machine to fill the equipment up to the mark and then all the water was removed from the equipment by suction. The pulp settled down at the bottom of the equipment on wire mesh in the form of sheet. The sheet of butter paper was placed above the pulp and pressed with roller. The sheet of filter was obtained after removing filter paper, which was kept for curing and drying. The dried paper was then tested for various properties in the laboratory as per TAPPI Standards.

Testing of Paper Sheets

All the tests of paper sheets were carried out under Standard condition (as per TAPPI standard,) i) Bursting Strength, ii) Tearing Strength: iii) Folding Endurance: iv) Tear factor: v) Tensile Strength, vi) Freeness, vii) Opacity, viii) Tensile Strength: ix) Brightness: The results of the comparison of characteristics were represented in Fig: 1.2

Development of Kinetics Model for Acetylation by using Integral Method of Analysis, (24-26)

The method assumed a particular mechanism (first order, second order and third order); and obtained correspounding time dependent form of rate equation by integration of differential form. The concentration data was fitted in concentration dependent form and plotted against time. If the graphical plot can be fitted in the form of linear plot passing through the origin, the assumption was correct and proves applicability of the reaction mechanisum. In case the plot was not linear; another reaction mechanisum was assumed and the procedure was repeated. The method has definite advantages over differenti--al method of analysis and hence was applied in present investigation for interpretation of kinetics data of acetylation of bagasse pulp, bamboo pulp and waste paper pulp.Initially, first order acetylation mechanism was assumed:

Cellulose + acetic anhydride = acetylated cellulose

A = Product

The rate of Reaction (- ra) = - d CA / d t = k CA ------- (1)

On integration of equiation 1 , We get ,

$$- \ln (CA / CA_0) = K t$$

The result of reaction can also be expressed in terms of fractional conversion

Concentration of A,

$CA = NA / V$, $= NA_0 (1 - XA) / V$, $= CA_0 (1 - XA)$ $= - d CA = CA_0 . d XA$

Substituting the value of - d CA in equation 1, we get, $d XA / d T = K (1 - XA)$

On Integration with respect to their variable, we get, $- \ln (1 - XA) = K t$

Where,

K = First order reaction rate constant in Sec^{-1}

CA = Concentration of reactant A, at specific time, (moles per liter)

CA_0 = Concentration of Reactant A at t = 0 (g mole per liter)

NA_0 = Moles of reactant A initially at t = 0 (g mole per liter)

V = Total volume of reactant in (ml)

(XA)= Fractionatioal conversion $(CA_0 - C_A) / CA0$

CA0 = Gram mole per liter of Acetic

TABLE: 1.5 Estimation of parameters for acetylation of Bagasse Pulp

Time (t) Hrs	CAo – CA Gram per liter	XA Conversion	-ln (1-XA)	K (1 / hr) Eq.Constant
0.0	0.0	0.0	0.0	0.0
1.0	0.01101	0.08320	0.08686	0.08686
1.5	0.02019	0.1524	0.1653	0.1102
2.0	0.03304	0.2495	0.2870	0.1435
2.5	0.04590	0.3466	0.4255	0.1702
3.0	0.05691	0.4298	0.5671	0.1890
3.5	0.06426	0.4853	0.6641	0.1897
4.0	0.06976	0.5269	0.7484	0.1871
4.5	0.07344	0.5546	0.8087	0.1797

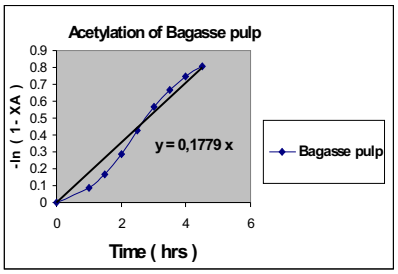


Fig: 1.3 Graph of-ln (1- XA) Versus time in hours for acetylation of bagasse pulp

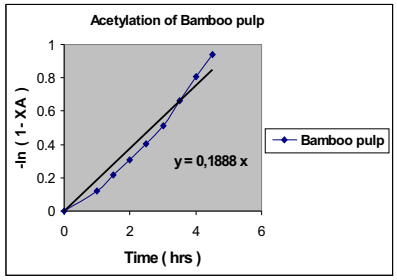


Fig: 1.4 Graph of-ln (1- XA) versus time in hrs for acetylation of bamboo pulp

TABLE: 1.6 Estimation of parameters for acetylation of bamboo pulp

Time (t) Hr	CAo – CA Gram per liter	XA Conversion	-ln(1-XA)	K (1 / hr) Eq.Constant
0.0	0.0	0.0	0.0	0.0
1.0	0.01468	0.1109	0.1175	0.1175
1.5	0.02570	0.1941	0.2157	0.1438
2.0	0.03488	0.2634	0.3057	0.1528
2.5	0.04406	0.3328	0.4046	0.1618
3.0	0.05324	0.4021	0.5143	0.1714
3.5	0.06426	0.4853	0.6641	0.1897
4.0	0.07344	0.5546	0.8087	0.2021
4.5	0.08078	0.6101	0.9418	0.2092

anhydride (Limiting Reactant) The calculated K value are represented in Tables No:1.5, 1.6, 1.7, and in Fig: 1.3, 1.4, and 1.5

Characterization of acetylated Bagasse Pulp, Bamboo Pulp and Waste Paper Pulp by IR Spectroscopy (27-29)

Procedure: The instrument used for IR characterization was Shimadzu Forrier Transform Infrared Spectrophotometer, (FTIR) of 800 series adding the thin film technique. The chemically modified paper was converted to thin film and % transmission (T) vs wave number (v) Spectrum was obtained. The peaks were examined and interpreted on the basis of Standard library, IR functional group analysis. Thus acetylation modification of bagasse pulp, bamboo pulp and waste paper pulp were expected to provide spectrum indicating replacement of hydroxyl group by acetyl ($-OCOCH_3$) group. Thus IR Spectroscopic characterization formed a significant modification monitoring technique. Spectroscopic characterizat--ion of acetylated bagasse pulp, bamboo pulp and waste paper pulp were represented in Table 1.8

The additional absorption band in IR spectrum of acetylated pulp are represented in Table no : 1.8 at 1870-1605 for

C= O of --- $\overset{O}{\overset{\|}{C}}CH_3$ group and at 1420- 1370 for CH_3CO group clearly confirm in corporation of acetyl group in the pulp.

Characterization of Un-acetylated Bagasse Pulp, Bamboo Pulp and Waste Paper Pulp by IR Spectroscopy (27-29)

Procedure: The instrument used for IR characterization was Shimadzu Forrier Transform Infrared Spectropho--tometer, (FTIR) 800 series and the thin film technique. The Un modified paper was converted to thin film and % transmission (T) vs wave number (v) Spectrum was obtained. The peaks were examined and interpreted on the basis of Standard library, IR functional group analysis. Spectroscopic characte--rization of Un-acetylated bagasse pulp, bamboo pulp and waste paper pulp are represented in Table 1.9 and

TABLE: 1.7 Estimation of parameters for acetylation of waste paper pulp

Time (t) Hrs	CAo – CA Gram per liter	XA Conversion	-ln(1-XA)	K (1 / hr) Eq.Constant
0.0	0.0	0.0	0.0	0.0
1.0	0.01285	0.09706	0.1020	0.1020
1.5	0.02203	0.1663	0.1770	0.1180
2.0	0.03855	0.2911	0.3440	0.1720
2.5	0.05140	0.3882	0.4913	0.1965
3.0	0.06242	0.4714	0.6375	0.2125
3.5	0.06976	0.5269	0.7484	0.2138
4.0	0.07344	0.5546	0.8087	0.2021
4.5	0.07711	0.5806	0.8690	0.1931

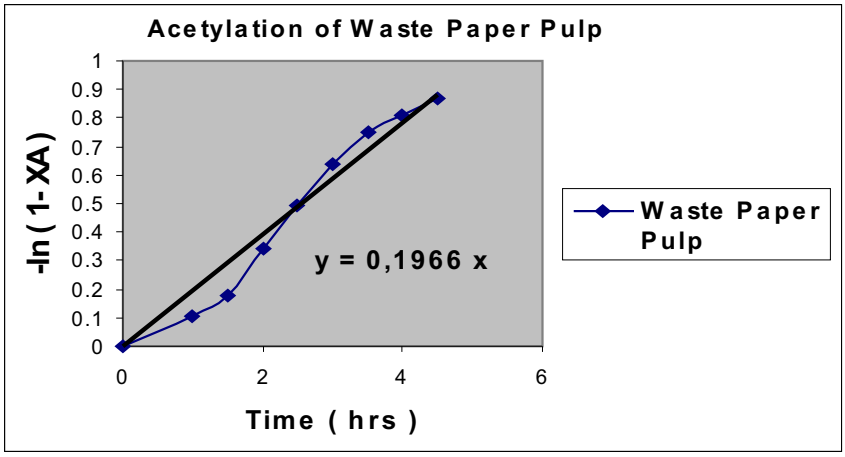


Fig: 1.5 Graph of-ln (1- XA) Versus time in hour for acetylation of waste paper pulp

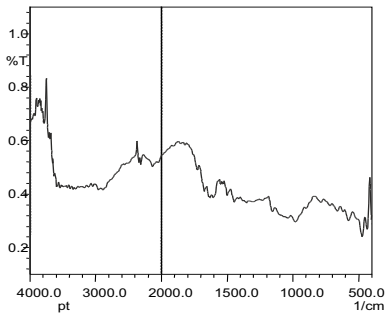


Fig: 1.6 IR Spectra for Acetylated Bagasse pulp

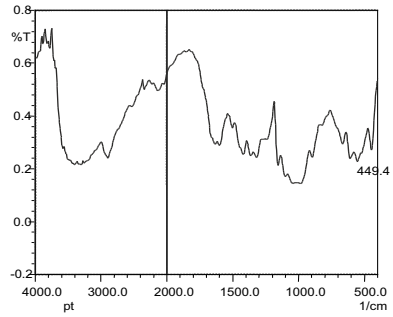


Fig: 1.7 IR Spectra for Acetylated Bamboo pulp

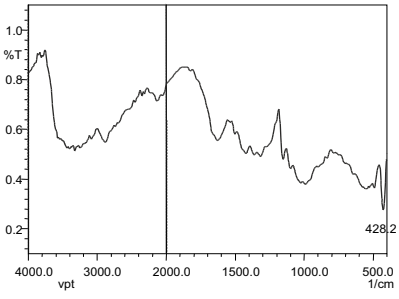


Fig: 1.8 IR Spectra for Acetylated waste paper pulp

figures are represented in Fig. 1-9, Fig-1.10 and Fig-1.11

RESULTS AND DISCUSSION

Acetylation involves reaction between hydroxyl group present in cellulosic structure and acetic anhydride. Acetylation was expected to reduce the hydrogen bond density between -OH groups, which increases water-repelling characteristics and enhance paper-making characteristics. The bagasse, bamboo, and waste paper pulps were acetylated using acetic anhydride in DMF solvent. The reaction was monitored by determinat--ion of hydroxyl value and degree of acetylation at regular reaction time intervals. The observations related to acetylation are reported in table 1.2, 1.3 and 1.4, and that for paper making characteristics represented in Fig 1.2. The observation and calculation related to the kinetics model study as-ln (1-XA) versus time are reported in table 1.5, 1.6,1.7 and Fig: 1.3,1.4,1.5. for bagasse, bamboo, and waste paper pulp respectively.

Euilibrium constant was calculated for different interval of time and it was observed that acetylation of bagasse pulp, bamboo pulp and waste paper pulp gave a first order kinetic model. The first order acetylation rate constants for bagasse pulp, bamboo pulp and waste paper pulp were 0.135, 0.168 and 0.176 hr^{-1}, respectively. Thus, the rate of acetylation of bamboo pulp was 2.5 and 1.5 times that of bagasse pulp and waste paper pulp. The idea was to determine the kinetics by using integral method of analysis.

Knowledge of rate constant is essential to design the reactors. A higher rate constant implies lower reactor volume for given conversion. Hence the volume of acetylation reactor was lowest for bamboo pulp amongst all the pulps. Though the reaction was first order, the acetylation was gradual unlike second order, where initial conversion was very rapid and hydroxyl value decreases exponentially in a terminal reaction. A considerable reduction in hydroxyl value with time was observed using bagasse pulp, bamboo pulp and waste paper pulp. As per table, 2.3 hydroxyl value for acetylation of bagasse pulp, equilibrium was established after 3 hours and low hydroxyl values were observed. In case

TABLE: 1.8 Spectroscopic Characterization of Acetylated Bagasse Pulp, Bamboo Pulp and Waste Paper

SR NO	Groups / Vibrations	IR absorption (cm^{-1})
1	* O--H stretching of -- OH groups ? O-H deformation	3650 – 3200 1400, 1350,
2	* C-H stretching of CH_3 -- CH_2 -- and $>C=CH$ groups * C-H deformation of CH_2 , -- CH2 O --- CH_3 , CH_3CO and $>C=C$ -- H	2960 –2805 1460, 1420- 1370
3	* C-O stretching of alcoholic C--OH Bonds * C-O of ether linkage (cyclic) * C-O -- O C – CH_3 group * C-O of CH_2O CH_2 groups	1350, 1305, 1107, 1050 1107 1245 1070
4	* C = O of --O C CH_3 group (H- bonding involved)	1670--- 1605

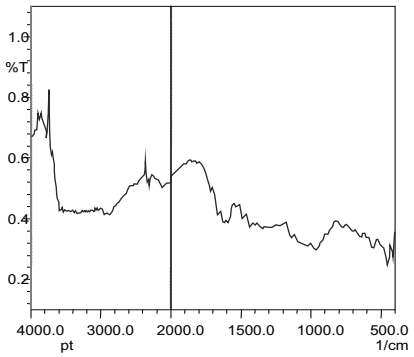


Fig: 1.9 IR Spectra for Un-Acetylated Bagasse pulp

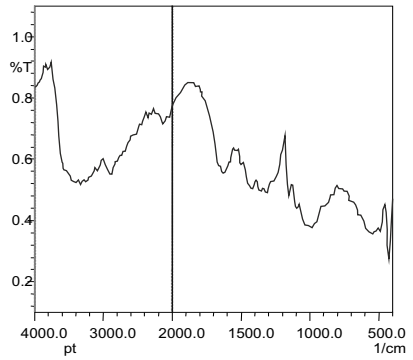


Fig: 1.10 IR Spectra for Un-Acetylated Bamboo pulp

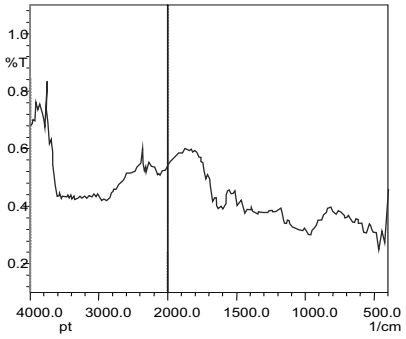


Fig: 1.11 IR Spectra for Un-Acetylated waste paper pulp

of bamboo pulp equilibrium was established within 4 hours. It had higher hydroxyl values in comparison to that of bagasse pulp. In case of waste paper pulp, intermediate hydroxyl value was observed and equilibrium was established after 4 hours. The empirical observations were strengthened by IR spectrophotometer analysis using Shimadzu IR-800 instrument and are shown in Fig: 1.6, 1.7, and 1.8. for bagasse, bamboo and waste paper pulp respectively.

Effect of Acetylation on Mechanical Properties

The unreacted hydroxyl groups as well as acetylated group of cellulose contribute to the properties of paper. Table: 1.3 reports the progress of acetylation reaction for the three different pulps, mainly bagasse pulp, bamboo pulp and waste paper pulp. The changes in properties of paper after acetylation can be visualized from observations recorded in a Table 2.5,2.6, and 2.7.The acetylation being partial, it did not bring any change in weight per unit area of acetylated paper. It is indicated by GSM values before and after acetylation for all three pulps. Thus acetylation did not cause any change in specific surface. The effect of introducing a hydrophobic group like acetyl into the cellulose molecules is a physical distortion of the fiber structure. . The partial introduction of acetyl groups prevents hydrogen bonding between cellulose hydroxyl in the vicinity of the acetyl groups.

I)Burst Factor and Bursting Strength

It was observed that bagasse pulp and waste paper pulp have a similar effect on burst factor and bursting strength after acetylation. At low GSM. (80), the partial acetylation caused no change in bursting strength. However with increase in GSM (or decrease in specific surface) the presence of higher number of acetyl groups per unit weight reduced hydrogen bonding in the vicinity of hydroxyl groups. Hence increase in GSM. had caused enrichment of bursting strength and bursting factor after acetylation. With bamboo pulp the degree of acetylation was more in comparison to that in bagasse and waste paper pulp. At 80 GSM, acetylated bamboo pulp exhibited 33 % increase in burst factor. No change in burst factor was observed

TABLE: 1.9 Spectroscopic Characterization of UnAcetylated Bagasse Pulp, Bamboo Pulp and Waste Paper

SR NO	Groups / Vibrations	IR absorption (cm^{-1})
1	* O--H stretching of -- OH groups	3660 – 3210
	O-H deformation	1416, 1342,
2	* C-H stretching of -- CH_2 -- and =CH groups	2971 –2812
	* C-H deformation of CH_2 , -- CH2 O ---	1462,
	and =C -- H	1422- 1365
3	* C-O stretching of alcoholic C--OH Bonds	1354, 1304, 1112, 1052
	* C-O of ether linkage (cyclic)	1110

with bamboo pulp at 85 GSM.

II) Tear force, Tear factor and Tearing Strength

The remarkable + ve and-ve effect of acetylation on tear force, tear factor and tearing strength of pulp was found. The degree of acetylation was increased in the decreasing order, bagasse pulp, bamboo pulp, and waste paper pulp. The enhancement in tearing strength was highest (70 %) with bagasse pulp and moderate with waste paper pulp (35%) however 20 % drop in tear strength was observed with acetylated bamboo pulp. Thus tear factor was found to be more sensitive with degree of acetylation than the burst factor. At lower degree of acetylation the enhancement in tear factor was very high.

III) Folding Endurance and Freeness:

With a partial acetylated bamboo bagasse and waste paper pulp, there was a positive effect on folding endurance and freeness. The enhancement in folding endurance of acetylated bamboo pulp was found to be excellent and almost double.

Thus acetylation at a lower degree was found to enhance tearing strength, bursting strength and folding endurance. In short acetylation was found to be useful chemical upgradation technique for improveme - -nt of paper making characteristics of pulps.

iv) Spectroscopic Characterization

In spectroscopic characterization of bagasse, bamboo and waste paper pulps by Shimndzu IR-800 Instrument, it is clear that acetic anhydride could incorporate acetyl group in the cellulose structure through acetylation of cellulose. This data confirms the proposed chemical structure and composition of the product

Acetylation of bagasse pulp, bamboo pulp and wastepaper pulp were carried out with acetic anhydride in DMF. The acetylated product was characterized by IR Spectroscopy to confirm the reaction. In this case, the **- OH** group of bagasse pulp, bamboo pulp and waste paper pulp was expected to convert into

group

The IR Spectroscopic Characterzation data of the acetylated bagasse pulp, bamboo pulp and waste paper pulp was summarized in table No: 1.8, Fig: 1.6, and 1.8. respectively

% Transmittance (T) verses wave number (v) in cm^{-1} clearly showed the presence of

* ---C--- (1670 - 1605 cm^{-1})
* C --O (12 45 cm^{-1}) and
* CH_3CO (1420 - 1370 cm-1) of

group

The IR Spectroscopic characterization data of the acetylated bagasse pulp, bamboo pulp and waste paper pulp is summarized in table No: 1.8, and Fig: 1.6, 1.7, and 1.8 .respectively and unacetylated data is summarized in table No:1.9

CONCLUSIONS

1. Estimation of hydroxyl values signified the degree of acetylation of paper pulp.

2. Degree of acetylation increased with increase in time for reaction between cellulose and acetic anhydride.

3. Degree of acetylation of bagasse pulp, bamboo pulp and waste paper pulp was 5.26 %, 4.96 % and 5.11 % respectively.

4. Acetylation of pulp was found to be useful in chemical upgradation Technique, for Improvement of paper making characteristics of pulp.

I) Acetylation of pulp improved the bursting strength. At higher degree of acetylation the bursting strength did not improve.

II) Tear factor was found to be more sensitive with degree of acetylation than the burst factor.

III) Tearing strength was highest 70 % with bagasse pulp and moderate with waste paper pulp 30 % and dropped by 20 % in bamboo pulp.

IV) The folding endurance of acetylated bagasse pulp, bamboo pulp, and wastepaper pulp were found increased.

V) Acetylation was observed to follow first order kinetics and reaction rate constants for bagasse, bamboo and waste paper

pulp were 0.135,0.168, and 0.176 hr.

5. IR Spectroscopy analysis indicated the formation of acety1 group.

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