Cellulose Derivatives from Jute Stick, An Agrowaste

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ABSTRACT

A study for making cellulose derivatives from jute stick has been carried out for utilization of large amount of jute stick available after extraction of golden jute fibre. For obtaining cellulose with high purity from jute stick, two stage pulping process was followed i.e. prehydrolysis followed by Kraft pulping. Different prehydrolysis and Kraft pulping conditions were used to produce pulp with different -Cellulose content to be used for different possible uses. Jute stick pulp containing 93% -Cellulose was to produce cellulose derivatives like CMC-Na and Microcrystalline Cellulose. Characterization of jute stick pulp was done. High -Cellulose containing jute stick cellulose pulp was compared with different standard commercial cellulose pulps available in the market. Specification for Microcrystalline Cellulose obtained from jute stick cellulose has also been listed.

INTRODUCTION

Cotton, linter, forest wood, bamboo etc. are the conventional sources of cellulose for manufacturing of various cellulose derivatives, viscose rayon, cellophane etc. A cheaper source of cellulose would be the agro-wastes, which may have no commercial value at present and which should contain appreciable amount of cellulose.

Jute Stick is one of such potential raw materials. It is the waste material left after extraction of jute fibre by retting process. The amount of stick, core portion of whole jute plant amounts nearly two and half times of jute fibre and is available to the tune of three millions tons a year. Its chemical composition is similar to hard wood, contains 40% of -cellulose but its physical structure is different; it is soft though fibres are short. Jute Sticks have been found to give good quality particle board[1], paper[2], charcoal[3], oxalic acid[4], etc., but its use as source of cellulose is yet to be developed. Jute stick chips are very clean material having low ash content, having no resin or pith. It does not require any further cleaning before pulping. So, in this work, attempt has been made to produce different cellulose derivatives from high - Cellulose containing pulp produced from jute stick.

EXPERIMENTAL

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Extraction of Cellulose from Jute Stick

For extraction of cellulose from jute stick, conventional two stage pulping procedure was followed. Jute stick chips were digested in electrically heated rotary digestor at a steam pressure 5-7 Kg / cm^2 (temperature 150-180 C). The pulp was washed and subjected to mild beating at the laboratory valey beater and then delignified by bleaching with chlorine, hypo and chlorine dioxide in the sequence C E H E D, as described earlier[5]. The bleached pulp was made into 150-200 GSM hand sheet with DM water. A part was washed with acetone and air dried to obtain in flake or powder form.

Analysis of pulp, -cellulose, pentosan & lignin was carried out by standard TAPPI method[6]. Viscosity was measured by Cuene method as in TAPPI standard method[6].

Preparation of Carboxymethyl Cellulose

Preparation of Sodium Chloroacetate[7]

A solution of 250 gm. of sodium hydroxide in two litres of absolute ethanol is added to 500 gm. of chloroacetic acid with cooling, the addition was stopped at the phenolphthalein end point. The precipitated chloroacetate was filtered, the excess solution was pressed out with the aid of rubber dental dam, and the product was air dried, yield about 85%.

Sodiun O-Carboxymethyl cellulose

10 gm. of jute stick cellulose pulp (containing 93% -cellulose) and 14 ml. of water are shredded for 30 min. in a laboratory shredder. The desire of amount of solid sodium hydroxide was added, and the shredder was run for 10 min. To this preparation of alkali cellulose was then added a portion of solid sodium chloroacetate (the molar ratio of sodium hydroxide to sodium chloroacetate was 1.02). The mixture was shredded for two hr. at 10º C and then removed from the shredder and stored until the reaction was complete. This reaction was carried out several times. The products were purified according to the method of dialysis[8]. D.S. of the product was found to be 2.5 by copper method[9].

Microcrystalline Cellulose (MC)

MC was produced from 93% α - cellulose pulp obtained from jute stick by following the procedure of Baltista & Co. workers[10], using 2.5 N HCl. The modified cellulose was dried through solvent exchange in steps-

50% alcohol ⟶ 95% alcohol ⟶ absolute alcohol ⟶ acetone ⟶ anhydrous diethyl ether. The dry powder was ball milled for 2 hrs. with 9% PH grade CMC until it makes stable dispersion with water at 5% solid content when mixed in warning blender for 10 min.

Table-1: Effect of Prehydrolysis on -cellulose content of jute stick pulp

No.	Prehydrolysis (160-165 °C 2 Hrs.	Kraft Pulping (160 -165 °C 2 Hrs.	Composition of Pulp				Ratio (Hemi-cell / -cell) in Bleached pulp
			Unbleached		Bleached		
			Hemi-cell	-cell	Hemi-cell	-cell	
1.	No	18% Na_2O 30% Sulfur	17.0	80.2	14.0	85.5	1 : 6.1
2.	No	18% Na_2O 22% Sulfur	14.0	83.2	11.1	88.6	1 : 7.9
3.	Yes	18% Na_2O 30% Sulfur	11.0	86.9	6.5	93.1	1 : 14.32
4.	Yes	22% Na_2O 30% Sulfur	8.0	90.0	3.8	96.0	1 : 20.5

Table-2: Effect of Prehydrolysis temperature on yield and -cellulose content of jute stick pulp

No.	Prehydro-lysis temp.	pH of the Prehydro-lysis solution	Kraft Pulping 18% Na_2O 30% Sulfur 160 -165 °C 2 Hrs.	Yield %	Final -cell %	Pulp content	*Loss of -cell %
1.	150-155 °C	5.1	Yes	35	88.0		5%
2.	160-165 °C	4.5	Yes	32	93.0		10%
3.	175-180 °C	4.0	Yes	27	96.0		13%
4.	175-180 °C	4.0	22% Na_2O 35% Sulfur	24	98.0		16%

* Loss is calculated on jute Stick, which contained 40% -cellulose initially

Pulp	-Cellulose content %	Yield %	Possible uses
A	88	35	Cellophane, Viscose staple
B	93	32	Medium tenacity Viscose filament, CMC, Microcrystalline cellulose
C	96	28	High performance Viscose Rayon, CMC, Other cellulosic derivatives
D	98	24	Rayon tyre-chord, Cellulose acetate, Nitrate

RESULTS AND DISCUSSION

From table-1, it is clear that for obtaining high purity cellulose, prehydrolysis of jute stick chips at elevated temperature by water was essential. In this step about 40-50% hemicellulose was removed at no cost of chemicals like alkali or sulfide. Unless a part of hemicellulose is removed by this process, it becomes very difficult to obtain a high -cellulose containing pulp. If the pulp is bleached, hemicellulose content decreases resulting in proportionate increase in -cellulose content. Pentosan content in the pulp obtained from normal Kraft cook was to high, on subsequent alkali extraction, it becomes resistant possibly due too formation of neutral xylan and cellulose pulp having very low pentosan content can not be obtained. The bleached pulp was found to contain only traces or no Uronic acid prior to alkali extraction in normal Kraft cooking without prehydrolysis treatment. After prehydrolysis jute stick contained good amount of Uronic acid as indicated by paper chromatography and such material after Kraft cooking, still contained some Uronic acid which perhaps favoured higher solubility of residual hemicelluloses in 8% alkali, resulting in higher -cellulose content in the pulp. Moreover, due to partial removal of low molecular weight xylan during pre-hydrolysis stage, the consumption of alkali in Kraft cooking is less, at the same chemical level, pulp containing lower pentosan and higher alpha content is obtained from prehydrolysed jute stick.

The temperature of prehydrolysis also was found to have some significant effect on final -cellulose content of the pulp and on the yield of -cellulose as seen from table-2. The drop in pH of prehydrolysis bath was due to liberation of acetic acid combined with hemicellulose. With increasing severity of prehydrolysis condition, the more hemicellulose is removed which increases alpha content which is good but at the same time -cellulose also is lost to some extent, which is appreciable at 175-185°C. prehydrolysis condition. At 150-155º C or 160-165º C prehydrolysis condition, the prehydrolysis solution was found to contain only traces of glucose, with some mannose besides large amount of xylose. But at 175-180º C, the solution was found to give stronger spot for glucose and also loss of -cellulose is higher on Kraft cooking, possibly due to depolymerisation of cellulose resulting in from high prehydrolysis temperature. But high prehydrolysis temperature is a Prerequisite for obtaining very high -cellulose pulp, which may be suitable for making cellulose acetate or high performance rayon. It seems we have to make sacrifice of some -cellulose in order to obtain very high alpha content in the final pulp. Thus at least four types of pulp has been prepared from jute stick which may be classified.

Because jute stick itself is a short fibred material, the pulp fibres are also short, 1-2 mm. Such short fibres present problem in making standard pulp sheet unless it is mixed with 10-20% long fibre bamboo pulp (chemical) or pulp from jute fibre. Jute stick pulp may be packed in flake from and is recommended for slurry streping in alkali in large scale production for making Viscose and CMC. Swelling in 18% alkali and dissolving character of 93% alpha jute stick pulp in Cuene was

Table-3: Comparison of crystallinity and viscosity of jute stick cellulose pulp with standard commercial pulp

Pulp	Prehydrolysis temp.	-cellulose % in final pulp	% Crystallinity	Cuene Viscosity of 0.5% Solution
I	150-155 °C	88-89	34	7.0
II	160-165 °C	92-93	35	9.5
III	175-180 °C	96-97	42	10.9
IV	*Imported AS-4 Pulp (International)	96-97	44	11.2
V	**K324N pulp (Alaska)	92-93	-	7.1
VI	**S.I.V. Pulp	92-93	-	7.0

* Received from International Pulp and Paper Research Centre, New York, U.S.A. as gift sample for research

** Received through the courtesy of Kesoram Rayon, West Bengal

Table-4: Specification for Microcrystalline Cellulose obtained from JUTE STICK CELLULOSE

Physical form	: White, water dispersible powder
Particle size	: Powder – 50% less than 350 mesh, less than 0.1% on 60 mesh Screen, Average particle size 30-35 micron
Moisture Content	: 6% at 60% RH
Heavy Metals	: > 10 ppm.
Ash	: 250 ppm.
PH of 2% dispersion	: 6.6
Solubility	: Insoluble in water, organic solvents, dispersible in water to form Colloidal solution. The dispersion is not coloured blue by iodine solution.
D.P.	: 180
Sp. Gravity	: 1.55

found to be good as domestic pulp, Mavoor or SIV and imported K324N pulp from Ketchikan Company Alaska.

The degree of crystallinity of jute stick pulp was determined by X-ray diffraction technique and the results are tabulated in table-3. An interesting observation was made that when high prehydrolysis temperature was used in pulping process, the degree of crysatllinity was higher and it was very close to high alpha cellulose containing AS-4 pulp from international pulp Company, U.S.A., which is used in America for HWM tyre chord rayon production. The reason for obtaining high crysatllinity of jute stick cellulose when prepared by prehydrolysis at high temperature (175-185º C) is not clear. But it may be related to reaching glass transition temperature of cellulose at that high temperature resulting in reorientation of cellulose chains and crystallisation of some amorphous area. Further basic research work to understand this change is under progress. The Cuene viscosity of jute stick pulps was fairly high, higher than conventional pulps available, which can be seen in table-3.

The reaction of alkali cellulose and sodium chloroacetate proceeded fairly well, D.S. ranging from 1.0 to 2.5. Low D.S. material is insoluble in 80% alcohol but for high D.S. absolute alcohol had to be used to Precipitate the product. The yield of CMC (Na form) having D.S. 2.5 was 80%. The free acid form CMC was obtained by Nitric acid reagent from sodium salt and the yield is 70%. CMC at Na-salt and free acid form is being evaluated for its use in detergent and in pharmaceuticals. The viscosity of sodium salt of CMC from jute stick was measured and was found to be at par with commercial CMC available in the market.

Use of MC cellulose in food, cosmetics and pharmaceutical products are well established in advanced countries. It is expected that in India such use of the product, if available, will soon start. Cellulose in crude form is water indispersible, even it may contain large amorphous area but when it is modified so that crystallite sizes become very small, then it becomes water dispersible. Such phenomenon occurs when cellulose is rapidly hydrolysed with 2.5 N HCI at 105º C until the limiting or level off D.P. stage is attained. It was also observed by Baltista and Co. workers at American Viscose Research, U.S.A. that incorporation of 9-10% CMC in MC Cellulose helps to make a stable colloidal dispersion which could be used in food or coating tablets in pharmaceutical industries. By following Baltista's technique MC cellulose in fine mesh was produced from jute stick cellulose in good yield, specifications of which are presented in the table-4.

The level of D.P. for jute stick cellulose on hydrolysis with 2.5 N HCl was found to be 80-220 as compared to 220-240 from k324N pulp used by F.M.C., U.S.A.Water dispersibility of jute stick MC cellulose was fairly good (3-5 days, 5% consistency) which improved above 10 days with 5-10% CMC. However, because of the lower D.P. and lower particle size, MC cellulose from jute stick may be more suitable for use in food and cosmetic products. Further development work for commercial application is in progress at our laboratory.

CONCLUSIONS

- Considering 3 million tons of jute sticks available in India, about 6-7 lakhs tons of cellulose could be isolated from this raw material which may solve the shortage of

good quality cellulose in our country.

- Prehydrolysis of jute stick removes about 40-45% hemicellulose resulting in pulp with low pentosan content. This pulp contains high uronic acid which help in removal of residual hemicellulose during subsequent alkali extraction process.

- Prehydrolysis of jute stick is a prerequisite for obtaining high cellulose containing jute stick pulp by Kraft pulping process, to be used for making cellulose derivatives.

- CMC-Na and microcrystalline cellulose can be produced from high cellulose containing jute stick pulp with good properties.

- Characteristics of high cellulose containing pulp obtained from jute sticks compares well with that obtained from standard cellulose pulps available in the market.

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