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Caustic Soda and Bio-Soda Pulping of Jute

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Abstract

In this study, new approaches for pulping jute have been evaluated using caustic soda and bio-soda pulping approaches. Although caustic soda pulps had good yield and strength properties, the delignification ability of the system was limited. Requiring higher temperatures and cooking times to achieve desired residual lignin around 5%. This resulted in yield and strength losses of the pulp. A comparison of pulps from bio-tretaed and untretaed samples of jute bast at 300ml CSF clearly demonstrates the advantage of bio-treatment over untretaed samples.

Ceriporiopsis subvermispora treatment prior to soda pulping synergistically affects on lignin removal. These preliminary results imply that white-rot fungi treatment was effective in pulp strength and lower residual lignin. This improvement is very important because the residual lignin in pulps had reducing effects on quality of paper products. In bio-soda pulps, the highest burst strength of 4.2 $kPa.m^2/g$ and tensile strength of 62.7 N.m/g were found at 200 ^{0}C and 45 min reaction conditions.

Key words: bio-delignification, white-rot fungi, ceriporiopsis subvermispora, pulp, paper strength

INTRODUCTION

The idea of preservation forests and elimination environmental problems from papermaking processes has led researchers to developed not only new alternative fibrous resources but also new environmentally benign papermaking processes with high quality paper based products.

Biotechnology have become provide environmentally solutions to problems that faced by the papermaking industry. Many researchers have opinion that biotechnology can provide environmentally friendly and extensive cost-effective alternatives to processes rather than totally replace traditional pulp and paper technologies [1-4].

In recent years the search for pulping processes that led to the development of several new methods capable of producing pulp with properties near those of conventional pulps [5-8]. The idea of using fungus in papermaking processes has a new idea and can be successfully use in conventional papermaking processes. Extensive research on the use of microorganisms for pulping [5,6], bleaching [7], resin removal [8] have been already done.

Biopulping could be defined as the treatment of ligoncellulosic materials with lignin-degrading fungi (white-rot) prior to pulping processes. The enzymes of white-rot fungi attact in the cell walls and selectively modify the lignin, which has the effect of "softening" the chips. As a result of these modifications, the energy use during pulping have been decreased and affects increasing in the paper strength properties. It was reported by Blanchette *et al.,* [9] and Akthar *et al.,* [10] that extensive energy savings have been possible if wood chips are pre-treated with fungal inocula in the biopulping process to reduce lignin.

The economical feasibility of bio-mechanical pulping was investigated in recent years [11]. It has now been scaled up to near industrial levels. It was reported that the use of the proper lignin-degrading fungus, at least 30% electrical energy could be saved in mechanical pulping, paper strength properties have improved, and pitch content is considerably reduced [10-12]. The advantage of using fungal treatment prior to mechanical refining of lignocellulosic materials with beneficial results has been proven in more recent studies [12].

Biological approaches using fungal strains for conventional pulping processes of woods were received wide spread attention in the past decade. However, fungal treatment with chemical pulping process has not been much attention yet due to some difficulties. Moreover, the use of fungi for non-woody plants prior to chemical delignification have received verly little attention.

Jute *(Corchorus capsularis)* is primarily grown in Bangladesh, India, China and Thailand. The plant grows to 2.5–3.5 meter in height at maturity. The outer bark or bast comprises about 40% of the stem by weight and is mainly used for low value-added products such as rope, cordage and gunny sacks. The inner woody core accounts for the remaining of the stem. Newly 2.2 million tons of jute bast alone (excluding core) are reported to be potentially available worldwide [13]. The chemical components of jute are similar to wood species, mainly cellulose, lignin and pentosan rich hemicelluloses. A major decline in jute exports from developing countries has accelerated research to diversify jute utilization for value added products [15].

Caustic soda is one of the original chemical delignifying agents for lignocellulose material and is also a major compound in kraft pulping liquor. It can be applied to a wide variety of lignocellulosics for pulping, especially to hardwoods and herbaceous material. But it has limited delignification ability compare to kraft method. Milder cooking conditions are required to obtain higher yields; but these conditions are not suitable for chemical pulping because the residual lignin content of the pulp remains high (> 5%).

In this investigation, the use of the white-rot fungi, *Ceriporiopsis subvermispora,* resulted in less chemical demand and/or shorter pulping times to produce the same or better jute pulp. Although exact mechanism of biodegradation of lignin is not clear, selective lignin modification is surely an important component of a successful bio-chemical process.

MATERIALS AND METHODS

Jute, was obtained from the Jute Research Institute in Bangladesh, was used in this study. Due to its high lignin selectivity and superior biopulping performance with wood and herbaceous materials, *Ceriporiopsis subvermispora* was selected to biological treatment. It was obtained from the Center for Mycology Research, Forest Products Laboratory, Madison, WI.

A number of caustic soda pulping trials using 200 g/L and 500g/L aqueous solutions were evaluated.

It was known that 175 °C is the most suitable temperature for pulping wood with the kraft process. For that reason only 175 °C was evaluated for kraft pulping at four different times for comparison delignification selectivity of the caustic soda system.

Inoculum and medium preparation: A solid culture medium was prepared with 100 ml of water containing potato dextrose agar (4.0 g) from Difco Laboraties, Detroit, MI. After the incubation, the petri plate fungal cultures were maintained in the refrigerator at 4 °C until used.

A sample consisting of 800-1000 g washed wet jute (350 g o.d basis) was placed in a bioreactor and autoclaved at 121 °C for 60 min. Inoculum suspension containing fungus, sterilized corn steep liquor, and water were mixed in Waring blender and mixed thoroughly with the jute. The 5 g corn step liquor and 0.1% fungus on dry weight basis were added to the medium prior to inoculation. Sterile water was then added to the Waring blender to make the total volume of the suspension to 100 ml. Temperature within the bioreactor was maintained using humidified air at 27°C for two weeks. The materials in the bioreactor was treated for 2 weeks under the same conditions. The corn step liquor and *C. subvermispora* were obtained from the Forest Products Laboratory, Madison, WI.

All equipment used in the biotreatment was covered with aluminum foil and autoclaved for 30 min at 121 °C and 15 psi.

Pulp preparation and evaluation: The one liter stainless steel labaratory type digester was used in all cooking trials. After cooking, samples were washed hot water and were refined in PFI mill directly until the specific level of Canadian Standard Freeness (~ 300 ml CSF) was reached according to Tappi Standard No T-248. Papers for evaluation were perpared with using labaratory type Sheet Mold Machine as described Tappi Test Method T-205.

Bulk, residual lignin content and strength properties were evaluated according to Tappi Test Methods, T-220, T-236, T-403, T-414, T-494 for all untreated and treated pulps.

Akthar and his group reported that Simons staining can be useful tool for evaluating the extent of biopulping esperimets [16]. It is a differential stain used to evaluate pore structure and degree of fibrillation. To carry out the simons stain procedure. The stain is composed of a 1% aqueous solution of Pontamine Sky Blue 6 BX and 1% aqueous solution of Pontamine Fast Orange 6 RN mixed in a 1:1 ratio was used to evaluate extent of fibrillation. The fibers are examined under the microscope, Nikon type 144, and immediately photographed.

RESULTS

Caustic soda and kraft pulping of jute

The effect of cooking time and temperature on selected physical properties were evaluated at ~300 ml CFS level and the results are given in Table 1. Lower temperatures and milder cooking conditions are essential to obtain higher pulp yields (68-78%); but those are not suitable for chemical grade pulps because the residual lignin of the pulp is too high. It is noteworthy that caustic soda pulping is not useful at lower temperature (i.e., < 175 °C) for jute. To get sufficient delignification such as; residual lignin ~ 3-4% in caustic soda pulping trials, high temperatures and cooking times are necessary. A yield of 64% was found at a good residual lignin (4.5%) at 200 °C and 60 min of reaction conditions.

The pulp properties for jute from the kraft process (20% active alkali and 25% sülfidity) are also given Table 1. As expected, kraft pulping could improve delignification and strength properties. At the same reaction conditions, the delignification selectivity of the caustic soda system was shown to be less than kraft pulping. At similar residual lignin such as; 4-5%, the yield of caustic soda pulp was about 15% lower than that from kraft pulping system (64% versus 74%). The lower selectivity of caustic soda results in greater yield losses in both low and high temperatures.

At the same freeness level which was 300 ml CSF, both system gave bulk properties of pulps in chemical pulp range. However, there were approximately 5-9% differences of bulkiness observed with caustic soda and kraft pulping of jute.

Figure 1 indicates an inverse tensile and tear strength relation to each other which is typical for many pulps when the tensile strengths are greater than 40 N m/g.

A plot of pulp yield against residual lignin (as kappa number) in Figure 2 reveals a close relationship. Whether delignification is controlled by hemicellulose removal cannot be ascertained because much slower carbohydrate losses couple with higher delignification rates.

Based on this preliminary investigation, it was decided to further explore the bio-soda pulping of jute. It would be expected more environmentally benign process and that could potantially give pulp properties equivalent and/or better for the jute pulps.

Table1. Caustic soda and kraft pulp properties of jute (at 300 ml CSF)

Temp. (°C)	Time (Min)	Yield (%)	Res. lignin (%)	Bulk (cm^3/g)	Tear Ind. ($mN.m^2/g$)	Burst Ind. ($kPa\ m^2/g$)	Tensile Ind. (N m/g)
CAUSTIC SODA PULPING (%20 NaOH)							
150	45-150	N/A	N/A	N/A	N/A	N/A	N/A
175	45	75	11.7	1.9	18.1	4.0	60.8
175	60	74	9.0	2.1	22.5	3.5	52.7
175	90	70	8.4	2.0	20.4	4.1	61.6
175	150	68	7.5	2.1	20.1	4.1	58.4
200	45	75	9.9	2.1	22.6	2.7	42.0
200	60	64	4.5	2.1	25.5	3.0	48.0
200	90	64	1.9	2.1	19.4	3.1	47.8
200	150	57	1.2	2.0	10.1	1.9	34.4
KRAFT PULPING (Active Alkali 20%; Sulfidity 25%)							
175	45	75	11.1	2.0	23.7	4.0	50.7
175	60	72	8.6	1.9	21.8	4.5	57.9
175	90	70	4.9	1.9	25.4	4.6	60.3
175	150	74	4.8	1.8	19.4	4.7	61.1

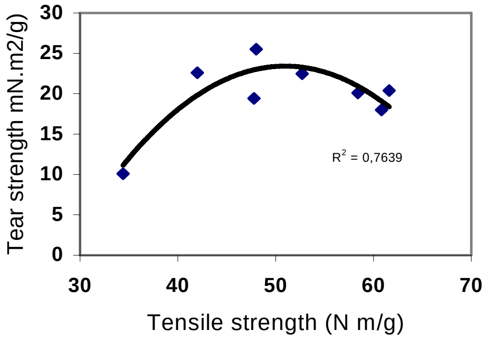

Figure 1. Tear and tensile strength relations of caustic jute pulps

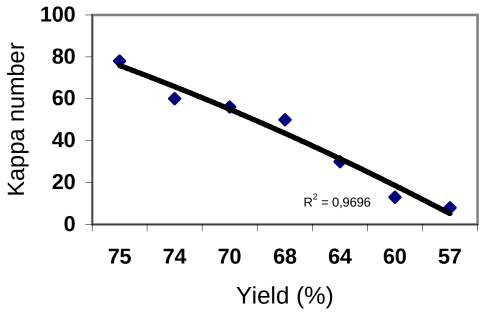

Figure 2. Yield and residual lignin relation of caustic soda jute pulps

Bio- soda pulping of jute

A number of experiments were run under various conditions. Comperative pulping conditions and residual lignin content of jute pulps are given in Table 2. Two concentrations of NaOH (20% and 50% by weight) at 175 °C for 150 min and at 200 °C for 45 min reaction conditions were summarized in Table 2. This comparison gives a general view of how soda pulping affects both untreated and bio-treated jute, and indicates which processes show the greatest promise for pulping. As it seen, lignin has removed considerably more for bio-treated jute (B) compared to the untreated (A) at the same reaction conditions.

Increased alkali concentration in pulping liquor gives a lower residual lignin with dramatically yield loss. The bulkiness of the biotreated sheets (B, C, D and E) decreased approximately 5-9% (Table 2). Reduced bulkiness imply, the fungus-treated jute pulps were separated into relatively intact jute fibers on beating (refining). Burst pressure is approximately inversely proportional to the spherical radius of water-swollen fibers. Figure 3 shows the burst strengths (as index) for control and bio-treated pulps. The marginally same burst strength of control as the 175 °C and 1.5 h cooking with bio-soda pulp could be obtained (A and B). However, the highest burst strength which was 4.2 kPa m^2/g obtained at 200 °C and 45 min cooking conditions with bio-treated jute (D). This indicate approximately 5% improvements in burst strength with lower residual lignin compared to control (A).

In Figure 4, the tensile strength shows similar pattern as burst strength. Bio-treatment did not help to improve tensile strength at the 175 ^{0}C. However, at the higher temperature at 200 °C and 45 min cooking (D), the tensile strength is approximately 8% higher than untreated soda pulps with about 40% lower residual lignin content.

The tear strengths of the pulps were marginally improved with bio-treatment. The biopulp in both 175 ^{0}C & 2.5 h and 200 ^{0}C & 45 min cooking conditions (B and D) had approximately 8% and 1% higher tear strength than untreated pulp at similar cooking and marginally same residual lignin content (Figure 5).

Simon stain is a two-color differential stain consisting of a blue small molecules and orange large molecules. The method is used to microscopically determine the fibrillation and mechanical damage of fibers [16]. If the micro-pores of the fibers are small and there is poor fibrillation such as with unbeaten or dried pulps, the small blue stain can penetrate, and the pulps stain blue. However, if the pulps are opened up and well fibrillated, then an orange/yellow color is obtained. Simons staining and ultrastructural observations provide additional evidence on modification in cell wall porosity.

Fibers obtained from jute biopulps under various experimental conditions showed different intensities of yellow-orange stain. However, this rating does not reflect any quantitative measurements and that the comparison should to be made only within each experimental set. In Table 3, at the same concentarion of chemical (20% NaOH) and reaction conditions (175 °C and 1.5 h), caustic soda pulps gave advance orange color (A) and bio-soda pulps gave with an intermediate orange color (B), which indicating good fibrillation of both pulps. However, high concentarion of caustic soda (50% NaOH) was used in bio-treated caustic soda pulps gave blue color (C), indicating limited fibrillation.

In summary, all pulps showed various Simon stain color distrubition, which indicates, these pulps where fibrillated some level. These results are also generally consistent with the strength properties of the pulps.

Table 2. Caustic soda and Bio-soda pulp properties of jute

Code	Pulping conditions	Temp. (^{0}C)	Time (min)	Res. lignin (%)	Yield (%)	Bulk (cm^3/g)
A	Caustic soda (20% NaOH)	175	150	7.5	68	2.1
B	Bio-soda (20% NaOH)	175	150	3.8	65	1.9
C	Bio-soda (50% NaOH)	175	150	1.2	50	2.0
D	Bio-soda (20% NaOH)	200	45	3.9	60	1.9
E	Bio-soda (50% NaOH)	200	45	1.5	51	1.9

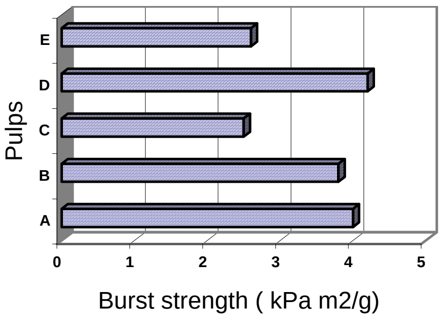

Figure 3. Burst strength properties of caustic soda and bio-soda jute pulps

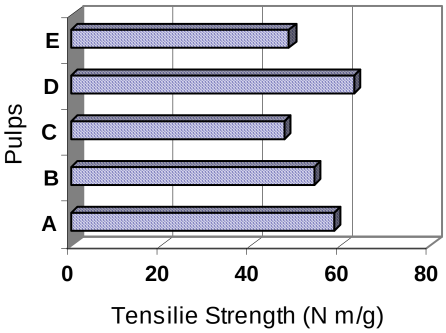

Figure 4. Tensile strength properties of caustic soda and bio-soda jute pulps

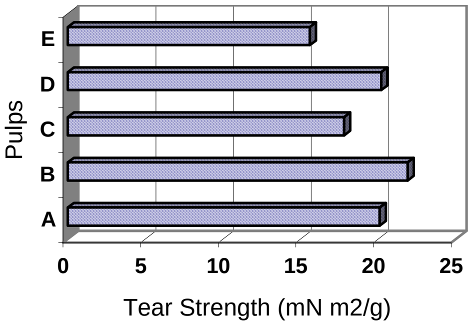

Figure 5. Tear strength properties of caustic soda and bio-soda jute pulps

Table 3. Simon stain properties on selected untreated and treated jute pulp fibers

Pulps	Blue	Slight orange-yellow	Intmed. orange-yellow	Adv. orange-yellow
A				+
B			+	
C	+			

DISCUSSION

As expected, 175 ^{0}C pulping temperature and shorter cooking were useful for higher yield in soda pulping. However delignification proceeded more rapidly in higher temperature (i.e.,200 ^{o}C) but it did not affect selectivity pulps. The high temperature and longer cooking promotes hydrolysis of carbohydrates resulting in strength and yield losses. In alkali caustic soda pulping of lignocellulosics, hydrolytic depolymerization of phenyl alkyl ethers could occur, thereby reducing the size of lignin molecules and simultaneously creating soluble phenoxide ions as sodium salts [17]. Also, the hydroxyl ions can act as nucleophilic agents that cleave lignin ether linkages. Sjostrom reported that some carbohydrate degredation occurs in alkali pulping by endwise depolymerization, a reaction known as peeling in which single monosacharide units are sequentially removed from the reducing end of the carbohydrate chain [17,18].

High reaction temperatures were needed to suffuciently remove lignin from jute. However, high temperatures not only affects lignin removal, but also carbohydrate degredation.

In caustic soda pulping, the highest tensile strength of 61.6 N m/g was found at 175 ^{o}C with 1.5 h of cooking. The tensile strengths were reduced at high temperature and reaction conditions. This is probably hydrophilic nature of the hemicelluloses. It is well known that hemicelluloses has a shorter chain length and is more hydrophilic than cellulose, thus it absorbs water better and produces a stronger bond with adjacent fiber surfaces in the dry state. However, the hydrophilic nature of the fiber surface is very important for good fiber-fiber bonding; therefore hemicellulose plays an important role in paper strength such as; breaking and bursting strengths.

The burst strength shows similar trends as tensile strength (Table 1). The highest burst strength of 4.1 N kPa m^2/g was also found at 175 ^{o}C with 1.5 h of cooking. However, the highest tear strength which 25.5 mN.m^2/g was found at 200 ^{o}C in 1 h of cooking with low residual lignin content.

It is well known that tear strength has a very complicated effect in the terms of fiber properties, especially morphological structure of the fibers. Fernandez and Young reported detailed information about tear strength developmets of pulps from acidic and alkali conditions [19]. They reported that if the density of paper is increased, it is more difficult to pull fibers out. Short fibers are more easily pulled out than long ones; also, they are not able to distrubute the applied load over as large area as long fibers [19]..

Pre-treatment of jute by white-rot fungi of *C. subvermispora* improved burst, tear and tensile strength compared to the untreated caustic soda pulp either similar reaction conditions and/or residual lignin content. The pulps obtained from fungal treated jute bast at freeness levels of 300 ml CSF had considerably enhanced strength and delignification selectivity. The highest burst strength of 4.2 kPa.m^2/g and tensile strength of 62.7 N.m/g were found at 200 ^{0}C and 45 min reaction conditions in bio-soda pulping trials.

Roughening and loosing the fiber surface, along with removing the fibril layer at the surface is commonly known as *external fibrillation*. External fibrillation increases fiber surface area and exposes cellular components which are important for inter-fiber bonding. In fact, the bond strength developed between fibers in sheet network is ultimately determined by the chemical nature of the fiber surface that makes intimate contact during water removal (drying). The unique phenomenon of obtaining stronger pulps in the case of fungal treated jute might be explained by *external fibrillation*.

It may be hypothesized that the enzymes act on the fiber surface producing a peeling effect and fungus induced physico-chemical changes in cell walls might improve chemical penetration and subsequently aid soda pulping. It is well known that the fungi hyphae penetrate woody and herbaceous lignocellulose very rapidly. Akthar and his friends suggested that the fungi attack lignocellulose by enzymes secreted from their hypha [20].

The mechanism of action for staining patterns in fibers with Simons stain is not completely clear. According to Akthar and his group [16] fungal pre-treatment modifies the cell wall that when the fibers are refined, the cut edges are to erode away with fibrils which removed from the wall. If such cell wall modifications due to fungal action, better penetration of high molecular weight orange dye in the biopulp fibers possible. The similar result were found in this study.

Biopulping, which uses natural decay organisms, appears to have the potential to overcome conventional papermaking problems. It may help to reduce chemical and energy usage in papermaking processes.

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