# High Yield Alkaline-Sulphite Pulping and Subsequent Enzyme Treatment of Agroresidues with Utilization of Spent Black Liquor

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***ABSTRACT***

*The present paper deals with a comparative study on the chemical cooking of wheat straw and Sarkanda using 100% caustic soda as well as combination of sodium sulphite and caustic soda. A combination of caustic soda and sodium sulphite in the ratio of 1:1 resulted in high yield at 47% in comparison to caustic soda cooking with 42-43% yield. The feasibility of the enzyme treatment on different types of the pulp was evaluated using a commercial cellulase-free xylanase enzyme. The effect of various parameters viz. temperature, reaction time, concentration of enzyme, consistency and pH of the pulp on enyzme pre-bleaching of the alkaline sulphite pulp was also studied to optimize the reaction conditions for maximum reduction in bleaching chemicals. An attempt was also made to find out the possibility of using the spent black liquor for developing value-added products.*

## INTRODUCTION

Although the paper industry exists for over a century, the problem of pollution associated with the paper manufacturing has always remained a subject of concern for all. Continuous efforts have been made to develop technologies for transforming paper making to a more economical and eco-friendly process. In this regard, the biotechnology coupled with pulp making has certainly an important role to play to improve the process at one end and to reduce the pollution load on the other. An important source of pollution, which has attracted the attention of scientists, is the use of chlorine in pulp bleaching. Paper mills have now started to find out possible alternatives to chlorine in bleaching of pulp to make the process elemental chlorine free (ECF) and total chlorine free (TCF). Efforts in this direction have resulted in the emergence of oxygen and ozone bleaching. However, the high capital cost of these processes has always remained a limiting factor to incorporate these processes for the paper mills particularly in small paper mills. The use of microbial enzymes in pulp and paper industry has come up as an alternative bleaching technology due to its positive environmental effects in terms of substantial reduction in chlorine consumption and economic feasibility.

## EXPERIMENTAL

### Raw Materials

Wheat straw (Triticum aestivum) and Sarkanda (Saccharum munja) were used as raw material for the studies. Botanically, Sarkanda commonly known as Kana Grass, is Saccharum munja and belongs to the family Grammineae (Poaceae). Sarkanda is a very large erect grass growing in clupms upto a height of 4-5 meters. It grows well on alluvial sandy banks of the river streams all over and is abundantly available in northern belt of India. Culms are biennial, pale, solid, smooth with an inconspicuous growth ring and root zone. Some species of Sarkanda grow in very dry climate. The proximate analysis of Saccharum munja is given in Table 1.

Table 1. Proximate analysis of Saccharum munja

| Particular | % |
|---|---|
| Ash | 4.67 |
| Solubility: | |
| 1% NaOH | 41.8 |
| Alcohol | 3.9 |
| Cold Water | 7.6 |
| Hot Water | 10.4 |
| Pentogen | 26.5 |
| Lignin | 22 |
| Cellulose | 58 |
| Holocellulose 79 | |

**Fig. 1 Sarkanda growing on wasteland**

**Fig. 2 Unloading of Sarkanda**

Sarkanda grass is a promising cellulosic raw material, which could easily supplement the growing need of agro-residue based paper mills for their raw materials.

Fig. 1 shows Sarkanda growing on waste land which is transported to the mill in tractor and then unloaded (Fig. 2) for storing. Sarkanda is cut in the cutter section and then it is loaded to the digestor (Fig. 3).

### Enzyme

Cellulase- free xylanase with an activity of 5000 U/g was obtained from a commercial source available in the market.

### Bleaching Sequence

Control: C-E-H

Enzyme: X-C-E-H

## RESULTS AND DISCUSSION

### Evaluation of Pulping Data

Sarkanda and wheat straw are cooked with NaOH + $Na_2SO_3$ and NaOH. It is observed that in case of

**Fig. 3 Loading of cut of Sarkanda in the Digester**

alkaline sulphite pulping the unbleached pulp yield is 53-54% as against in soda pulping (48-49%). The detailed chemical composition, cooking parameters and pulp properties are shown in Tables 2-4.

### Enzyme Bleaching

The lignocellulosic raw material used in paper manufacturing is composed of cellulose, hemicellulose and lignin in the ratio of 3:2:1. Cellulose fraction of the lignocellulosic agro-residue is utilized for making pulp by digesting it with cooking chemicals during pulping process. The second most abundant polysaccharide in lignocellulose, called hemicellulose, derives its name generally on the basis of predominant sugar fractions resulting after hydrolysis. These polymers (1) are made up of D-xylose, D-mannose, D-glucose, L-arabinose and 4-O-methyl-D glucuronic acid. Depending on the raw material source, the hemicellulosic fraction can be as high as 85% xylan (2).

Since large molecules of hemicellulose can not pass through wall membranes, the microorganisms secrete extracellular hydrolytic enzymes called hemicellulases. Xylan, the predominant fraction of hemicellulose is hydrolysed by a group of hemicellulases, collectively called as xylanolytic enzymes or xylanase complex consisting of generally two enzymes i.e. endoxylanase (endo-1, 4-B xylanase; EC 3.2.2.8 and B-xylosidase (1,4-B-D-xylan, exylohydrolase: EC 3.2.1.37), the coordinated action of which brings about the total xylan breakdown. Endoxylanase is responsible for the initial breakdown of xylan chain by hydrolysing the B, D-xylopyranoxyl linkage of xylan to form oligosaccharides. B-xylosidase, on the other hand catalyses the gradual hydrolysis of xylobiose or xylo-oligosaccharides from the non-reducing end to form D-xylose. The enzymes responsible for clearing several side groups attached to main polymer chain of xylan are also released by

Table 2. Results of Pulping

| Particulars | Alkaline Sulphite Pulping | | Soda Pulping | |
|---|---|---|---|---|
| Raw Material | Sarkanda | Wheat Straw | Sarkanda | Wheat Straw |
| B.D. Qty. MT | 5.0 | 5.0 | 5.0 | 5.0 |
| Loading time (hour) | 2.30 | 1.30 | 2.30 | 1.30 |
| Steaming time (hour) | 2.0 | 2.0 | 2.0 | 2.0 |
| Chemical charged % NaOH % | 9.0 | 9.0 | 14.0 | 15.5 |
| $Na_2SO_3$ % | 9.0 | 11.0 | - | - |
| Cooking time (hour) | 3.30 | 3.30 | 3.30 | 3.30 |
| Temperature (°C) | 165-170 | 165-170 | 165-170 | 165-170 |
| Pressure ($Kg/cm^2$) | 6.5-7.0 | 6.5-7.0 | 6.5-7.0 | 6.5-7.0 |
| Total duration (hour) | 8 | 7 | 8 | 7 |
| Bath ratio | 1:3 | 1:3 | 1:3 | 1:3 |
| Unbleaced Yield (%) | 53 | 54 | 48 | 49 |
| Reject (%) | 2.5 | 2.0 | 2.5 | 2.0 |
| pH- wash pulp | 8.0 | 8.0 | 8.5 | 8.5 |
| Kappa no. | 28 | 28 | 30 | 30 |
| Viscosity (cps) | 12 | 12 | 15 | 15 |
| **Black liquor** | 11.0 | 11.0 | 11.5 | 11.5 |
| pH | | | | |
| R.A.A. (Gpl) | 0.2 | 0.2 | 0.8 | 0.8 |
| Total Solids (%) | 12.5 | 14 | 12.5 | 14 |
| Inorganic (%) | 37.0 | 37.5 | 37.5 | 38.0 |
| Organic (%) | 63.0 | 63.5 | 62.5 | 62.0 |

the microorganism in addition to endoxylanase and B-xylosidase and act synergistically (3-5). The reports available in literature reveal that enzyme pretreatment with cellulase free enzymes result in substantial reduction in bleach chemicals and extraction chemicals with improvement in strength properties. A number of commercial enzymes are available for the treatment of pulp. However, optimization of reaction and process conditions for individual raw materials used in different mills have to be examined at laboratory and pilot scale to make the process of enzyme bleaching feasible on the plant scale. The selection of a suitable chemical cooking process for making pulp that is more prone to enzymatic treatment also plays an important role in this regard.

Comparison of bleach chemical consumption and strength properties of untreated and enzyme-pretreated alkaline sulphite pulp of Sarkanda is made in Table 5. It is evident that pretreatment with enzyme brings down the chlorine consumption with marginal improvement in strength properties.

## Economics

$Cl_2$ reduction @ 20% from present level of 15% i.e. 30 Kg @ 6/- Kg = Rs.180/- T

NaOH reduction @ 15% from present level of 3.5% in 'E' stage, i.e. 5.25 Kg @ 15/- Kg = Rs. 78/- T

Total Savings = Rs.258/-T of Pulp

Cost of Enzyme Rs. 100/- Kg and dose @ 1.8 Kg/T of Pulp = Rs.180/-T of Pulp

## Lignosulphonates

The alkaline-sulphite cooking process generates black liquor at pH of 11 and at about 8% TS, which is sulphonated and then evaporated upto 40% TS. The product is called Lignosulphonate.

The composition is:

| | | |
|---|---|---|
| The composition is: | % Lignin | 60 |
| | % Sugar | 6-8 |
| | pH | 6.5-7.0 |
| | % TS | 40-42 |

It is sticky syrup in nature.

## Application of the product

a) It is used as a grinding aid in Cement Industry.

b) It is a "Retarder" and used in Cement to delay

Table 3. Results of bleaching (CEH sequence)

| | | | | |
|---|---|---|---|---|
| **Chlorination stage** | | | | |
| Chlorine Added (%) | 7.0 | 7.0 | 7.5 | 7.5 |
| Initial | 1.8 | 1.8 | 1.8 | 1.8 |
| Final | 2.2 | 2.2 | 2.2 | 2.2 |
| Retention time (min) | 45 | 45 | 45 | 45 |
| Residual Chlorine (Gpl) | 0.0142 | 0.0142 | 0.02 | 0.02 |
| $Cl_2$ consumption (%) | 7.0 | 7.0 | 7.4 | 7.4 |
| pH-wash pulp | 3.2 | 3.2 | 3.2 | 3.2 |
| Kappa no. | 11 | 11 | 12.5 | 13 |
| **Alkali extraction stage** | | | | |
| Temperature (°C) | 60 | 60 | 60 | 60 |
| NaOH Added (%) | 3.5 | 3.5 | 3.5 | 3.5 |
| pH Initial | 11.2 | 11.2 | 11.5 | 11.5 |
| Final | 10.5 | 10.5 | 10.8 | 10.8 |
| Retention time (hr.) | 2.0 | 2.0 | 2.0 | 2.0 |
| pH wash Pulp | 8.5 | 8.5 | 8.5 | 8.5 |
| Kappa No. | 4.0 | 4.0 | 4.5 | 5.0 |
| **Hypo stage** | | | | |
| Temperature (°C) | 40 | 40 | 40 | 40 |
| Chlorine Added (%) | 8.0 | 7.5 | 7.5 | 7.5 |
| pH initial | 8.7 | 8.7 | 8.7 | 8.7 |
| Final | 6.5 | 6.5 | 6.5 | 6.5 |
| Retntion time (min) | 3 | 3 | 3 | 3 |
| Residual Chlorine (Gpl) | 0.0071 | 0.0071 | 0.0142 | 0.0142 |
| Chlorine consumed % | 3.99 | 4.49 | 4.486 | 4.98 |
| Total $Cl_2$ consumption (%) | 11.42 | 11.9 | 11.89 | 12.38 |
| Losses (%) | 11.6 | 12.0 | 11.8 | 12.0 |
| BLD yield (%) | 46.85 | 47.52 | 42.3 | 43.12 |
| Final Brighness (%) | 80 | 80 | 80 | 80 |
| Viscosity (cps) | 6.5 | 7.0 | 6.7 | 7.2 |

the setting time of concrete in case of mass construction to avoid cracking.

c) It is used as a plastisizer in Cement Industry.

d) It is used as a disperser in Dye Industry.

e) It increases viscosity of low density oil and used as emulsifier and thus various burnt oil are converted into "Grease".

f) It is used to increase the sensitivity for explosive, since the hygroscopic characteristics of ligno sulphonate can hold tiny water particles, resulting in increased conductivity.

g) It us used for "Core" making in the Foundry-shop.

h) It is a coal dust/particles binder and hence used for briquetting industries to give smokeless combustion.

i) It is used as a soil stabilizer while drilling, by oil industries. It is mixed with bentonite and gives an adhesive coat on the drilled well and thus avoids "Cave in" of the well. When lignosulphonate is added with the crude oil it also acts as a Catalyst and decantation of the oils becomes faster.

Table 4. Evaluation of strength propreties of hand sheets

| Properties | Alkaline-Sulphite Pulping | | | | Soda-Pulping | | | |
|---|---|---|---|---|---|---|---|---|
| | Sarkanda | | Wheat Straw | | Sarkanda | | Wheat Straw | |
| | Unbld | Bld. | Unbld | Bld | Unbld | Bld | Unbld | Bld |
| °SR | 24 | 30 | 25 | 32 | 25 | 29 | 24 | 31 |
| Substance $gm/m_2$ | 60 | 59 | 59 | 60 | 61 | 60 | 60.5 | 60 |
| Breaking Length (mtrs) | 2750 | 2500 | 3050 | 2850 | 2800 | 2650 | 3240 | 3100 |
| Burst Factor | 14.0 | 13.0 | 17.5 | 16.5 | 14.5 | 14 | 17.5 | 17 |
| Tear Factor | 47.5 | 44.5 | 49.5 | 46.0 | 47.5 | 45.0 | 49.0 | 46.4 |
| Ash Contents % | 4 | 3.6 | 6.7 | 6.0 | 4.2 | 3.7 | 7.0 | 6.5 |

Table 5. Comparison of bleach chemical consumption and strength properties of untreated and Enzyme pretreated Alkaline Sulphite Sarkanda pulp.

| Parameter | Control | Enzyme treated pulp |
|---|---|---|
| Bleaching Sequence | CEH | X-CEH |
| Enzyme Dosage | Nil | 9 U/g |
| Total $Cl_2$ Consumption (%) | 11.42 | 9.85 |
| Alkali used in extraction (%) | 3.5 | 3.0 |
| Breaking Length (mtr) | 2500 | 2701 |
| Tear Factor | 44.5 | 41.5 |
| Burst Factor | 13.0 | 14.1 |
| Viscosity | 7.16 | 6.52 |
| Final Brightness (%) | 80.0 | 81.0 |

j) It is used to increase the strength properties of high Alimina Content Refractory bricks.

However, further advanced R&D efforts are needed to optimize the process for individual mills.

### Utilization of Spent Black Liquor

The black liquor which comes out as a result of digestion of raw materials with chemicals also raises an environmental threat, if not removed from the system. In this context, agro based paper mills generate higher pollution load in the absence of a chemical recovery system as compared to large integrated mills. Therefore, the utilization of black liquor for developing value added products like lignosulphonates seems to be a possible cost effective and technically viable solution of black liquor removal particularly in small and agro based paper mills.

## CONCLUSION

The enzyme pretreatment resulted in approximately 20% and 15% reduction in terms of chlorine and alkali consumption respectively under optimized reaction conditions in subsequent steps of bleaching. The enzyme treatment has also shown a positive effect on strength properties of the pulp. The spent black liquor obtained in the process was evaporated to increase the concentration of solids to approximately 40%. The concentrated black liquor was sulphonated to convert to lignosulphonates. Lignosulphonate is a versatile by-product with commercial value for various industries. However, further R&D efforts are needed to address some critical areas to optimize the process to an acceptable level for agro-based paper industry.

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