# Development of Lignosulphonates from Spent Black Liquor generated from Optimized Bisulphite Pulping of Saccharum munja

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***Abstract***

*The utilization of lignosulphonates, a byproduct of the manufacture of pulp and paper has two fold benefits of eliminating a black liquor disposal problem while improving manufacturing performance in other consumers ranging from food to concrete industries. The present paper elaborates the efforts to utilize the black liquor generating in the pulping of a wild grass Saccharum munja commonly known as Sarkanda or Kahna Grass. The conditions for cooking of this wild grass and subsequent CEH bleaching pulp have also been optimized to develop pulp with acceptable strength properties for making writing and printing paper. The process for development of lignosulphonates, their properties and the utilization of sodium lignosulphonates so obtained in various consumer industries, have also been summarized.*

## INTRODUCTION

Lignosulphonates from bisulphite pulping of wood have been developed and used in commercial applications for over 50 years. However, a critical review of the literature available on Lignosulphonates reveals that comparatively very little work has been done on bisulphite pulping of agro-residue and consequently on lignosulphonates production. Presently, countries with pulp mills, which supply lignosulphonates, are the United States, Canada, Norway, Sweden, Finland, China, Japan and South Africa.

In developing countries, about 60% of cellulose fibres originate from nonwood raw materials. In India, agro residues used in pulp and paper industry are mostly bagasse (Saccharum officinarum), wheat straw (Triticum aestivum), rice straw (Oryza sativa), wild grasses commonly known as kahi (Saccharum spontaneum) and Sarkanda (Saccharum munja). The pulping process used for agro residues is basically alkaline pulping or alkaline sulphite pulping. 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 possible cost effective and technically viable solution of black liquor removal particularly in small and agro based paper mills. Keeping in view the problem of pollution associated with the black liquor and at the same time, market potential of lignosulphonates, studies were carried out to optimize bisulphite pulping of Sarkanda and subsequent development of lignosulphonates from spent liquor.

## EXPERIMENTAL

### Raw materials

Sarkanda (Saccharum munja) was used as raw material for the studies.

### Description of Sarkanda

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 clumps up to 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, pithy, 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.

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 wasteland. The unloading of this raw material in the mill is shown in Fig. 2 and Fig. 3 shows its loading in the digester.

### Cooking Chemical

Sodium Bisulphate (60% purity)

Table 1. Proximate analysis of Saccharum munja

| Parameters | % |
|---|---|
| Ash | 4.67 |
| Solubility-1% NaOH | 41.8 |
| Alcohol | 3.9 |
| Cold Water | 7.6 |
| Hot Water | 10.4 |
| Pentogen | 26.5 |
| Lignin | 22.0 |
| Cellulose | 58.0 |
| Holo-cellulose | 79.0 |

### Bleaching sequence C-$E_P$-H

The Cooking conditions have been summarized in Table 2.

### Production of ligonosulphonates

The black liquor generated in the pulping operations was clarified in the clarifier followed by filtration to remove all the impurities. The clarified liquor thus obtained was evaporated to 45% solids. The lignosulphonates so obtained were further modified through chemical and biotechnological routes depending on the requirement of various consumer industries.

### Analysis and compliance of properties of lignosulphonates

The sodium lignosulphonate developed from spent black liquor from bisulphite pulping of Sarkanda was analysed as per IS: 9103-1999 for compliance as water reducing admixure.

### Comparison of sodium lignosulphonates with commercial chemical admixure

The effect of crude sodium lignosulphonate as admixure was studied on Portland Pozzolana cement and also compared with commercial chemical admixure.

Table 2. Pulping conditions and results

| | |
|---|---|
| B.D. Qty. MT | 5.0 |
| Loading time (hours) | 2.30 |
| Steaming time (hours) | 2.0 |
| Chemical charged % $NaHSO_3$ (as Sulphur) | 12 |
| Cooking time (hours) | 2.30 |
| Temperature °C | 165-170 |
| Pressure Kg/cm² | 6.5-7.0 |
| Total hours | 7 |
| Unbleached yield % | 48.7 |
| Reject % | 2.0 |
| PH-wash pulp | 4-5 |
| Kappa No. | 18 |
| Viscosity cm³/g | 545 |
| Black liquor pH | 6.5 |
| Residual $NaHSO_3$ as $SO_2$, gpl | 1.5 |
| Total solids % | 15 |

## RESULTS AND DISCUSSION

The results of the bisulphite pulping of Sarkanda, subsequent processing and bleaching have been shown in Tables 2-5. It was observed that in case of bisulphite pulping, the unbleached yield is 48.7% which is quite comparable to soda pulping with 48%-49% yield confirming the suitability of bisulphite pulping for sarkanda grass.

### Lignosulphonates

The composition of sodium lignosulphonates developed from bisulphite liquor is shown in Table 6. The results of analysis of sodium lignosulphonate and effect of sodium lignosulphonate as admixure on Portland pozzolana cement in comparison to control and commercial chemical admixure have been summarized in Table 7 and Table 8.

### Applications of Lignosulphonates

The opportunities are substantial as far as commercial applications of lignosulphonates are concerned. To list a few, the major ones are as follows:

Table 3. CEpH bleaching sequence

| | |
|---|---|
| **Chlorination Stage:** | |
| Chlorine added % | 4 |
| pH Initial | 1.8 |
| Final | 2.05 |
| Retention time 'Min' | 45 |
| $Cl_2$ consumption % | 3.96 |
| (as available $Cl_2$) | |
| pH- Wash pulp | 2.98 |
| Kappa No. | 8 |
| **Alkali Extraction Stage:** | |
| Temperature °C | 60 |
| NaOH added % | 3.0 |
| $H_2O_2$ added % | 0.62 |
| pH Initial | 11.2 |
| pH Final | 10.68 |
| Retention time (hrs.) | 2.0 |
| pH Wash Pulp | 7.89 |
| Kappa No. | 3.5 |
| **Hypo Stage:** | |
| Temperature °C | 40 |
| Chlorine added % | 3.0 |
| pH Initial | 8.0 |
| pH Final | 6.0 |
| Retention time (hrs.) | 3 |
| Chlorine consumed % | 2.97 |
| (as available $Cl_2$) | |
| Total $Cl_2$ consumption % | 6.93 |
| Losses % | |
| BLD yield % | 40.85 |
| Final brightness % | 80.5 |
| Viscosity $Cm^3/g$ | 332 |

Table 4. Evaluation of strength properties of hand sheets

| Properties | Sodium Bisulphite Pulping | |
|---|---|---|
| | Unbleached pulp | Bleached pulp |
| °SR | 30 | 30 |
| Substance gm/m² | 59.5 | 61.0 |
| Breaking Length mtr | 2195 | 1955 |
| Burst Factor | 12 | 11 |
| Tear Factor | 41.7 | 37.8 |
| Ash % | 4.36 | 3.0 |

**a) Oil and grease industry**

The lignosulphonates are used to stabilize the emulsions containing water and dispersants used in drilling of oil wells. These emulsions are used to improve the properties of drilling mud in terms of reduction of torque on the drill stem, control of water loss etc. It is also used as a decanter to separate oil from other heavy impurities. Due to its emulsifying property and ability to increase the viscosity of low density oil, lignosulphonates are used to make grease.

Table 5. Summary of chemical consumption in bisulphite pulping and strength properties of Sarkanda pulp

| Parameter | Control |
|---|---|
| Bleaching sequence | CEpH |
| Total $Cl_2$ consumption % | 6.93 |
| Alkali used in extraction % | 3.0 |
| $H_2O_2$ used % | 0.62 |
| Breaking length (mtr) | 1955 |
| Tear Factor | 37.8 |
| Burst Factor | 11 |
| Viscosity ($Cm^3/g$) | 332 |
| Final Brightness, % | 80.5 |

**b) Tissue culture**

Lignosulphonates have been reported to be use as fertilizers. Effect of lignosulphonates as culture medium additive has been studied on plant in vitro culture systems. The application of lignosulphonates at optimum concentrations on different plants have resulted in stimulation the growth of sugar beet callus, improvement in multiplication rate and vigor of a shoot proliferating poplar cluster and increase in the rooting percentage of poplar shoots.

**c) Cement industry**

The lignosulphonates have got wide spread use in cement industry. Lignosulphonates are used as grinding aids in cement grinding mills. In grinding process, lignosulphonates reduce the agglomeration of the ground particles and surface tension at the solid-air interference of the particles and at the same time keep the surface of the grinding media free and clean. Lignosulphonates are also used as a retarder in cement to delay the setting time of concrete in mass construction, to avoid cracking. Lignosulphonates also increase the durability and compressive strength of the cement.

**d) Adhesives**

Lignosulphonates can be used as an ingredient alongwith other chemicals for the production of adhesives for plywood and chip board. The linoleum cement containing mainly

Table 6. Composition of sodium lignosulphonates

| Parameter | Limit |
|---|---|
| Total solids % | 45-46 |
| pH | 6.14 |
| Lignin % | 58-60 |
| Sugar % | 8-10 |
| Sp. Gravity gm/cc | 1.32 |
| Organic % | 65 |
| Inorganic % | 35 |
| Sodium % | 3.34 |
| Calcium | 1.202 |
| Methoxyl content | 7.5 - 8.0 |

lignosulphonates and clay are used as adhesive for ceiling tiles.

**e) Binders**

Lignosulphonates are used as binders for pellets and briquettes. The pellets formed from iron ore with a very low concentration of lignosulphonates are many times harder than the pellets made with bentonite binder.

**f) Explosives**

Lignosulphonates are used to increase the sensitivity for explosive. The hygroscopic nature of lignosulphonates allow it to hold tiny water particles, resulting in increased conductivity.

**g) Other applications**

Lignosulphonates are also used as disperser in dye industry, additive in rubber industry, brightening agent in electrolytic refining etc.

## Role of Biotechnology

The biotechnology could also play an important role in widening the scope of applications of lignosulphonates. The microorganisms have been used to remove the impurities such as carbohydrates from the lignosulphonates. Various literature reveal that lignosulphonates could have several used because of their dual properties of hydrophilicity and hydrophobicity, if modified with lignin transforming enzymes from microorganisms.

Lignosulphonates have been used for the production of gel if treated with a phenol oxidising enzyme system (oxidase or peroxidase) from microorganism. Since the gel can absorb and release waste and/or organic solvents, these are useful in treatment of waste water from paper manufacturing process by adsorbing unwanted chemicals.

Table 7. Analysis and compliance of sodium lignosulphonate as water reducing concrete admixure.

| Particulars | Test results | Requirement of IS-9103-1999 |
|---|---|---|
| **Water content** | | |
| % of control sample, Max | 90 | 95 |
| **Compressive Strength** | | |
| % of control sample, Min | | |
| 3 days | 120 | 110 |
| 7 days | 116 | 110 |
| 28 days | 115 | 110 |
| **Flexural Strength** | | |
| % of control sample, Min | | |
| 3 days | 106 | 100 |
| 7 days | 105 | 100 |
| 2 days | 113 | 100 |
| **Length Change** | | |
| % increase over control,max | | |
| 28 days | 0.008 | 0.010 |
| **Bleeding** | | |
| % Increase over control sample, max | 3 | 5 |

A method has been developed for preparing wooden tiles with increased strength for the building industry using a binder composed of lignosulphonates, sodium dichromate and Penicillium sp. mycelium. The results of the study revealed that the addition of fungal mycelium has increased the strength of the product by upto 70% in comparison to the product without mycelium.

The sodium lignosulphonate obtained from sarkanda based black liquor has been tested and found to be suitable as use as water reducing admixure as per IS 9103-1999 (Table 7). Fruther, studies carried out on the effect of sodium lignosulphonates on Portland cement indicate that even the crude form of sodium lignosulphonate developed from agro-based black liquor is quite comparable to the commercial chemical admixtures available in the market (Table 8). However, the acceptability of lignosulphonates from agro-based black liquor over chemical

Table 8. Comparison of the effect of crude sodium lignosulphonates as admixure with commercial chemical admixure on Portland Pozzolan Cement M 20. a grade of cement concrete

| Description | Slump range (mm) | Compressive strength (Mpa) | | | | Flexural strength (Mpa) | |
|---|---|---|---|---|---|---|---|
| | | 1 day | 3 day | 7 day | 28 days | 7 day | 28 day |
| Control 12-17 (w/c=0.6) | 7.9 | 15.5 | 22.7 | 34.0 | 4.6 | 5.8 | |
| With 0.6% Lignosulphonate (w/c = 0.6) | 50-52 | 5.8 | 12.8 | 20.5 | 32.3 | 4.4 | 5.6 |
| With 0.6% Chemical Admixure (37% solids) (w/c=0.6) | 54-58 | 7.0 | 16.5 | 23.3 | 36.0 | 4.5 | 5.5 |

admixtures may be enhanced further by adopting various purifying methods such as desugarization. The evaluation of the sodium lignosulphonate obtained from sarkanda based sulphite liquor for other consumer industries is under progress.

## CONCLUSION

Bisulphite pulping of Saccharum munja results in acceptable yield when compared with Soda pulping of agro residues. Moreover, the spent black liquor obtained in the process may be processed for the production of lignosulphonates, a versatile and meaningful byproduct of the paper industry, which at one end eliminates the pollution problem associated with the pulp mill effluent and generates revenue in the form of value added consumable by-product.

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## REFERENCES

1. Anderson, M.B. and Yde, B., Gel Production from lignosulphonate waste from paper manufacturing Patent Novo-Nordisk Biotechnol. Abs. (1982/07-2000/09).
2. Chatterjee, A.K. lignosulphonates-The Potential By-product from Black Liquor. In Paper International 16-17, (July-Sept 2000).
3. Cherkasov, V.D., Solomatov, V.I., Indzemtsev, V., Gselyaev, V.P., Rusakov, V.A. Revin, V.V., Buzulukov, V.I. Merkulov, A.I. and Potavtsev, S.I. Wood tile binder, Composition Patent Moscow-Inst. Eng. Ry. Transp. Biotechnol, Abs (1982/07-2000/09).
4. Egan, E.M. Lignin transforming Enzymes, Their Characterization and Potential Industrial Applications. Abstr. Pap. Am. Chem. Soc. 192 MEET BTEC 54, (1986).
5. Kevers, C., Soteras, G., Baccou, J.C. and Garpar, T. lignosulphonates: Novel promoting additives for plant tissue culture. In vitro-cell Dev. Biol. Plant 35(3) 413-416 (1999).
6. Managaonkar, N.D. and Kulkarni, A.Y. Preparation and Utilization of Lignin byproducts and lignosulphonates obtained from wood black liquor, IPPTA Conv. Issue 40 (1987).
7. Srinivasan, G.K. and Chatterjee, A.K. Improved Environmental Management in an Agro based mill- A case study IPPTA J., 7(4) 49-56 (1995).
8. Chatterjee, A.K. Sharma N., Bhatt, A.K. et.al. High yield Alkaline Sulphite Pulping and subsequent Enzyme treatment of agro-residues with utilization of spent black liquor. IPPTA Conv. Issue, 81-84 March (2002).
9. Chatterjee, A.K., Sharma, N., Bhatt, A.K. and Azmi, W. lignosulphonates : A Viable Ecofriendly Approach for Paper Industry. Workshop on Biobusiness & Entrepreneurships, DBT, Shimla, India Aug. 19-20 (2001).