ISSN: 0379-5462
IPPTA: Quarterly Journal of Indian Pulp and Paper Technical Association
Vol. 30, E2, 2018, pp.1-5

A Novel Approach to Utilize Straw Black Liquor from Mills Producing Unbleached Packaging Grade Paper

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Abstract: *Effective processing as well as efficient utilization of straw based black liquor is the need of the hour to make straw based integrated biorefinery and papermaking processes commercially successful. This study reports two such strategies for processing and utilization of straw black liquor from an unbleached pulp producing paper mill. The first strategy looks into the formulation of lignin phenol formaldehyde resins for application in plywood industry while the second involves the development of lignosulphonates as black liquor viscosity reducing additive. The lignin phenol formaldehyde resins were produced by substituting phenol with straw based soda black liquor lignin in various percentages. The formulations thus obtained were used to make boiling water proof plywood panels which were further subjected to test their ability to bind plywood as per standard specification for synthetic resin adhesives. It was found that up to 30% substitution of phenol in phenol formaldehyde with black liquor lignin can yield good quality phenol lignin formaldehyde resin for manufacture of boiling water proof plywood panels conforming to relevant standard specification. The lignosulphonates generated during straw pulping were studied for reducing viscosity of soda bagasse and soda straw black liquor. Various doses of lignosulphonates were added to above mentioned weak black liquors and viscosities were determined for control and lignosulphonates added black liquor at different solid concentrations. Substantial reduction in viscosity led to the generation of additional steam along with energy savings. This study emphasizes that packaging grade pulp mill employing straw as fibrous raw material may utilize the black liquor as by-product which will help in pollution abatement and will also improve the economics of the small mill.*

Key words: Straw, Black Liquor, Lignosulphonates, Lignin, Pulp and Paper

1. Introduction

Presently, the wood based, Agro based and waste paper based paper mills contribute 20% (4 million tons), 10% (1.56 million tons) and 70% (11.81 million tons) respectively to the total paper production (17.37 million tons) in India. Projections indicate that the total production would increase to 30-33 million tons in 2030. The agro based paper mills have a present growth rate of 3.22% in comparison to that of 2.3% and 5.6% for wood based and waste paper based mills respectively. India has emerged as one of the leading countries using substantial proportion of non-wood raw materials such as cereal straws, grasses, bagasse, etc. in paper furnish. Black liquor is a potential source of energy and cooking chemicals. Large mills are equipped with conventional chemical recovery and are recovering energy and chemicals from black liquor. Small mills operating on Agro based raw material have adopted Copeland recovery process and are recovering cooking chemicals in sodium carbonate form but energy is not recovered. Most of the large mills having conventional chemical recovery system could not marginally expand their pulp mill capacity and cannot adopt oxygen delignification due to capacity of chemical recovery.

High capital cost of chemical recovery system and bottleneck on the existing capacity left no scope for these mills to handle the additional black liquor generated by adopting oxygen delignification and marginal expansion of pulp mill. Separating part of lignin from black liquor is an alternate to reduce load on chemical recovery unit thereby allowing these mills to cope up with this additional black liquor. Further small mills which are having very low capacity and cannot afford chemical recovery system may opt for sulphite pulping under optimized conditions and generate this sulphite black liquor as a by-product which may find applications in various industries. The waste lignin can be used as a potential raw material for several new products such as chemicals, carbon fibres/materials, phenols, adhesives/binders, dispersant, metal chelating agents etc. [1] In view of the above, this study explores the novel possibilities of use of lignin in plywood industry by developing lignin phenol formaldehyde resins and use of sulphite liquor based lignosulphonates as black liquor viscosity reducing additive in paper mills. This will form a basis for more effective utilization of lignin biomass for resource conservation, environment protection and to improve the economics and competitiveness of agro based mills under biorefinery mechanism in the years to come.

2. Material and Methods

2.1 Separation of lignin from black liquor

Black liquor collected from a nearby Agro based paper mill was subjected to partial lignin removal by acidification. The black liquor pH was reduced to ~ 2 by adding sulphuric acid. The precipitated lignin was allowed to settle and separated through centrifugation. The separated lignin was dried, powdered and passed through 100 mesh for maintaining uniform size.

2.2 Preparation and evaluation of lignin-phenol-formaldehyde (LPF) resins

The lignin-phenol-formaldehyde (LPF) resins were produced by substituting phenol with black liquor lignin as obtained in various percentages. Phenol was replaced by various percentages of lignin to keep the phenol to formalin weight ratio constant to 1:1.8. 10%, 20% and 30% replacement of phenol by lignin were adopted in making LPF Resin. The resin preparation method incorporates concentration of the black liquor/ precipitated lignin followed by its reaction with phenol and formaldehyde. The co-polymerisation of the lignin with phenol-formaldehyde under alkaline catalytic conditions takes place and a structure similar to the one shown in Figure 1 is attained. The resin was discharged and then the flow properties of PLF resin were determined. The plywood panels of 4 mm thick, 30 X 30cm were made from rotary cut veneers of *Grevillea robusta* (Silver oak), *Shorea assamica* (Makai) and *Populus* spp. (Poplar). The panels were subjected to test as per IS: 848:2006, specification for synthetic resin adhesives for plywood (Phenolic and Amino plastics).

2.3 Development of lignosulphonate and viscosity determination

Lignosulphonates were obtained by performing sulphite pulping of rice straw. In order to determine the effect of lignosulphonate on the viscosity of concentrated soda black liquor, varying amounts of lignosulphonate in the form of slurry were added to the black liquor. Lignosulphonate were added to the weak black liquor prior to concentration so as to achieve through mixing of the lignosulphonate with the black liquor during concentration. Various doses of lignosulphonate (1 & 2 %) were added to weak black liquor. Viscosity determinations were then made using Anton Paar Rheometer (MCR 100) for the control black liquor at different black liquor solids concentration and compared with those obtained after addition of lignosulphonate

3. Results and Discussion

3.1 Properties of lignin and lignosulphonates

Table 1 and **2** gives the results of characterization of the lignin biomass and lignosulphonates produced in the laboratory. Under optimized conditions, lignin product/lignosulphonate with high purity and desirable pH and solid content were obtained.

Table 1. Characteristics of lignin obtained from rice straw based black liquor

Parameters	Results
Silica as SiO_2, % w/w	2.25
Lignin purity, % w/w	78.50
Lignosulphonate purity, % w/w	66.15
Total sugars, gpl	1.04
Chloride as NaCl, % w/w	0.59
Carbon as C, % w/w	53.83
Hydrogen as H, % w/w	4.02
Nitrogen as N, % w/w	0.49
Sulphur as S, % w/w	4.23
Sodium as Na, % w/w	1.22

Table 2. Characteristic of lignosulphonate (sulphite black liquor) slurry

Parameters	Results
pH	8.76
Ash, %	22.38
Total solids, %	29.16
Lignosulphonate purity as % sodium lignosulphonate	93.24
Sodium (OD basis) %	10.16
Silica, %	2.42
Chloride, %	0.27
Calcium, %	0.12

3.2. Application of lignin in Plywood Industry

In the manufacture of the plyboard and particle boards, phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins are most commonly used. The major advantage of UF resins are their low cost, lack of colour and short curing time. However, the glue line is not water proof and during recent years, a great deal of attention has been drawn to the emission of formaldehyde from the particle boards made from UF resins for a length period after production. The advantage of PF resin is the weather resistance of the manufactured product, their chief drawback lies in their high cost. In view of this, it was decided to substitute phenol with lignin which has a phenolic structure. Due to its lower cost and environment friendly nature, it can be preferred to urea and phenolic components with respect to the end product quality and cost of the product respectively.

PF resins are made by condensing phenol with formaldehyde using alkaline catalysts. As phenol has three reactive sites, the first stage of the reaction with formaldehyde gives five hydroxymethyl phenols in varying proportions depending on the reaction conditions. The hydroxymethylol groups subsequently condense during the formation of methhlene bridges. Lignin is the most important of the natural polyphenols. It is the composed of phenyl propane units which are connected by carbon-carbon and ether bonds forming a polymeric product. In chemical pulping, part of the bonds between the phenyl-propane units is broken and lignin gets dissolved in the pulping liquor in the form of various sizes. **Figure 1** illustrates a comparison between the structural detail of lignin and PF resin.

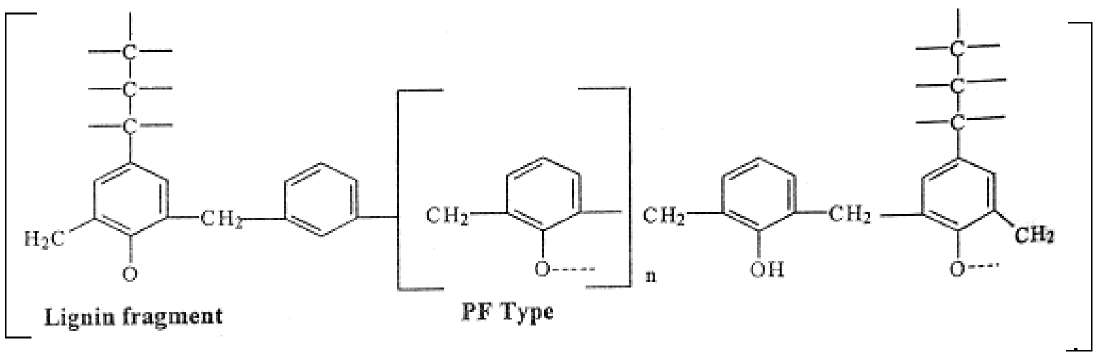

Figure 1: Copolymerization of lignin with phenol formaldehyde

It can be seen that similarities exist and therefore attempts were made to co-polymerize lignin with PF resin. Work carried out with softwood and hardwood black liquor lignin caused deterioration in the properties of the PF type substituted resins which required longer press time, higher press temperature and poorer water resistance than pure phenolic resins. Several studies have illustrated that lignin from the Agro residues show much promising prospects for its use in phenol substitution, the prime reason being that unlike the wood kraft lignin, its ortho position are comparatively less blocked, which do not hinder the co-polymerization reactions. It has been found that the soda lignin from Agro based fibrous raw material contain approximately 0.7 reactive sites per phenyl propane units. This value is about twice as high as that of wood kraft lignin. The lignin derived from the Agro based raw materials is therefore expected to be a good substitute for phenol in LPF resin than wood kraft lignin. The properties of resin with different formulations are mentioned in **Table 3**. It can be seen that flow time increases by gradual substitution of phenol with lignin. It is also evident from the corresponding increase of solid content.

Table 3. Lignin phenol formaldehyde (LPF) resin formulations and properties

Particulars	Batch 1	Batch 2	Batch 3
Phenol (98-99%), g	180	160	140
Lignin, g	20	40	60
Flow time in B4 flow cup at room temperature, sec	21.50	22.9	27.2
Water tolerance	1:14	1:14	1:14
pH	9.79	10.0	9.91
Solid content,%	50.47	50.55	50.55
Spread in g/m^2	320-350	320-350	320-350
Open assembly time to bring down glue coated moisture content to 14%-16%, min	65	60-95	60-95

Table 4 shows the evaluation test of lignin as a substitute of phenol in PF resin. These results indicate that up to 30 % substitution of phenol in PF resin yields good quality LPF resin for manufacture of boiling water proof plywood conforming to relevant BIS specification. The shear strength of lignin modified adhesive bond was also found good in all the three plywood panels as shown in **Table 5.** It was confirmed by continue six cycles of the test. Each cycle consisting of 72 hours boiling in water and thereafter drying at 65 ± 2 °C for 16 hours. No separation of plies at the edges and/or surface at the end of three cycles was observed.

Table 4. Evaluation of lignin as substitute of phenol in PF resin

Test	Specification	Result		
		90% Phenol +10% lignin	80% Phenol +20% lignin	70% Phenol +30% lignin
Boiling water proof testing	No separation of piles at edges	√	√	√
	Forcible separation with knife	Passed the test Excellent Bond	Passed the test Excellent Bond	Passed the test good

The use of this resin makes it practical to make ply boards and particle boards for exterior use. The major advantages of production of lignin substituted phenol formaldehyde type of resin is that a substantial reduction in resin/adhesive cost can be attained as lignin is much cheaper than PF resin, a petrochemical product dependent upon the price and availability of phenol. The product thus produced saved substantial quantity of phenol, a carcinogenic petroleum based product, providing a greener product to the consumer. The cost of phenol is more than ₹ 150 per kg. Replacement of phenol by black liquor laden lignin could fetch good price. It is therefore clear that resins of the type of LPF can be produced from black liquor lignin or lignin isolated from the black liquor. However, the advantage with the dissolved black liquor lignin is its lower base catalyst requirement in comparison to the resin prepared from precipitated lignin. The curing time of the LPF resins are comparatively longer than the PF resins. A suitable catalyst to reduce the curing time of the resin prepared needs to be found.

Table 5. Properties of the plywood panels

Test	Criteria for conformity	Actual observed Results		
		Makai	Silver oak	Popular
BWP GRADE (Boiling Water Proof) Six cycles : Each cycle consisting of 72 hours boiling in water and thereafter drying at 65 ± 2 °C for 16 hours	No separation of plies at the edges and/or surface at the end of three cycles On forcible separation of plies with knife, wood failure shall be predominant and shall be more than 75% for excellent bond and not less than 50% for pass standard. For less than 50% wood failure, the specimen shall be considered as failed	80%	47 %	72%

3.3 Utilization of sodium lignosulphonate as black liquor viscosity reducing additive

Soda based agro black liquors are known for high viscosity. The high viscosity leads to the formation of very large liquor droplets that creates problems during combustion of black liquors, increase energy consumption in pumping and higher scaling in evaporators. Firing of black liquor at lower concentration due to high viscosity is a measure concern of soda based pulp mill. There are several approaches to reduce the high viscosity such as increasing the firing temperature of the black liquor [2], salting-in [3], heat treatment [4] etc. This study proposes a novel approach of using sulphite black liquor as viscosity reducing agent. The alkaline sulphite liquor is basically a sodium lignosulphonate. The delignification process during sulphite pulping involves acidic cleavage of ether bonds, which connect many of the constituents of lignin. The electrophilic carbo-cation produced during ether cleavage reacts with bisulphate ions HSO_3^- to give sulphonates.

$$R\text{-}O\,R^- + H^+ \rightarrow R^+ + R\text{-}OH$$
$$R^+ + H\,SO_3^- \rightarrow R\text{-}SO_3H$$

The concentrated black liquors are known as high solids content black liquor. However, the single most important drawback to firing high solids content black liquor relates to its viscosity which dramatically increases with its solids content. The more the black liquor is concentrated in evaporators and the like, the more it tends to cause plugging of the evaporators, concentrators, transport lines, and the boiler firing nozzles. Consequently, although it is possible to currently obtain solids content of about 85%, black liquor solids content is generally maintained at approximately 60-65% to avoid plugging and fouling of equipment. Therefore, there remains an important need for the discovery of improved viscosity reducing additives. Studies were therefore initiated to develop viscosity reducing additive which will allow the firing of black liquors having solids content higher than 62 %. In order to determine the effect of lignosulphonate on the viscosity of concentrated soda black liquor, varying amounts of lignosulphonate in the form of slurry were added to the black liquor. Lignosulphonate was added to the weak black liquor prior to concentration so as to achieve through mixing of the lignosulphonate with the black liquor during concentration. Viscosity determinations were then made for the control black liquor at different black liquor solids concentration and compared with those obtained after addition of lignosulphonate. The results obtained for the study are presented in **Table 6**. The table shows a marked drop in black liquor viscosity after addition of even 1 % lignosulphonate at black liquor solid concentration of 58 %. Higher black liquor solid concentration can therefore be attained with use of Lignosulphonate based additive resulting in energy savings in the form of additional steam generation. Application of sulphite black liquor based lignosulphonate as viscosity reducing additive can increase black liquor firing solids from 62% to 67%. This will lead to the production of higher steam to the tune of ~ 70 tonnes per day and hence will contribute to substantial energy savings.

Table 6. Effect of Lignosulphonate based additive on Soda Black Liquor Viscosity

	Black Liquor Viscosity in mps at different solids		
	45% BL Solids	50 % BL Solids	58 % BL Solids
Control Black Liquor	115.0	263.0	1230.3
Black Liquor + 1% lignosulphonate on w/w	104.7	260.0	805.0
Black Liquor + 2 % lignosulphonate on w/w	56.2	177.8	619.8

4. Conclusions

- Lignin rich agro residue Black liquor can be effectively used in making PLF resin where it can replace phenol up to 30%.
- Lignosulphonate can be used as additive in soda black liquor to reduce viscosity. The results obtained showed that 2% addition of Lignosulphonate reduced the viscosity by more than 30% resulting in achieving higher black liquor solids.
- Firing at Higher black liquor solids improves thermal efficiency of chemical recovery boiler.

Utilization of sulphite black liquor directly as a viscosity reducing additive can help small pulp and paper mills in improving their economy and effective use of agro residue as raw material for pulp and paper.

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