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

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IPPTA Seminar

August 17-18, 2018, Muzaffarnagar

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Structure of Presentation

This presentation is divided in the following points:

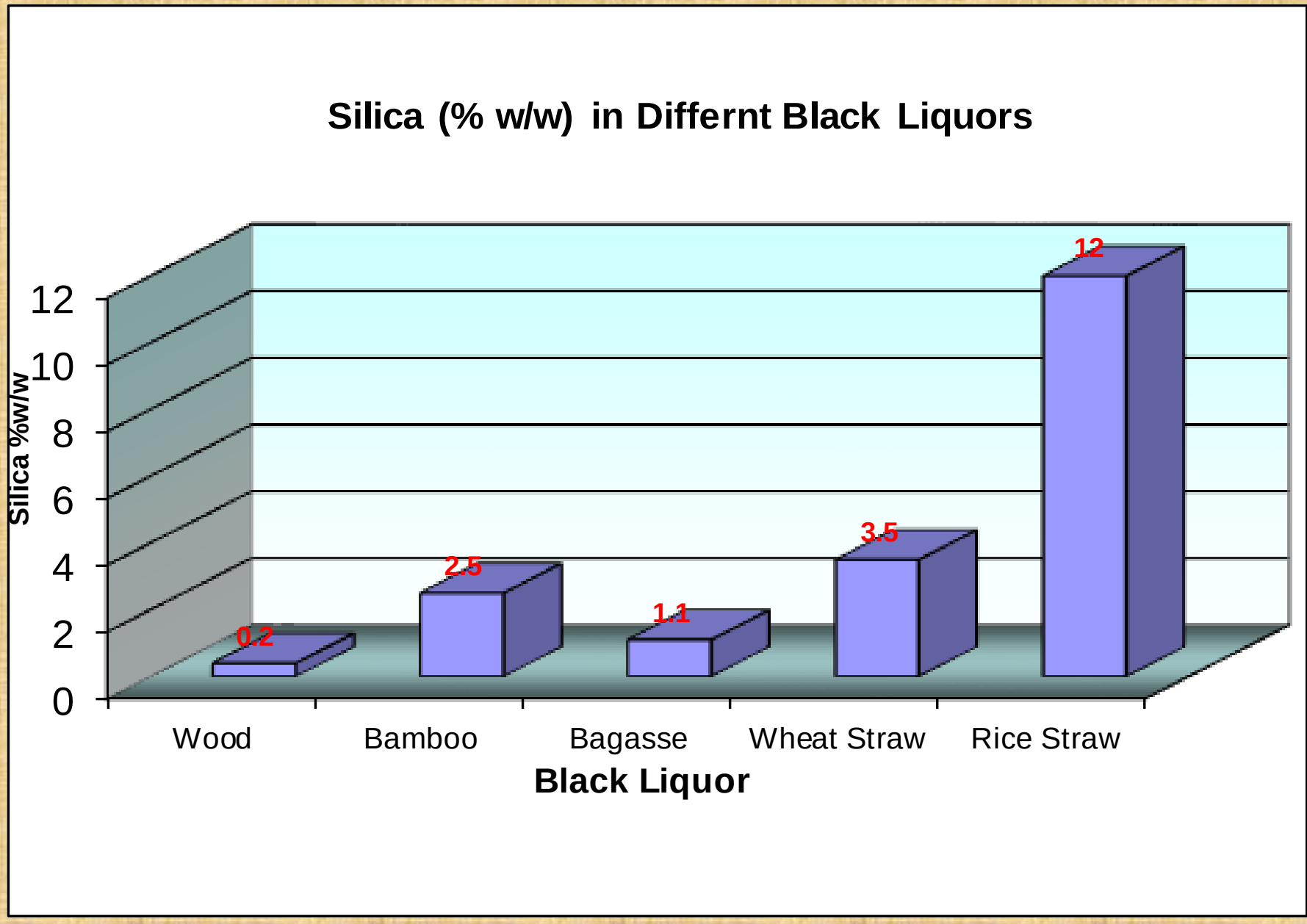
- **Background of work**
- **Objective of the study**
- **Agro Black Liquor and Associated Problems**
- **Utilization of Lignin rich Black liquor Biomass in:**
  - Phenol-Lignin-Formaldehyde Resin
  - Reducing viscosity of soda black liquor
- **The way forward**

Background of the Study

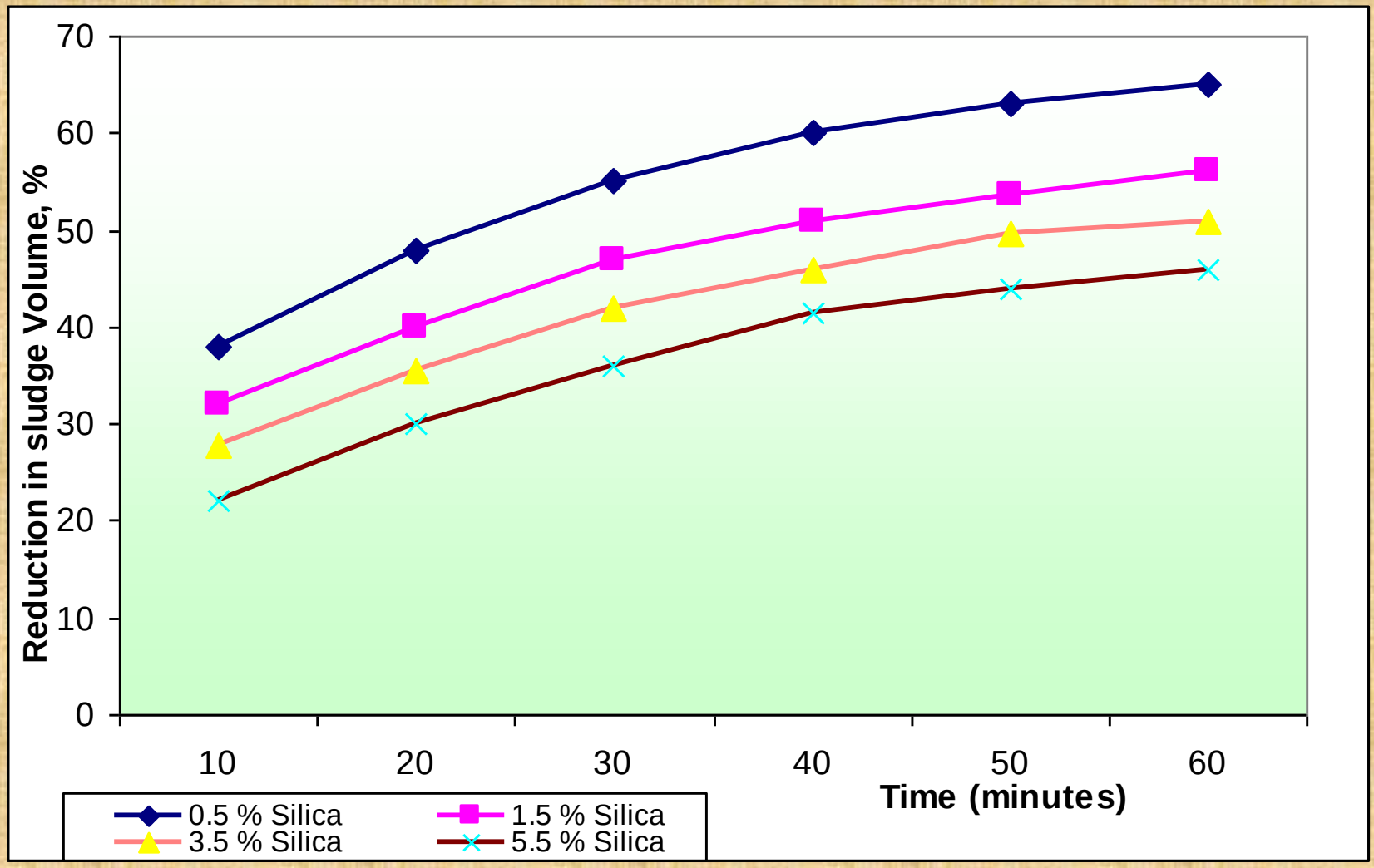
- **Black Liquor is a potential source of energy and cooking chemicals. Large mills are equipped with conventional chemical recovery and are recovering energy and chemicals from black liquor.**
- **Small Mills based on agro Based raw material have adopted Copeland recovery process and are getting back the sodium compounds but energy is not recovered.**
- **Large mills having conventional chemical recovery system could not marginally expand their pulp mill capacity and can not adopt ODL as capacity of chemical recovery is a bottleneck.**

Background of the Study

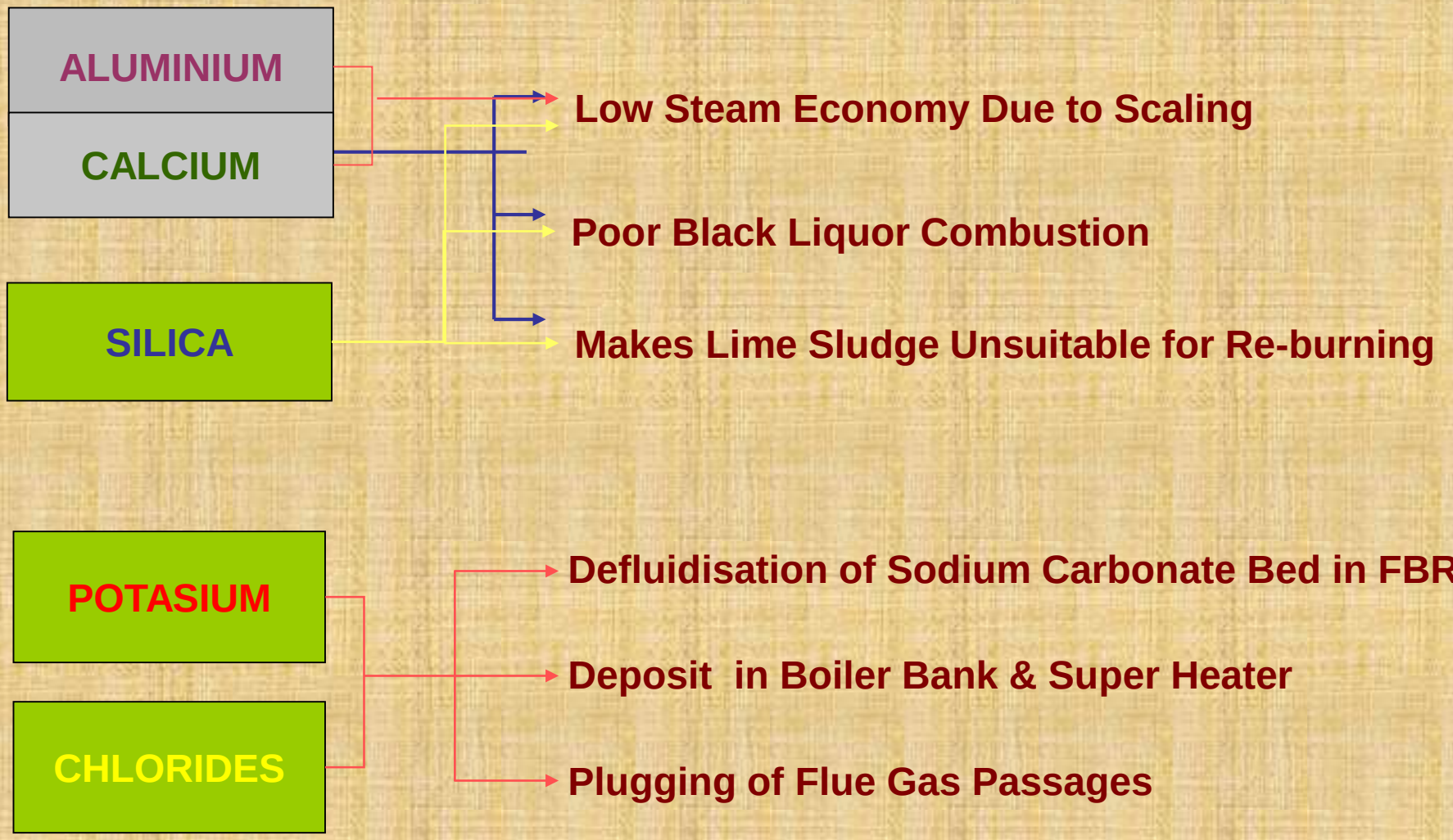
- CPPRI has been working on the process to marginal expand recovery capacity and in this process lignin as a waste biomass is generated.
- In this background studies were initiated at CPPRI to find some industrial application of this lignin which is being generated as waste biomass.
- Small mills producing packaging grade of paper from Agro residue are looking for black liquor based lignin utilization.
- Studies on utilization of this agro-residue soda or sulphite black liquor based waste lignin were conducted in plywood industry and paper industry as black liquor viscosity reducing agent.


Silica (% w/w) in Differnt Black Liquors
Silica %w/w
12
10
8
6
4
2
0
0.2
2.5
1.1
3.5
12
Wood
Bamboo
Bagasse
Wheat Straw
Rice Straw
Black Liquor

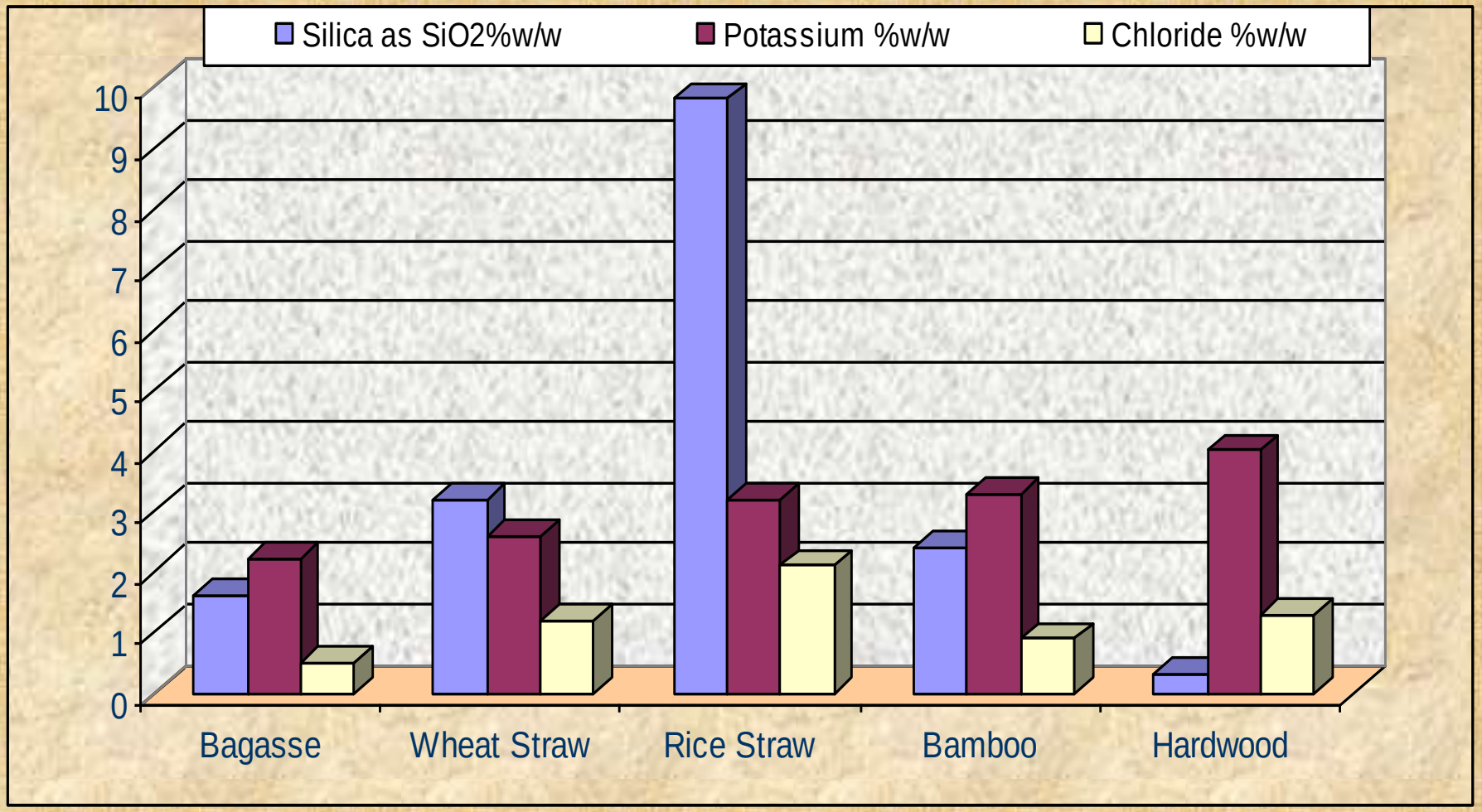
Settling Rate of Lime sludge at Different Silica Concentrations



IMPACT OF NON-PROCESS ELEMENTS ON VARIOUS RECOVERY UNIT OPERATIONS



Non Process Elements in Black Liquor



Utilization of Lignin rich Black liquor Biomass in various industries

Studies On Development of Phenol Lignin Formaldehyde Resin

Phenol-formaldehyde (PF) resins are characterized by their high strength and moisture resistance. The costs of PF resin is the main factor limiting its use, have been the subject of considerable fluctuation, largely as a result of variability in the world oil market, but there is no trend indicating any long-term reduction of phenol costs. An alternative, cheaper source of phenols would be of great interest to all users of PF resin. Utilization of black liquor lignin as a partial replacement of phenol could be a route to this.

Studies On Development of Phenol Lignin Formaldehyde Resin

- Lignin-phenol-formaldehyde (LPF) resins were produced by substituting phenol with black liquor lignin in various percentages. Phenol was replaced by various percentages of lignin to keep the phenolic to formalin weight ratio constant to 1:1.8.
- 10%, 20% and 30% replacement of phenol by lignin were adopted in making lignin phenol formaldehyde resin (LPF Resin).
- The plywood panels of 4 mm thick, 30 X 30cm were made and the panels were subjected to test as per IS: 848:2006, specification for synthetic resin adhesives for plywood (Phenolic and Amino plastics).

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

Lignin modified phenol formaldehyde resin (PLF) adhesive formulations

Particulars	Batch 1	Batch 2	Batch 3
Phenol	180 gm	160 gm	140 gm
Lignin	20 gm	40 gm	60 gm
Flow time in B4 flow cup at room temperature	21.50 Sec.	22.9 Sec.	27.2 Sec.
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 gms/sqm	320-350	320-350	320-350
Open Assembly (min. to bring down glue coated moisture content to	65	60-95	60-95

Application of PLF Resin in Plywood Industry

The objective of this study is to investigate the extent to which black liquor lignin solids could replace phenol in PF resins designed for application as an adhesive to bond plywood. A Panel of 4 mm thickness (1 sq. Feet) boiling water proof was made and properties of lignin modified phenol-formaldehyde (LPF) resins were tested as per IS: 848:2006

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

Properties of the 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^{0}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%

Application of lignin in Plywood Industry

- Up to 30 % substitution of phenol in PF resin yields good quality Phenol Lignin Formaldehyde (PLF) resin for manufacture of Boiling water proof plywood conforming to relevant BIS specification

- 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 Rs. 150/kg. Replacement of phenol by Black liquor laden lignin could fetch good price.

Utilization of lignosulphonate as Black liquor viscosity reducing additive.

- **Objective:** To achieve higher black liquor solids with enhanced energy generation potential in soda pulping based agro pulp and paper mill

Utilization of lignosulphonate as Black liquor viscosity reducing additive

- Soda black liquor in agro based mill is known for high viscosity & makes it difficult to achieve higher total solids concentration of firing black liquor.

- Low solid concentration of black liquor is the main reason for lower steam generation per ton of black liquor in these mills.
- Concentration of black liquor fired in recovery boiler has great influence on energy saving, boiler through- put capacity and abatement of pollution

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

Utilization of lignosulphonate as Black liquor viscosity reducing additive.

- Lignosulphonate due to their inherent chemical nature can be used as Black liquor viscosity reducing additive.

- Lignosulphonate generated during project study were tried for reducing viscosity of soda bagasse and soda straw black liquor

- In order to determine the effect of lignosulphonate on the viscosity of concentrated soda black liquor , varying amounts of lignosulphonate in the form of a slurry were added to the black liquor

Utilization of lignosulphonate as Black liquor viscosity reducing additive.

- 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 for the control black liquor at different black liquor solids concentration and compared with those obtained after addition of lignosulphonate

Effect of Lignosulphonate based additive on Soda Black Liquor Viscosity

	Black Liquor Viscosity in mps		
	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

Energy Savings from firing of higher black liquor solids

Gross Calorific value of Black liquor = 3100Kcal /Kg

Net Calorific value at 62 % black liquor solids = 1922 Kcal/ Kg
(Before addition of lignosulphonate)

Net Calorific value at 67 % black liquor solids = 2077 Kcal /Kg

Difference in calorific value = 155 Kcal/ Kg

Additional steam generated by combustion of = 300X155X1000

300 t/d black liquor solids with higher = 70 t steam /day

Assuming that 10 tons of steam is produced from 1 ton of RFO
Energy saving in oil equivalents = 2555 tons of oil / annum

Conclusion

- Lignin rich agro residue Black liquor can be effectively used in making PLF resin where it can replace phenol upto 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.
- Pulp and paper industries in India should opt for biorefinery approaches to compete with global industries. Industry should look for the possibility of producing green energy, value added chemicals from lignin to be substitute.


THANK YOU