Desilication of Wheat Straw Black Liquor

A. K. Dixit[1], R. M. Mathur[1] and A. G. Kulkarni[2]

Although wood is the most widely used raw material for pulp and paper industry, its availability is limited in many forest deficient countries. With the shortage of forest-based raw material and to preserve the depleting forest, the paper industry in Asia and other parts of the world is forced to use non-woody fibrous raw materials. India is also one of the leading countries using substantial proportion of non-wood raw materials such as bamboo, cereal straws, bagasse, etc., which constitute about 35% of the total raw material furnish used in Indian paper industry. Non-wood raw materials are characterized by high silica content which varies between 1.5 to 15%. Major portion of this silica gets dissolved in spent pulping liquor during alkaline pulping. Presence of this silica in black liquor creates innumerable problems in operating chemical recovery system. Evaporator, Recovery furnace, causticization and lime kiln operations are adversely affected by the presence of silica in black liquor. Presence of silica in lime sludge from a wheat straw based mill does not allow installation of lime kiln. This causes severe solid waste pollution. Central Pulp & Paper Research Institute (CPPRI) is an apex R & D organization dedicated to applied research in the area of pulp and paper. The Institute has carried out extensive work on utilization of non-wood raw materials for pulp and papermaking and also to address the problems associated with these raw materials during processing in pulp & paper industry. Wheat straw and bagasse are the two main agro-residue raw material used in the Indian subcontinent. Silica content in bagasse black liquor is in the range of 0.4- 0.5% while in wheat straw it is 4.0 -5.0 % w/w. Due to the presence of this high amount of silica processing of wheat straw black liquor in chemical recovery is very difficult. Looking into this problem CPPRI initiated detailed studies on desilication of wheat straw black liquor. The objective of this study was to effectively remove silica from wheat straw black liquor. Black liquor was collected from an integrated wheat straw based mill. Silica content in the original black liquor was in the rage of 3.5 – 5.0 g/l. The black liquor was subjected to carbonation under controlled conditions using recovery boiler flue gas as source of carbon dioxide. Controlled pH reduction led to selective precipitation of silica without co-precipitation of lignin. Residual silica content in the black liquor after desilication was 0.4 g/l and nearly 90% desilication was achieved. Black liquor properties before and after desilication were evaluated. The results show improved black liquor properties after desilication. Viscosity was reduced to nearly 60% while swelling volume ratio increased by 1.5 times. The black liquor was colloidally stable up to 65% total solid concentration and no precipitation was observed. Improved black liquor properties of wheat straw black liquor after desilication makes it suitable for processing in conventional chemical recovery system & lower amount of silica in lime sludge will allow installation of lime kiln. This will reduce solid waste pollution.

INTRODUCTION

The Indian Pulp & Paper Industry is more than a century old industry. The first paper mill was established in the year 1832, based on imported raw materials. Increasing rate of literacy, industrialization and better packaging of all general use products, presents a high rate of demand growth for the pulp & paper sector.

Rising cost of inputs, stringent environmental regulations, poor infrastructure facilities and non-availability of raw material have resulted in closure of many Paper mills. Due to scarce availability of forest based raw material non-wood raw material will be the major renewable source of fibers. In contrast to wood, the nonwood raw materials contain a significant portion of silica. During pulping this silica gets dissolved in cooking liquor at high temperature and alkaline conditions and passes into black liquor.

The presence of silica in black liquor causes serious problems in the

1 Scientists

2 Director

Central Pulp & Paper Research Institute, Post Box No. 174, Saharanpur- 247001 (U.P.)

operation of chemical recovery plant (1). The major problems are:

- Scaling on heat transfer surfaces in the evaporator
- Silica rich black liquor burns at slower rate and causes problem in recovery furnace.
- Retards settling rate during causticization process.
- Lime reburning kiln becomes uneconomical when high percentage of silica are present in lime kiln.

Due to these problems the mills using silica rich raw materials are unable to install chemical recovery system. So there is a strong need to remove this silica from black liquor.

Efforts for removal of silica from pulping and chemical recovery loop are going on for last five decades. Research work was carried out on desilication of black liquor and green liquor using different techniques like addtion of cations (lime and alumina) and reduction of pH.

The methods developed earlier did not live up to the expectations and none of the technique was scaled up to commercial scale. The methods involving addition of cations did not become popular as enormous quantities of sludge is produced when desilication is carried out by addition of lime or alumina. There is an additional problem of suspended residual flocculant (Lime or alumina) which does not settle readily and can cause similar problems like silica.

Reduction of pH either by acid or CO_2 were tried. But the ultimate choice was use of CO_2, as it is impossible to control the pH by mineral acids. The critical silica precipitation pH lies very close to lignin precipitation pH. The conventional methods of gas – liquid mass transfer like direct bubbling of CO_2 or in a counter current fashion using packed bed column did not work satisfactorily due to over carbonation and foam flooding (2).

Technology developed by CPPRI

Central Pulp & Paper Research Institute initiated work on desilication in early eighties and did extensive basic research on mechanism of silica precipitation and reactions involved in desilication by carbonation. CPPRI adopted the carbonation technique essentially because the process does not produce sludge like lime treatment method where massive quantities of sludge is generated.CPPRI initiated work on desilication of black liquor and has developed a desilication technology based on stepwise carbonation technique. The performance of full scale desilication plant has been successfully demonstrated on bamboo black liquor. Studies were further conducted on straw black liquor.

Other than bagasse, Wheat Straw is the major non-wood raw material used by Indian paper industry. Wheat straw contains 3.0-3.5 % silica. A major portion of this passes into black liquor during soda pulping. Wheat Straw black liquor contains 4.0 -4.5% silica. Looking into the problem faced by the wheat straw based mills there was a need to prove the efficacy of the technology on wheat straw black liquor.

During desilication by carbonation, black liquor undergoes a number of physical and chemical changes. A number of articles have been published on desilication of black liquor but not much information is available on change in black liquor properties after desilication. Looking into this, for the first time studies were concentrated on change in wheat straw black liquor behaviour after desilication.

The present paper highlights studies carried out on desilication of wheat straw black liquor on pilot plant scale. The studies cover the optimization of desilication parameters and black liquor behavior after desilication.

MATERIALS & METHODS

- **Source of Wheat straw black liquor**

Wheat straw Black liquor was collected from a wheat straw based mill employing soda pulping process. The mill is equipped with conventional chemical recovery process.

- **Source of flue gas**

Flue gas was tapped from chemical recovery boiler stack.

- **Chemical Analysis of Black liquor**

The TAPPI method T-625 CM –85 was used for black liquor analysis.

- **Elemental Analysis of Black liquor**

Elemental analysis was carried out by using CHNS analyzer and atomic absorption spectrophotometer.

- **Viscosity Determination of Black Liquor**

Viscosity of black liquor was determined by using HAAKE Rheometer.

Black Liquor Desilication

Black liquor desilication studies were conducted on semi pilot scale. The reactor consists of two communicating tubes of about 2.5 meter height and 10 cm diameter, through which a high speed centrifugal pump circulates the black liquor to be treated. Near the upper end of the tube provision is made for the upward flowing liquor to suck in by ventury action the flue gas through two openings. The gas stream is broken up into discreet particles, the size and speed of which can be regulated. Due to the shearing action of the liquor, the gas bubbles are continuously replaced exposing new surfaces for efficient mass transfer over the liquid/gas boundary.

The pH of the circulating liquor was continuously measured and recorded by temperature compensated electrodes. Rotameters were used to determine & regulate the gas intake into each reactor. Reaction temperature was kept above 75°C initially and

Table 1

Physico-chemical Characteristics of black liquor

Parameter	Value
pH at 30°C	12.5
RAA g/l as NaOH	4.5
Silica as SiO_2, g/l	3.5
Inorganics as NaOH, % w/w	36.7
Organics , %w/w	63.3
Swelling Volume Ratio (SVR), ml/g	9
Calorific Value, Cals/gm	2797
Carbon as C, % w/w	28.5
Hydrogen, % w/w	3.10
Nitrogen as N, % w/w	0.23
Temperature of Ignition, °C	590

Table 2

Viscosity of Wheat Straw Black liquor

Total Solids, % w/w	Viscosity at 90 °C, mpasec.
50	79
55	199
60	446.7
65	Could not be determined

maintained around 70°C. Filtration was carried out using laboratory vacuum equipment and ordinary filter papers.

The plant was put into continuous operation and about 60 liters of black liquor was carbonated in each trial.

RESULTS & DISCUSSION

Black Liquor Evaluation

Black liquor is one of the highest ash containing fuel used commercially. Black liquor properties play an important role during its processing in chemical recovery plant(3). Therefore knowledge of black liquor properties is essential for designing and operation of chemical recovery boiler efficiently. Wheat straw black liquor collected for the study was analysed for various parameters. The results are shown in Table 1 and 2.

It is clear from the results that wheat straw black liquor contains high amount of silica, which causes problems in smooth functioning of chemical recovery system. This high amount of silica in wheat straw black liquor makes recovery of chemicals very difficult and does not allow lime reburning. Viscosity of the wheat straw black liquor is also on higher side and black liquor becomes unstable above 65% total solids concentrations. High viscosity of black liquor also causes numerous problems in evaporation section.

Desilication of Wheat straw Black liquor

Black liquor was carbonated at different pH levels in order to optimize the conditions for desilication of wheat straw black liquor. The results obtained are shown in table 3.

The results obtained has clearly revealed that optimum pH for desilication is 9.9-10.0. Residual silica level is 0.25 g/l which is as good as wood black liquor. Following observations were made during desilication studies.

- The carbonated black liquor was easily filtrable
- No lignin precipitation is observed
- Foam generation was moderate
- More than 90% desilication was achieved.

Realkalization of Desilicated black liquor

The degree of desilication is a function of pH. During carbonation, pH of the black liquor drops down to 10.0. Residual active alkali of the black liquor drops during carbonation. Carbonated black liquor has a RAA level below 1.0 in most cases. This leaves the lignin in unstable state. Concentration by evaporation of such liquor causes early viscosity rise and precipitation, long before the concentration required for self sustained combustion arrived(4). For stability of black liquor certain level of residual active alkali is essential in black liquor. Realkalsation of carbonated black liquor by addition of different dosage of alkali is carried out in order to make the black liquor stable. Around 4.0 gpl of caustic is required to check the precipitation during evaporation.

Change in black liquor behavior after desilication

The chemical and thermal recovery efficiency of silica rich black liquor based chemical recovery plant is low as compared to wood based mills. The primary reason is the nature of raw material and its effect on black liquor properties like organic to inorganic ratio etc. These components ultimately influence the processing of black liquor in chemical recovery section.

Nature of black liquor changes after desilication. Physico-chemical and rheological properties of black liquor were examined after desilication and were compared with original black liquor.

Physico-chemical characteristics of desilicated black liquor

Desilicated black liquor was analyzed

for its physico-chemical prioperties and the same were compared with original black liquor. The results are shown in table-4.

The results shown in table 4 have revealed that there is no significant change in physico-chemical properties of wheat straw black liquor after desilicaion. Silica has goes down to 0.25% as against 3.2 in original black liquor.

Improvements in Thermal properties of desilicated black liquor

Thermal properties of black liquor are important for efficiency of chemical recovery boiler. Swelling Volume Ratio, Calorific value and Temperature of Ignition were determined before and after desilication. The results are shown in table–5.

The results shown in table 5 revealed that there is a marginal increase in calorific value. Temperature of ignition has gone down to 575 from 590°C.

Swelling Volume Ratio (SVR) increased from 9 to 15 ml/gm after desilication. Figure-1 shows the improvement in swelling characteristics of wheat straw black liquor after desilication.

Increase in Swelling Volume Ratio and lower Temperature of ignition value is a pointer towards better burning behaviour of desilicated black liquor. Marginal increase in the calorific value will improve thermal energy recovery from black liquor.

Improvement in viscosity of desilicated black liquor

Black liquor is a colloidal system and its viscosity depends largely upon the colloidal stability of lignin, macromolecules present. Higher pH and presence of free alkali ensures that lignin remain in colloidal form. On carbonation, free alkali is almost completely destroyed and lignin becomes colloidally unstable. Therefore addition of caustic is necessary to retain the fluidity of the liquor at higher concentration. Viscosity of the realkalised desilicated black liquor and original black liquor were determined at increasing dry solids concentrations. Figure-2 represents the viscosity curve of original and desilicated wheat straw black liquor showing the influence of silica on viscosity. The figure shows that significant reduction in viscosity is achieved after desilication of wheat straw black liquor. High viscosity values of black liquor are generally the

Table 3
Results of desilication trials

Black Liquor Characteristics			
Before Desilication		After Desilication	
pH	SiO_2, g/l	pH	SiO_2, g/l
12.5	3.5	10.4	3.0
		10.2	0.7
		10.1	0.6
		10.0	0.35
		9.9	0.25
		9.8	0.25

Table 4
Physico-chemical characteristics of black liquor before and after desilication

Parameter	Value	
	Before Desilication	After Desilication
pH at 30°C	12.5	12.3
RAA g/l as NaOH	4.5	3.5
Silica as SiO_2, g/l	3.2	0.25
Inorganics as NaOH, % w/w	36.7	36.8
Organics , %w/w	63.3	63.2
Carbon as C, % w/w	28.5	28.1
Hydrogen as H, % w/w	3.10	2.99
Nitrogen as N, % w/w	0.23	0.28

Table 5

Improvements in Thermal properties of desilicated black liquor

Parameter	Value	
	Before Desilication	After Desilication
Swelling Volume Ratio (SVR), ml/g	9	15
Calorific Value, Cals/gm	2797	2813
Temperature of Ignition (Tig) , °C	590	575

function of hemicelluloses content in the black liquor. As desilication is carried out at a temperature much below the hemicelluloses degradation temperature, it is obvious that removal of silica caused the marked reduction in black liquor viscosity.

Analysis of silica sludge separated from black liquor

Silica sludge obtained in different desilication trials were collected after washing with hot water. Precipitated silica was analysed for various parameters. It has whitish appearance, having a brightness of 68.4 % ISO. It had about 82% ash, and on ash basis it had 95% silica. On O.D. sludge basis, silica content is 79.8%. Only traces of lignin are found in the silica sludge. Results are depicted in table-6. Wheat straw silica may find application in paints, rubber, pesticides and tyre industry. Figure -3 shows precipitated silica from wheat straw black liquor before and after hot water washing.

CONCLUSIONS

The presence of high amount of silica in wheat straw black liquor causes numerous problems in chemical recovery installations. The desilication process developed by Central Pulp & Paper Research Institute has shown that silica can be effectively removed from wheat straw black liquor to the tune of 90%. Detailed black liquor analysis after desilication has shown that burning and rheological properties of black liquor are improved. This will help in improving chemical recovery and thermal efficiency of chemical recovery boiler. Residual silica content in only 0.3 gpl which is very much close to wood black liquor. With this silica content in black liquor lime kiln installation can be reality in wheat straw black liquor.

Table 6

Analysis of Wheat straw Silica

Parameter	Value
Ash, %w/w	82.2
Silica, %w/w, ash basis	95.0
Silica, %w/w, Sludge basis	79.8
Lignin, %w/w	0.1
Brightness, % ISO	68.4

(Hot water washed)

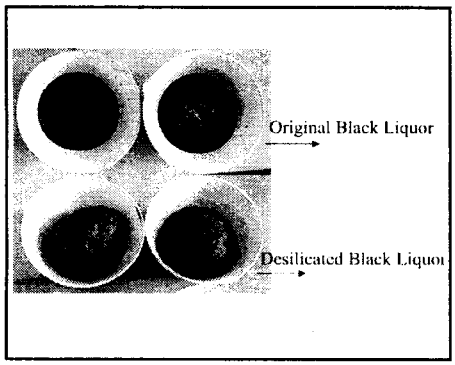

Fig. 1 Improvement in Swelling Volume Ratio after desilication

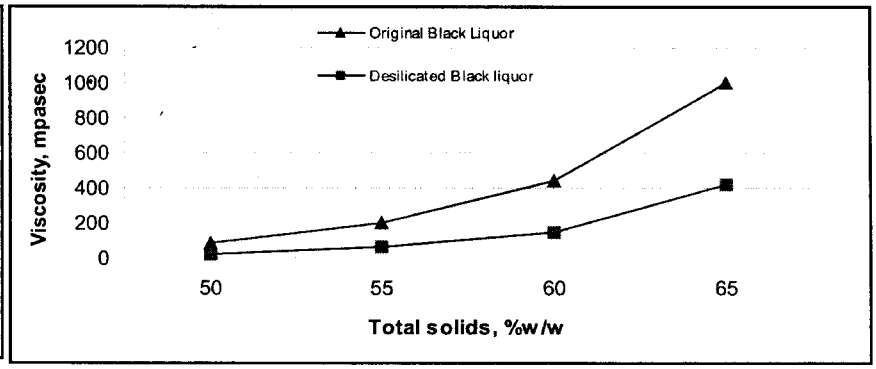

Fig. 2 Viscosity of Original & Desilicated Black Liquor

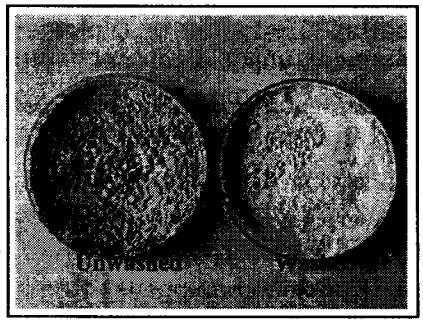

Fig. 3 Silica separated from Wheat straw black Liquor

REFERENCES

1. Panda, A. – Indian Pulp & Paper 26 (7) : 1 (1962)
2. Kulkarni, A.G., Kolambe, S.L., Mathur, R.M. & Pant, R. – Ippta, 21(1) : 37 (1984).
3. Fubes, G.S., JPPS, 10 : J57 (1984)
4. Soderhjelm, L., Paperi Ja Puu, 68 : 642 (1980)