

# Chemical recovery from small rice/wheat straw based pulp and paper mills prospects.

Dr. RAO N. J.\*

## INTRODUCTION :

In India most of the small mills using pulping depend on non-wood fibers like Rice straw, wheat straw, bagasse and some of the locally availables agri-residues like sarkanda. The mills use soda or lime-soda pulping and manufacture chemical, semi-chemical pulps. The black liquor coming from brown stock washing is usually very dilute (4-8% total dissolved solids). This is essentially due to poor washing and drainage characteristics. Further practically no mill in the country using these non-woody raw materials in the capacity range of 30 TPD practices chemical recovery. The technical feasibility to recover chemicals and energy from black liquors using conventional recovery systems did not meet with success due to the problems of high viscosity and high silica (and hence scaling) of

these B.L. These mills have hence become a source of major water pollution and face the threat of not meeting the set national environmental standards.

Against this back drop, there are several mills in other countries particularly China which use non wood fibers like wheat and rice straw and are small, but are adopting chemical recovery for black liquors from chemical/semi-chemical pulps<sup>1,2</sup>. These developments alongwith other attempts to find plausible alternatives to chemical recovery should be viewed seriously to find a solution for indian small mills.

Before analysing the problems of chemical recovery of small mills it is essential to see first the different pulping techniques used for nonwood fibers. Non wood fibers are essentially characterized by lower

Table 1—Comparison of Different Pulping Processes for non-wood fibers.

Detail	Soda Process	Kraft Process	Green liquor Sulphite Process	Neutral Sulphite Process	Alkaline Sulphite Process
Chemicals	4-14% NaOH	8-14% as Na <sub>2</sub> O (NaOH, Na <sub>2</sub> S) 18-25% Sulphidity	6-14% as NaOH (Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> S and Na <sub>2</sub> SO <sub>2</sub> )	Na <sub>2</sub> CO <sub>3</sub> -0.2 SO <sub>2</sub> -2%	Na SO <sub>3</sub> -12% NaOH-3% (18-20% as NaOH 20% as SO <sub>2</sub> ) AQ 0.02-0.5%
Bath Ratio	1:3 to 1:6 in all cases				
Starting pH	11-12	10-11	9-10	7-9	10-13
Max. temp.	150°C - 170°C in all cases				
Final pH (Black liq. pH)	8.5-9	9	7.5	7.0	9.5-11
Yield, % (Unbleached screened)	40-46	40-45	52-54	48-50	50-52

\*Institute of Paper Technology, Saharanpur-247001 (U.P.)

lignin, lower cellulose, shorter fiber lengths. It has higher pentosans, higher hemicelluloses, higher silica. They have lower extractives. The possible pulping methods and their specifications are shown in Table—1. There are several advantages and limitations of each of these processes.

#### INDIAN SCENE :

In Indian small mills processing non wood fibers, caustic soda is used as a cooking liquor with a bath ratio ranging between 1:4 to 1:6 at a cooking temperature of 165°C. The alkali charge is 8-14% NaOH on O.D. raw material basis. The charge is lower for semi-chemical/chemi-mechanical pulps while it is on the higher side for chemical pulps. The volume and concentration of black liquor generated varies depending on the yield, and washing. The silica content in black liquor is dependent not only on the raw material used, but equally on pulping process followed and raw material preparation. Some information relating to black liquor characteristics from small mills in India is given in Table No. 2.

Table -2 : Characteristics of Black Liquors From Small Non-wood Fiber Pulp Mills In India.

(Cooking-soda process, bath ratio 1:4-1:6 or more  
Alkali charge 6%—14% NaOH).

Parameter	Range (Average)	Remarks
pH	7-11 (~90)	Based on 14 mills of capacity varying from 8 TPD
Sp.gr. at 20°C	1.014-1.045 (~1.022)	
Total solids,%(W/W)	4-9.07 (~5)	30 TPD using rice straw, wheat straw bagasse, sarkanda grass and other agriresidues.
Residual alkali, g/l	0-7.32 (~3)	
Total alkali as Na <sub>2</sub> O, g/l	7.59-18.5 (~11)	
Silica as SiO <sub>2</sub> ,% dry solids	0.73-12.85	
IOM/OM	1:2.09-1:3.46	
Calorificvalue, KCal/kg.	2932-3853	
Swelling volume Index, SVI, ml/g	4.0-18.6	

For any chemical recovery it is essential to concentrate the weak black liquor and burn the same to recover the energy and chemical values. Initial low dilution of weak black liquor, very high viscosities of black liquors at medium/higher concentrations, high silica content are major obstacles in any recovery process. The concentration of silica in spent Black liquor for different raw materials is shown in table—3.

Table—3.: Concentration of silica in spent Black Liquors (3)

Raw Material	Silica %
Rice straw	16—30
Cereal straw	3—6
Bamboo	2—5
Bagasse	1—3
Eucalyptus	0.1—0.8

The concentration of silica is particularly high in rice and wheat straw black liquors. The result of this high silica is fouling of heat transfer surfaces and difficulties in pulping and concentration.

The characteristics of black liquor which have influence on processing further for recovery of chemicals and energy can be classified as chemical, Physical, thermophysical, rheological and polymeric. There are scattered studies which indicate such data for non-wood materials mostly for kraft or soda black liquors.

Black liquor contain practically all alkali and sulphur originally charged into the digesters along with almost over 50% of the original weight of the non-wood fibrous raw materials. The liquor is intense black tending to reddish brown on dilution.

Even at very low concentration of 0.04% with water, the liquor retains the dark yellow colour of straw. The liquors are foamy at lower concentration. Foam increases with increase in resin content of raw material and is more for sulphate liquors than soda black liquor.

Specific gravity of the liquor depends on the concentration of solids and temperature. At any concentration specific gravity increases with increase in Inorganic matter.<sup>(13)</sup>

Specific gravity, concentration, degree Baume and degree Twaddell are correlated for a given liquor as under.

$$^{\circ}\text{B}_e = 145 - \frac{145}{\text{Sp. gr.}}$$

$$^{\circ}\text{T}_w = \frac{\text{Sp. gr.} - 1}{0.005}$$

Specific gravity is taken at 15.5°C with respect to water at the same temperature. A rough estimation of total solids concentration as wt. % is obtained by multiplying degree Baume (0 Be) by 1.5.

Increase in temperature causes a fall in oBe value as specific gravity falls. A 20°C rise in temperature shows a fall of 1°Be at low concentration. Similarly at higher concentrations a fall of 1°Be is observed by a rise of about 14°C.

Table-4 shows some correlations for predicting major design properties from Bamboo and Bagasse soda/kraft black liquors. These include specific gravity, specific heat, thermal conductivity and boiling point rise.

Table-4: Correlations for major design properties of Bamboo and bagasse black liquors (4)

Property	Correlation
Specific gravity (S)	$S = 1.012 + 0.763 C - 4.7 \times 10^{-4} T$ $T = 4.86 \times 10^{-4} CT$
Specific Heat KCal/kg° K, (CP)	For Bamboo B.L. $CP = (1.8 \times 10^{-3} T - 0.540)C + 1.0$ For Bagasse B.L. $Cp = (1.04 \times 10^{-3} T - 1.26)C + 10$
Thermal conductivity, KCal/h m°K, (K)	$K = 0.504 - 0.282 C + 1.35 \times 10^{-3} T$
Boiling Point Rise, CP (BPR)	$BPR = 84C^2 - 107.5C^3 - 255C$

NOTE: C-is concentration of black liquor solids, wt%.  
T-is Temperature of B L. °C.

Surface tension of black liquors decreases with increase in concentration of solids and with increase in temperature of the liquor. Surface tension values are lower for Bamboo B.L. compared to bagasse B.L. under similar conditions.

The chemical composition of black liquor is strongly dependant on the nature of raw material, cooking chemical used and conditions set in pulping. Most alkali is present as Na<sub>2</sub>CO<sub>3</sub> or organic Na. Some of the organic sodium compounds are in the form of rosin soap

which accounts for the intense foaming characteristic of the black liquors. In sulphate process, organic sulphur compound are present alongwith Na<sub>2</sub>S, Mercaptans. Small amounts of Na<sub>2</sub>SO<sub>4</sub> may also be present. The black liquor from soda pulping is distinctly alkaline, but is not caustic as large part of alkali is in the form of neutral compounds. The proportion of organic to inorganics increases with increase in alkali (cooking chemicals) in digester, increase in cooking temperature and increase in cooking time particularly at maximum temperature. Typical chemical composition of B L for non woods for soda/alkaline sulphite process are shown in Tables 5,6, and 7.

Table-5: Typical composition of non wood black liquors from kraft pulping of Bamboo and Bagasse (4,5)

Component	g/l	Component	g/l
Organics : Lignins	30-40	NaOH	4-8
Degraded	45-65	NaHS	6-10
carbohydrates		Na <sub>2</sub> CO <sub>3</sub>	10-15
Soaps & Mercaptans	Small	Na <sub>2</sub> SO <sub>4</sub>	2-4
		SiO <sub>2</sub>	4-8
		Na <sub>2</sub> S	
		Na <sub>4</sub> SO <sub>3</sub>	Small

Table-6: Composition of Soda and alkaline sulphite rice and wheat straw black liquors.

Details	Rice Straw		Wheat Straw	
	Soda	ASP	Soda	ASP
Chemical charge to				
Digester				
NaOH %	17	13	11	7
Na <sub>2</sub> SO <sub>3</sub> %	—	3	—	3
(on O. D raw material)				
Black Liquor				
Pentosans %	10.5	7.44	10.55	8.55
AA on total solids %	11.2	9.23	8.71	1.24
SiO <sub>2</sub> %	1.86	1.19	3.57	1.83

TABLE 7  
Composition of soda B. L. From straw and bagasse (7)

Detail	Bagasse	Rice Straw
Alkali charge NaOH%	12	10
B L. generated m <sup>3</sup> /t pulp	10.9	12
Inorganics %	29.9	22.8
Organics %	70.1	77.2
Lignin %	45.3	33.4

The major parameters of concern in recovery of chemicals from spent black liquors are silica, viscosity and combustion characteristics. Presence of silica leads to problems related to scaling, clarification, precipitation. The viscosity being high, concentration of black liquor is very difficult. It is these parameters which have been a major bottle neck in adopting chemical recovery systems for non-woods black liquors in small pulp mills. Let us review these parameters in greater detail.

#### SILICA IN BLACK LIQUOR :

The non-wood fiber black liquors have a high percentage of silica, nearly 4.8% (even more) in case of straw and 1-2% in case of bagasse, Silica enters both as intrinsic and external silica with raw material and cooking liquors. In black liquor it is present essentially as Na<sub>2</sub>SiO<sub>3</sub> which undergoes hydrolysis to silicic acid as pH is decreased. This happens with dilution by wash water leading to silicic acid scale deposition on filters, wires, screens and plates

Black liquors become unstable and form precipitations on standing. This is prominent with pH falling to 10-10.6. In fact in 48 hours with precipitation pH goes down from 10 to 8. Silica contained in precipitated sediments settle down in the bottom of the black liquor tanks and become very hard scales. Volume of such sludge is 10-30% of black liquor volume and most silica can be transferred to sludge from Black Liquor. The important parameters influencing this are pH and time of storage.

Semichemical pulps and high yield pulps have more silica in pulp and less silica in black liquor due to milder cooking. Higher alkali or pH in black liquor leads

to greater dissolution of silica. The solubility of SiO<sub>2</sub> in rice and wheat straw black liquors with pH is shown in table-8.

TABLE 8  
Solubility of SiO<sub>2</sub> in straw black liquors (8)

pH of black liquor	9	10	10.4	11	11.5	12
SiO <sub>2</sub> in B.L. W/W, %	0.2	0.5	1	2.5	3.5	7

This clearly indicates that silica precipitation can be effected by lower pH while scale can be avoided by increasing pH with alkali addition. At higher availability of alkali (more than 5%), no hydrolysis of Na<sub>2</sub>SiO<sub>3</sub> occurs. Result is reduced viscosity and avoiding scaling. If pH is reduced to 10.3 or below the silica content in B.L. is less than 1%. This can be achieved by pulping process modification or by desilication. There after elevating pH will ensure no precipitation of silica. For best precipitation of silica from black liquor, the conditions are pH below 10.3, temperature around 80°C and the time of storage of around 8 hours.

The soluble silica in black liquor as weight % of black liquor solids (Y) is related to active alkali in black liquor in g/l as NaOH (X) by the following relation (8) for 6 10° Be B.L. at 20°C.

$$Y = 0.65 + 1.21 X$$

The precipitated silica sludge from straw B.L. in settling tanks can be separated. The volume of such sludge can be reduced from 30% of black liquor volume to 6-8% in 2 hours at 80°C. The sludge, dark yellow in colour, has more than 10 times SiO<sub>2</sub> than in clear black liquor. The black liquor with only 0.6% SiO<sub>2</sub> can be easily processed for recovery with proper alkali addition to ensure no precipitation in evaporators. The sludge on the other hand has almost 15% SiO<sub>2</sub>.

In another study (9) it has been shown that silica in the rice straw soda black liquor reduced from initial value of about 9.32% to 7% in 5 days and 6.6% in 10 days due to settling of precipitates when the cooking liquor has 8% alkali in alkali. Soda black liquors will

have more silica at high amount of Alkali in cooking liquor. Under similar cooking condition soda AQ black liquor has less silica than Soda black liquor for rice straw.

Straw black liquors have NPK. At lower pH and lower temperature they help propagate bacteria which drops pH further leading to lignin precipitation below pH of 8. This is one of the main causes of decay of straw black liquors.

During evaporation of black liquor scales are formed in various heat transfer surfaces. These scales contain 35—70% silica.

Non wood black liquors have low swollen volume index (SVI) or volumetric iso-thermal expansivity (VIE). This is expressed as ml/g of dry black liquor solid roasted at 300°C for one hour. High value indicates a porous ignited bed with free air passage and complete incineration. The values reported for various non-wood are give in Table—9.

TABLE 9

SVI values of Different Black liquors (6,10)

Material	SVI ml/g
Rice Straw	3.13—6.2
Wheat straw	5.05
70% wheat straw + 30% Rice straw	4.97
Bamboo	12
Wood	26.77
Bagasse	15.5

Addition of Alkali to black liquor first increase SVI values marginally and then decrease. Ratio of organic to inorganic matter in B.L. influences SVI value. SVI values decrease with increase in IOM/OM. The optimum values for best SVI values for straw appear to be 4% active alkali in B.L. Solids and IOM/OM in the range of 1 : 1.5 to 1 : 1.65. Decrease in silica improves SVI values. SVI values can be increased by reducing hemicellulose in B.L. It may be noted that a higher swollen volume index refers to better thermal decomposition of black liquor solids and better combustion. The Straw BL decompose slowly. Due to low values of SVI, proper height of charred black liquor solids is not formed in the combustion zone and unsteady combustion results.

The calorific value of Black Liquors from non-woods are lower than woods. Some of the reported values are given in Table—10. The calorific value is strongly dependent on 10M/OM. Further removal of silica sludge (6—8% by volume) results in reduction in calorific value by 5%. But it helps in concentrating the black liquor from straw pulps to 50—55% concentration.

TABLE—10

Calorific value of Black Liquor.

Material	Calorific value KCal/kg. Solids
Rice Straw	2600—2700
Wheat straw	2800—3000
Bagasse	3200—3400
Bamboo	3200—3340

Silica presence increases the smelt melting temperature. This causes problems in flow with possibilities of freezing near the spout. The smelt melting temperature of wheat straw is 850-870°C while that for bagasse is 850-890°C and for bamboo it is 825-850°C.

With more silica in green liquor, a large proportion of this is transferred to lime during causticization. The lime mud volume increases with silica resulting in poor clarification. These adversely effect the sedimentation. At more than 5 g/l silica in green liquor the use of poly propylene bag filters will not be possible as high content of fines and granules will clog the filter pores. Silica that can be tolerated in B.L. is 2-6 g/l for no lime mud reburning and only 1% if reburning of lime is to be attempted.

The green liquor sulphite process uses a cooking liquor which essentially consists of Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub>. The milder cooking essentially ensures greater retention of silica in pulp and lesser silica in black liquor. Such black liquor if properly handled by storing at 80°C and pH less than 10.3 will lead to silica precipitation. Proper filtration of such liquor will give black liquor with less than 1% silica. The black liquor can easily be concentrated and by proper adjustment of pH by alkali addition during evaporation will ensure much less scaling and good concentration. The green liquor can be used directly for cooking with no causticization to produce semi-chemical pulps and

chemical pulps. The silica recirculation in GSP (green liquor sulphite process) will be only 5-6% of total silica entering.

Alkaline sulphite processes can also give similar result with regard to silica reduction. The principles of reducing silica in black liquor is to ensure minimum time at maximum cooking temperature and two stage cooking with varying AA.

#### VISCOSITY OF BLACK LIQUORS :

Non-wood black liquor have higher viscosity than wood black liquors due to higher hemicelluloses and pentosans. Semi-chemical pulp black liquors are more viscous than chemical pulp black liquors. Increased quantity of hemi-cellulose dissolution, lower alkali cooking more quantity of sodium unsaturated lignin, incomplete hydrolysis of hemicelluloses to lower molecular weights, low IOM/OM ratio result in increased black liquor viscosity.

Kraft Black liquor is generally newtonian at low concentrations upto 50% solids. It becomes thixotropic at high concentrations. With apparent decrease in viscosity with increased shear rates. Presence of increased quantity of hemicelluloses and colloidal fines in Non-wood black liquors make the black liquors non newtonian in character. Generally log viscosity Vs temperature plots are straight lines. The viscosity ratio of black liquors from chemical pulp of wood to chemical pulp of straws to semi chemical pulp of straws are in the range of 1-10:10-200:1000-10000. Viscosity of a black liquor increases with increase in solids concentration, decrease in temperature and decrease in available alkali in black liquor. Table-11, 12, 13 present some of the data on viscosity of non-wood black liquors.

These tables reveal some interesting information. These can be summarised as under : (10-13)

- In general viscosity of Rice straw BL > viscosity of wheat straw BL > viscosity of bagasse B.L.
- In general viscosity of soda BL > viscosity of Alkaline sulphite BL > viscosity of kraft BL. Bagasse appears not to follow this trend.
- For any BL, higher the concentration higher is the viscosity.
- Higher the free alkali in BL, lower is the viscosity. This effect is more pronounced at higher temperatures.
- Green Liquor sulphite pulping Black liquors viscosity is significantly lower than corresponding values for soda pulp for straws.
- Semi-chemical pulps Black liquors have very viscosity compared to chemical pulps.

Thus the methods of reducing black liquor high viscosity can be by maintaining higher free alkali in BL and processing at higher temperature. This can be possible by addition of alkali at appropriate stage during evaporation. Higher OM/10M in BL means higher higher viscosity and higher calorific value.

For black liquors to be recoverable the viscosity values should be as under :

At 30° Be and 30°C	Viscosity <	3000 CP
60°C	"	< 600 CP
90°C	"	< 200 CP

Table—11 : Viscosity of Black Liquors (11) (At 80°C in centi poise)

Conc. of BL Wt%	Rice Straw			Wheat Straw		Bagasse	
	Soda	A. Sulphite	Kraft	Soda	Kraft	Soda	Kraft
35	57	15	8	58	—	35.5	16.7
40	125	26	13	105	20	50.1	31.6
45	316	45	23	251	—	105.9	50.1
50	1000	83	46	759	35	251.1	84.1
55		144	96		—	596	158.4
60		287	232		250		
65		661	—		—		
Pulping Condition	10% NaOH	3% Na <sub>2</sub> SO <sub>4</sub> 12% NaOH	12% Na <sub>2</sub> O 22% Sulphidity	10% NaOH		18% NaOH	16% Na <sub>2</sub> O

Bath Ratio 1:5, Max. temp. 165°C. in all cases.

Table—12 : Effect of free alkali on viscosity (12)  
Soda wheat straw Pulp, 60% solids Black Liquor

Free alkali g/lit.	Viscosity, in Centi Stockes	
	Temp. 50°C	Temp. 90°C
4.48	20,500	1430
8.00	8,000	660
12.80	6,000	570
15.83	5,700	75

Table—13 : Effect of Pulping process and temperature on viscosity (8)  
of Black Liquor (30°Be liquor at 20°C), Viscosity in (°P)

Temp. °C	Wheat Straw		Bagasse		Rice Straw			
	Soda CP	GSP CP	Kraft	GSP CP	Soda CP	GSP SCP	GSP CP	Soda CP
30	1270	630	1600	1900	78000	3200	760	—
60	300	170	500	850	8100	680	150	455 (70°C)
90	80	50	50	96	3600	240	50	388 (80°C)

Presence of ligno-sulphonates formed during alkaline sulphite and Green liquor sulphite process reduces B.L. viscosity as these are good dispersants with high surface activity. At higher free alkali, the possibility of decomposition of  $\text{Na}_2\text{SiO}_3$  is reduced as acids if formed are neutralized. This prevents silica and lignin precipitation and helps in smooth operation. It is important that BL must be well settled and filtered before evaporation. Viscosity increase in BL is sharp at a 20-24°Be (30-35% solids) for non-woods and at 45-50% solids for hard woods. Thus viscosity reduction must be effected before these concentrations set in. In case of nonwood black liquors, pH adjustment to above 11 by alkali addition may be done at a concentration of 15°Be (20-22% solids). Presence of anthraquinone tends to reduce BL viscosity. Alkaline sulphite pulping of non-woods (8% NaOH with 4%  $\text{Na}_2\text{SO}_3$ ) for chemical pulps gives black liquors with nearly half to one fourth viscosity values of soda black liquors.

One can grade B.L. from decreasing viscosity point of view as under SCP Rice Straw > CP Rice Straw > CP Bagasse > CP wheat Straw > Bamboo CP > Wood CP. Pulping process can be graded with respect to decreasing B.L. viscosity as Soda Pulp > Soda AQ > Alkaline Sulphite = Green liquor sulphite.

Thus for straw it appears pertinent to look to Alkaline Sulphite and GSP Pulping process if Chemical Recovery is to be attempted.

The evaporation of non-wood black liquors can be done more efficiently in short tube vertical evaporators (STV) than in long tube vertical evaporators (LTV). This is because LTV is suitable upto viscosity of 50 CP while STV can be used for viscosity upto 100 CP. Free flow falling film evaporators (FFFF) are good when viscosity goes upto 400 CP. The specific evaporation rates vary from 10-17 kg/m<sup>2</sup>h for STV while it ranges from 7-12 kg/m<sup>2</sup>h for LTV for non-wood black liquors. The over all heat transfer coefficient for LTV is proportional to viscosity to the power-0.44. The heat transfer coefficient values get greatly reduced if scaling on heat transfer surface is present or OM/10 M is increased. Control of pH around 11 helps in avoiding hydrolysis of  $\text{Na}_2\text{SiO}_3$  and lignin precipitation and keeping heat transfer surfaces clean.

In order to keep evaporator tubes clean, descaling is necessary. This is done by water boiling, mechanical cleaning, acid/alkali boil out. These are more frequent in straw based systems with high silica. Scaling is maximum in bodies handling higher concentration black liquors.

The evaporation load is normally high as the initial weak black liquor concentration is low (8-10% solids). One of the first requirement would be to see that initial concentrations are raised by proper pulping followed by efficient brown stock washing. Steam economies are usually low in case of non-wood black liquor evaporation.

#### 5. Choice for viable Chemical Recovery for small non-wood based Mills.

The discussions clearly indicate that prime requirements in chemical recovery from non wood black liquor are (a) removal of silica to a level of 1 g/l (b) Ensuring the black liquor viscosity to be at acceptable levels

In order that these are achieved for both chemical and semi-chemical pulp black liquors, the choice is not soda pulping or kraft pulping as is being followed. Instead the choices appear to be Alkaline sulphite pulping and Green liquor sulphite pulping.

In alkaline sulphite (ASP) pulping sodium hydroxide (10-13%) alongwith sodium sulphite (2-4%) are taken and cooking is done at 165°C with a bath ratio of 1 : 3 to 1 : 5 for straws. In green liquor sulphite (GSP) process the cooking liquor comprises of a mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$  or NaOH. These process offer advantages over conventional soda process in terms of 2-3% extra yield, more silica going to pulp, less silica in black liquor. The washing characteristics of the pulps are better. The hemicellulose retention is more in the pulp and hence the black liquors are less viscous. The presence of ligno sulphonates in BL, a dispersant, further reduces the viscosity. Since the process uses more chemicals, the 10M/OM in black liquor is more giving lower calorific value, but lower viscosity. The pulps have better strength, easy to bleach and have less stickness on press rolls and less breaks in paper machine than soda pulps. The foaming tendency is also less.

The digester operation must be coupled with good wet cleaning of raw material to remove extreneous silica input, alongwith proper washing in horizontal belt washers. The black liquor which usually comes out at pH around 10 can be stored for 8 hours at 80°C This will precipitate silica and residual silica in BL is only around 1 g/l against an initial value of 6-8 g/l. There after the active alkali in BL is increased to more than 4% (pH > 11) to ensure lower viscosity.

The chemical recovery will essentially comprise the following :

- Step 1. Storing BL at pH 9-10 (below 10 3) for 8 hours at 80°C. The leads to hydrolysis of  $\text{Na}_2\text{SiO}_3$  to colloidal hydrosilicic acid. The coagulation/setting followed by filtration will remove, silica rich sludge with fines. The silicious mud 6-10% by volume of BL is disposed off.
- Step 2. The filtered black liquor around 6°Be (9-10 conc.) is partly concentrated to about 12°Be (18% conc.).
- Step 3. B.L. is mixed with Green Liquor or white liquor to increase pH to 11 to reduce viscosity and increase solubility of silica. The liquor is concentrated in MEE and DCE to 30-40° Be (45-66% conc.).
- Step 4. The black liquor is burned in recovery furnace to give a smelt comprising of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{CO}_3$ .
- Step 5. The green liquor is clarified and sent to digester as cooking chemical in GSP. Make up chemicals ( $\text{Na}_2\text{SO}_3$ ) is added in digester.

In case of Alkaline sulphite, the Green Liquor is treated with  $\text{SO}_2$  from flue gases/sulphur burner to give  $\text{Na}_2\text{SO}_3$  alongwith  $\text{Na}_2\text{CO}_3/\text{NaOH}$  and  $\text{Na}_2\text{S}$ . There are many well established recovery process for Alkaline Sulphite liquor like stora process, Rauma System, Tampella liquor sulphitation, Ebara process and Sonoco process. (2.)

#### 6. Conclusion :

The situation warrants that priority exploration of processes for viable chemical recovery from black liquor of non-wood fiber small mills be taken up. In this regard following national projects may be considered :

- (a) Possibilities of modifying existing soda pulp mills to GSP/ASP/AS-AQ Process.
- (b) Detailed studies on generation of data pertaining to silica contents, viscosity, and other Physico-chemical, Thermal and rheological properties of GSP/ASP black liquors.



- (c) Economic analysis of GSP/ASP recovery systems.
- (d) Studies on comparison of GSP/ASP process with soda/kraft from process and pollution angle.

Present state of knowledge and experience indicate that GSP/ASP may be attractive alternatives for small non-wood pulping mills to have effective chemical recovery.

#### 7. References :

1. Lin Zhi Jun & Huang Yun Ji—  
— Proceedings of the International Non-Wood fiber Pulping and Paper Making Conference, Beijing (China), Vol. II, PP-911-921, July 11-14, (1988).
2. "Pulp and Paper Manufacture". Vol. 4 "Sulfite Science and Technology" Editors Ingruber, OV; Kocurek, M.J., & Wong; A—Published by Joint Text Book Committee of Paper Industry-TAPPI-CPPA, Montreal-(1985).
3. Blidberg, G.—Proceedings of "Environmental Aspects of Non-wood Fiber Pulp and Paper Manufacture"—Hang chou, China, Vol. II PP. 17. UNEP, ROAP, Bangkok, September (1987).
4. Veermani H.—Non-wood Plant Fiber Pulping Progress report No. 9, TAPPI, PP-97-106 (1978).
5. Veermani, H.—Non-wood Plant Fiber Pulping progress report No. 13, PP 35-45 (1982).
6. Chou Bei Chang—Proceedings of Beijing Non-wood fiber Pulp and Paper Making Conference, Vol. 2, PP-839-843, July, 1988.
7. Kulkarni, A G etal—IPPTA. Vol. 25, No. 1, PP 1-9, March (1988).
8. Chen. Ren Yue—Proceedings of the workshop on "Environmental Aspects of Non-wood Fiber Pulp and Paper Manufacture", Hangzho, Vol. II, PP. 391-426, UNEP, ROAP. Bangkok, September (1987).
9. "Project Report on Pulping studies of Rice Straw using Soda and Soda AQ. Proccss"—Sanjeev Kumar Goel etal IPT, Saharanpur May, (1987).
10. Kulkarni, A.G.—etal-Proceedings of Nonwood Fiber Pulping and Paper Making Conference, Beijing, Vol. II, PP-890-909, July (1988).
11. PrivateCommunication
12. Mishra, D.K.,—Non-wood Plant fiber Pulping progress Report No. 3, PP 119 (1972).
13. Ray, AK, Bansal, M.C., Rao, N.J.—Pulp and Paper Canada PP. 82-86 (T 325-T 329) Vol. 90, No. 9 (1989).