Innovations & Process Development For Efficient Operation of Chemical Recovery System In Paper Industry

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ABSTRACT

The Indian Paper Industry utilizes diversified ligno-cellulosic raw materials viz. woody and agro residue based requiring different process conditions during pulping. Due to the inherent nature of these raw materials black liquor resultant from the pulp mill is characterized by poor thermal properties & abnormally higher viscosities besides the presence of higher contents of non-porcess elements viz. Silica, Potassium & chlorides etc. which has a strong bearing on the operation of chemical recovery system.

CPPRI with its long experience on working with these black liquors carried out extensive research work and developed various innovative process & technologies to overcome the problems being faced by the Indian paper industry which has resulted in the improved efficiency of chemical recovery system.

The present paper describes the dedicated research & development efforts of CPPRI in the last more than two decades which has emerged in the form of development of various process technologies viz. Desilication of Silica rich black liquor, Thermal treatment of bagasse black liquor and removal of potassium & chlorides (Non-process elements) etc. These innovative technologies have been upscaled on the pilot scale and being commercialized for improved efficiency of chemical recovery system.

Key words: *Non-wood black liquor, desilication, potassium, chlorides, viscosity, lignin-carbohydrate complexes, thermal treatment, non-process elements, silica*

Introduction

The present production of paper, paper board & newsprint in India is more than 10 million tons contributed by wood based (32%), Agro based (21%) and the Recycled waste paper (47%) industry and is projected to grow with an average growth rate 7% reaching to around 22 million tons by the year 2025. Though the country is self sufficient in meeting its demand for paper, paper board however certain speciality paper including the newsprint is being imported.

The Industry employing wood & non-wood based raw materials requires different processing conditions in respect of pulping & bleaching to achieve the desired quality of paper. Due to the inherent nature of these raw materials and the pulping condition employed to produce the desired quality of pulp, the quality of the resultant black liquor varied significantly. The black liquor resulting from the woody & agro residue based raw material are also characterized by the presence of higher contents of non-process elements and also abnormally higher viscosities & poor thermal properties having adverse effect on the operation of chemical recovery.

Nature of the Black Liquor

Nature of black liquor has pronounced impact on its processing in chemical recovery system. Entire economics of the chemical recovery unit is solely governed by black liquor properties. The properties of black liquor are significantly influenced by the chemical composition of the black liquor. Table. 1 shows the black liquor characterization of different Black Liquors and Table. 2 indicate the viscosity levels of the different black liquors. The results clearly indicate that bagasse black liquor shows high viscosity whereas straw black liquor shows the high amount of silica.

Table-1 Characterization of Different Black Liquor

Parameter	Bagasse	Wheat Straw	Wood
pH	12	12.35	12.5
Total solid % w/w	10 - 11	10 - 11	16 - 18
Inorganic as NaOH % w/w	34	36.4	35.4
Organics,% w/w	66	63.6	64.7
Chloride as NaCl% w/w	1.4	1. 7	1.2
Silca as SiO2 % w/w	1.3	3.15	0.05 -0.1
Residual Active Alkali, g/l as Na2O	7.0	7.0	5-6
Swelling Value Ratio. ml/g	12 - 14	8 - 10	20 - 25
Calorific Value as GCV, cal/g	3300	3110	2990
Carbon as C % w/w	38.6	33.4	31.7
Hydrogen as H, % w/w	4.1	2.9	3.2
Nitrogen as N, % w/w	0.3	0.4	0.4
Sulpher as S, % w/w	0.5	0.5	2.0

Table-2

Viscosity & Total Solids relationship of Black Liquor from various Raw Material

Raw Material	Viscosity at 100° At Total Solids % w/w					
	35	45	50	55	60	65
Pine	2.9	9.1	18	40	---	---
Eucalyptus	3.4	2.3	83	380	490	640
Eta Reeds	8.7	41	100	395		
Bamboo	---	---	11	31	125	398
Wheat Straw	---	---	89	299	450	1000
Bagasse	84	125	161	912	---	---
Rice Straw	33	112	316	---	---	---

Agro based black liquors show poor chemical and thermal energy efficiencies mainly due to:

- Lower weak black liquor solids concentration.
- Higher quantities of inert materials like silica and other non-process elements like potassium and chlorides.
- Poor flow behaviour resulting in higher black liquor viscosity.
- Poor combustion behaviour due to poorly dispersed macro-molecular structure of the organic molecules.

Due to these, significant changes are observed in nature of black liquor from wood & agro based raw materials. Utilizing the well equipped laboratory facilities of CPPRI, we could successfully explore the reasons for poor liquor behaviour in case of agro based black liquors.

Higher inerts like silica and its compounds, higher suspended matter and also higher proportions of hemicelluloses- lignin complexes in non wood black liquor are found to be the major reasons of poor black liquor behaviour of agro based liquors during chemical recovery operations, which makes handling of these liquors a more difficult process in comparison to wood black liquors.

Problems are being faced even in wood based chemical recovery system in the recent time due to system closing. This close cycle system leads to accumulation of certain non-process elements in Chemical Recovery System. Chloride and potassium are two such non-process elements, which can accumulate to high levels in closed pulp-mills and cause serious problems, particularly in the recovery boiler operations. High levels of chloride and potassium impurities in kraft liquors are known to accelerate recovery boiler plugging. The problem is being faced by all mills whether using hardwood or non-wood raw material.

In order to overcome some of the above mentioned problems of wood and agro based black liquors, CPPRI successfully came out with desilication technology to control the problems of evaporator scaling, poor black liquor combustion and lime sludge settling rates commonly encountered in silica rich black liquors . Further to improve the black liquor flow behaviour in terms of viscosity reduction, black liquor thermal treatment technology especially for bagasse liquors having very high viscosities has been successfully tried on pilot scale commissioned at CPPRI. Removal of chlorides and Potassium is a matter of concern in chemical recovery cycle. CPPRI has developed a process for removal of the same. The process has been successfully scaled up to pilot plant level.

The present article covers the details of the above mentioned initiatives undertaken by CPPRI to improve chemical and energy recovery efficiency of chemical recovery system.

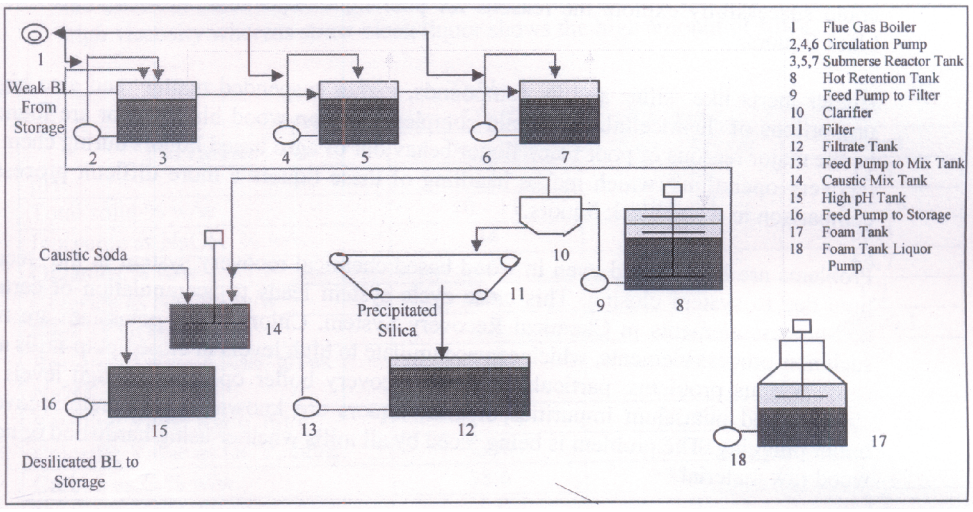
Desilication of Silica Rich Black Liquor

Higher quantity of silica, a non- process element has always been a matter of great concern as it gets dissolved in the black liquor and poses severe problem in the evaporator, recovery boiler and causticization operations (1). CPPRI did extensive research on desilication of black liquors and developed a desilication technology for selective precipitation of silica adopting stepwise gentle carbonation technique employing flue gas from the recovery stack.

Process Description

The basic principle of the desilication process developed by CPPRI is the slow and stepwise reduction of pH using CO_2 rich flue gas so that only silica gets precipitated and lignin precipitation could be prevented as the pH for silica precipitation and lignin precipitation lie in close proximity.

Fig -1 shows the schematic of desilication process.



Results of Desilication of Wheat Straw Black Liquor

Wheat Straw black liquor is rich in silica and processing of this black liquor in evaporator is a matter of concern due to scaling problem (2). Studies conducted on wheat straw black liquor desilication show encouraging results. Results are shown

Table - 3 Results of Desilication Trials

Black Liquor Characteristics				Desilication %
Beore Desilication		After Desilication		
pH	SiO_2, %w/w	pH	SiO_2, %w/w	
11.6	7.1	10.2	0.95	86.6
		10.1	0.85	88.0
		10.0	0.60	91.5
		9.8	0.42	92.9

Table - 4 Physico-Chemical Analysis of Black Liquor Before and After Desilication

Parameter	Original Black Liquor	Desilicated Black Liquor	Realkalized Black Liquor
pH at 30°C	11.6	10.0	11.8
RAA g/l as NaOH	3.2	0.4	3.5
Silica as SiO_2, %w/w	7.1	0.42	0.42
Inorganics as NaOH, % w/w	31.9	30.7	31.8
Organics, % w/w	68.1	69.3	68.2
SVR, ml/g	14	18	17
Calorific value, Cals/gm	3215	3385	3230
Carbon as C, % w/w	35.14	37.7	35.6
Hydrogen as H, % w/w	4.01	3.96	4.0
Nitrogen as N, % w/w	0.50	0.49	0.48

Table 5 Viscosity of Original and Desilicated Black Liquor

Particulars	VISCOSITY, m.Pa.S at 98^0 C	
Total solids, %w/w	Original Black Liquor	Desilicated, Realkalised Black liquor
40	37	36
45	81	82
50	191	184
55	501	439
60	1202	1109

Original Silica from Black liquor Hot Water Washed silica

below in Table 3 & 4. Figure shows the silica separated from wheat straw black liquor.

The above results indicate that desilication efficiency as high as 92% can be achieved with a residual silica content around 0.4%.

Optimum pH for desilication is 10.0 to 10.1. At this pH more than 85% desilication can be achieved without lignin co-precipitation. Remarkable improvement in the swelling volume ratio of desilicated black liquor was achieved when compared for the original black liquor, which is a pointer towards better combustibility of desilicated black liquor.

Thermal Treatment For Reduced Viscosity Of Black Liquors

The black liquor viscosity characteristics, specifically from non- wood based pulp & paper mills is such that even at normal operating temperatures of 100- 115 ^{0}C, the viscosity at 55% w/w total solids concentrations exceeds 500cps as can be seen from Fig.- 3. These high viscosities in case of non- wood black liquors make it difficult to handle in evaporators. Thus, the higher viscosity problems lead to firing of black liquor at low solids concentration and thereby lower steam generation.

With increased understanding & in- depth studies carried out at CPPRI on basic aspects of black liquor , it could be inferred that high molecular weight organic residues like polysaccharides linked with lignin- carbohydrates complexes.(LCC's) and the high molar mass lignin molecules are mainly responsible for abnormally high viscosities of bagasse black liquors. Unlike straw black liquors, where silica contributes substantially to high viscosity.

Thermal Depolymerisation of Lignin- Carbohydrate Complexes:

The process of thermal treatment basically incorporates heat treatment of semi- concentrated black liquor at temperatures higher than pulping in presence of residual alkali for specified time period, which results in depolymerisation of high molecular weight lignin- carbohydrate complexes in to lower mass components. The findings are supported from gel chromatograms, where it is clear that the thermal treatment of black liquor resulted

in cleavage of Lignin- carbohydrate complexes., which caused decrease in molar mass of the lignin entity. Schematic of thermal treatment process is shown in figure 3.

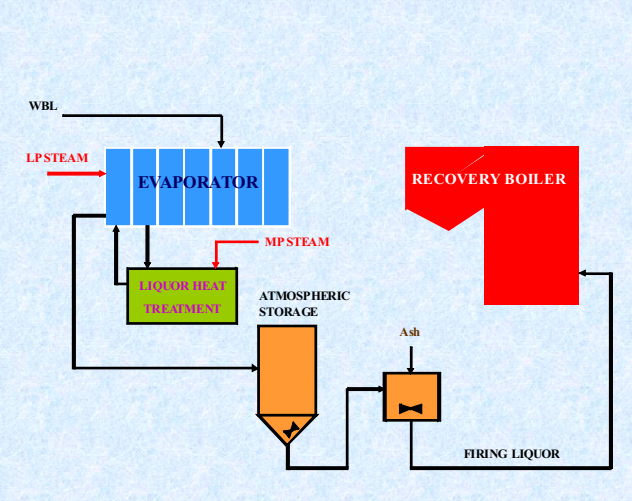


Fig 3 -Schematic of Black Liquor Thermal Treatment

Effect of Thermal Treatment on Viscosity of Black Liquor.

As a result of thermal treatment of black liquor, there was remarkable reduction in viscosity making it possible to achieve higher dry solids during evaporation. Reduction in viscosity after thermal treatment could help in handling the black liquor by keeping it in a less viscous form even at atmospheric pressure. Figure 4 shows the comparative viscosities of bagasse black liquor before and after thermal treatment.

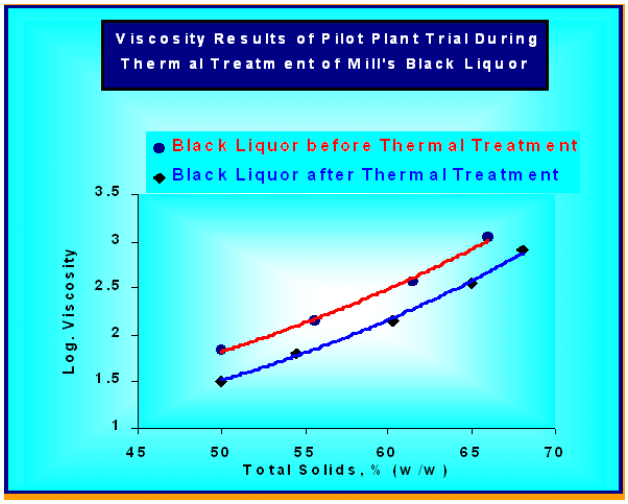


Figure 4 Viscosity before and after Thermal treatment

Effect of Thermal Treatment on Combustibility of Black Liquor.

Positive impact of thermal treatment is not only limited to reduction of viscosity of black liquor, Combustibility of black liquor also improves after thermal treatment in terms of swelling behavior & temperature of ignition. Results of combustibility are given in following Table. 6

The results indicate that thermal treatment of bagasse black liquor have shown improved black liquor properties with respect to viscosity and combustion behavior leading to higher energy efficiency of chemical recovery system.

Removal of Chloride and Potassium from Chemical Recovery Cycle

Product quality standards as well as environmental and economic factors are increasing the interest in progressing towards low effluent, closed cycle operation in pulp and paper mill. For system closure to be realized, several problems need to be addressed (*1*). These includes chemical imbalance and build up of non process elements such as Chlorides, Potassium, silica etc. in chemical recovery cycle. Accumulation of non process elements (NPE's) is widely recognized as the major limitation to increased mill closure. High levels of chloride and potassium impurities in kraft black liquors are known to accelerate recovery boiler plugging. As mills move towards higher levels of closure the current outlets for these elements are reduced. This will result in even higher chloride and potassium concentration in kraft recovery cycle. Presence of high levels of chlorides and potassium in chemical recovery causes following problems in the operation of the system.

Table - 6
Results of Combustibility of black liquor before & after Thermal Treatment

Particular	Before Thermal Treatment	After Thermal Treatment
Calorific Value, KJ/Kg.	14,200	13,990
Swelling Volume Ratio, ml/gm	8.0	17.0
Temp. of Ignition, ^{o}C	765	735

- adversely impacting the operation of the boiler.
- plugging in the super-heater, boiler bank and economiser
- corrosion in the recovery boiler
- increased steam demand
- reduced steam generation
- increased downtime

Looking into above problem due to presence of chlorides and potassium CPPRI initiated studies on removal of these NPEs from chemical recovery cycle. The process has been scaled up to pilot plant level.

Levels of Non Process Elements in Cellulosic Raw Materials

Various raw materials used by Indian paper industry were analyzed for NPEs content. Results are depicted in Table 7 & 8.

The above results shows that agro residues contains more amount of NPEs as compared to hardwood but even this low value of NPEs in hardwood accumulates in chemical recovery system and causes problems in operation of chemical recovery. Therefore their reduction/removal becomes necessary.

Table 7 Levels of Non process elements in different cellulosic raw materials*(3)

Name of NPE	Bagasse	Wheat Straw	Rice Straw	Bamboo	Hardwood
Silica, %w/w	1.7	5.1	10.9	1.5	0.1
Calcium, %w/w	0.1	0.1	0.1	0.08	0.1
Potassium, %w/w	0.2	1.2	1.7	0.1	0.1
Chlorides, %w/w	<0.1	0.9	0.90	<0.1	<0.1

*Results are expressed as percent o.d. by mass.

Table 8
Levels of Non process elements in different hardwoods

Name of NPE	Casurina	Cashew	Poplar	Saubabool	Eucalyptus
Silica, %w/w	0.06	0.03	0.03	0.02	0.08
Calcium, %w/w	0.1	0.2	0.02	0.2	0.07
Potassium, %w/w	0.11	0.26	0.2	0.25	0.27
Chlorides, %w/w	0.03	0.03	0.02	0.04	0.02

Fig 5 Photograph of the NPE removal pilot plant at CPPRI

Process for Removal of Chloride and Potassium

Leaching of chlorides & potassium from ESP ash is the advantageous point to reduce their amount from the system as they accumulate in ESP ash.

Table 9 Removal of Chloride and Potassium from ESP Ash

Parameter	Mill A	Mill B
Potassium Removal Efficiency, %w/w	54	58
Chloride Removal efficiency, %w/w	81	82.1
Sodium Sulfate Recovery , %w/w	87	87.9

Process Description

A part of the ESP ash is mixed with water at a temperature around 40^{0}C in a tank to a concentration of 40-45%. This saturated solution is subjected to temperature drop to 10-15^{0}C. At this temperature, Crystals of Sodium sulfate gets precipitated. Most of the Chlorides and potassium remain in the filtrate.

The above process was established on laboratory, bench and pilot plant scale. Schematic of the pilot plant is given in fig 5.

Results and Discussion

ESP ash collected from two mills were tried on pilot plant for removal of chlorides and potassium from chemical recovery cycle. Following results were obtained.

The results indicate that chlorides and potassium can effectively be removed from ESP ash by employing process technology developed by CPPRI. More than 80% chlorides can be removed with around 88% sulphate recovery.

Conclusion

i. Silica is no longer a problem in chemical recovery system as it can be easily removed from black liquor by employing CPPRI desilication technology. Bamboo and straw black liquor can effectively be desilicated to achieve a level of 0.4 gpl silica concentration in black liquor.
ii. Bagasse black liquor can be evaporated to high dry solid concentration as its viscosity can be reduced to 60% by employing thermal treatment process. Combustion behavior is also improved by thermal treatment.
iii. Removal of chloride from wood and non wood based mill will improve thermal efficiency of chemical recovery boiler and will reduce down time.

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