Dr. R. K. Jain
Director

INNOVATIVE APPROACH FOR IMPROVED ENERGY & CHEMICAL RECOVERY EFFICIENCY IN STRAW BASED PAPER MILL

Dr. A. K. Dixit
Sr Scientist

Tarun
Sr Reserch Fellow

Smooth operation of Conventional chemical recovery system in a straw based mill has always been a challenge for achieving desired efficiency level both in terms of chemical and energy recovery efficiency. These mills encountered with severe problems in evaporator section, boiler as well as in causticization section. These problems are due to the inherent nature of raw materials containing higher quantity of silica and resulting in black liquors with high viscosities and higher content of dissolved silica causing severe scaling problems in evaporator, poor combustion in boiler, inefficient operation of causticization section and huge solid waste generation in form of lime mud which is non recyclable

The paper discusses the innovative approach through development of a process consisting of removal of silica followed by Heat treatment of the black liquor under specified process conditions which has helped in achieving remarkable improvement in energy efficiency and chemical recovery efficiency .The process also helps in reducing environmental pollution by reduced solid waste generation and reduction in gaseous emissions.

The process has been demonstrated on pilot scale in few of the agro based paper mills using wheat straw as the major raw material and is being scaled up on commercial scale.

Introduction

Operation of chemical recovery system based on agro residue black liquor is not as efficient in case of wood black liquor. Presence of high content of silica and higher viscosity of black liquor from agro residue based raw material viz. wheat straw & bagasse etc. leads to lower chemical recovery and energy recovery efficiency of chemical recovery system. Silica causes scaling in evaporators reducing heat transfer coefficient thereby increasing steam demand in evaporation, slows down the settling rate of white liquor clarifier, poor dryness of lime mud and also makes lime sludge unsuitable for reburning to recycle lime.

Presence of high Lignin carbohydrate complexes (LCC) bond in agro residue black liquors caused higher viscosity of black liquor which limits its firing concentration in recovery furnace at a lower level. Firing at lower solids leads to less steam generation

due to higher viscosity in an agro based chemical recovery (*1 & 2*). Due to low steam generation from burning of black liquor mill required more coal to meet out its steam demand. Firing at lower solids also causes higher level of harmful gas emission from chemical recovery boiler stack.

Wheat straw is one of the major agro based fibrous raw material being used by Indian pulp and paper industry. Integrated pulp and paper mills based on wheat straw are facing problems of low energy and chemical recovery efficiency in processing of black liquor in Chemical Recovery system due to presence of higher content silica and higher viscosities of the black liquor.

In view of above, Central Pulp & Paper Research Institute, Saharanpur has conducted extensive research and development work incorporating process of Liquor Heat Treatment of desilicated black liquor to overcome the problems being faced by Agro based pulp & paper mills which may help the mill in reduction of black liquor viscosity by mill than 70%. Thereby, helping to achieve higher black liquor solids before firing in to the chemical recovery operation. This results in improved energy & chemical recovery efficiency of the chemical recovery operation. The present paper highlights the results of laboratory and pilot scale trials on black liquor wheat straw based mills in Punjab.

Experimental

Desilication followed by LHT: - Black liquor was collected from a pulp & paper mill (employing wheat straw as major raw material producing bleached variety of paper) located in Punjab. 3 sets of experiments on Desilication of black liquor each set of 50 litres of black liquor were carried out in pilot scale desilication plant using carbonation technique for selective precipitation. Desilicated black liquor was filtered and realkalized. The realkalized black liquor was evaporated in rotary flash evaporator to a concentration level of 30% w/w and was subjected to Heat treatment in LHT Pilot plant with a reactor capacity of 25 litres. The process conditions for LHT were optimized in respect of temperature, retention time and presence of residual alkali to obtain maximum possible reduction of black liquor viscosity after LHT.

Process Details

The process involves desilication of wheat straw black liquor followed by Liquor Heat Treatment of desilicated realkalized black liquor. Weak black liquor as received from brown stock washer is subjected to desilication by step wise carbonation employing flue gas as a source of carbon dioxide. pH of black liquor is reduced to around 10 by carbonation in a specially designed reactor so that localized carbonation is avoided and lignin co precipitation is stopped. At this ph silica gets precipitated and is separated by filtration. This desilicated black liquor is decarbonated and realkalised by addition of caustic.

Desilicated and realkalized black liquor is evaporated to a concentration around 30% and is subjected to heat treatment under optimized conditions. Level of residual active alkali, temperature of heat treatment and duration are important parameters for obtaining best results of LHT.

Results and Discussions

Desilication of Wheat Straw Black Liquor

Weak black liquor collected from brown stock washer was subjected to desilication. Stepwise coronation was carried out and desilication was monitored at different pH levels to optimize the pH for maximum desilication. Results are shown in table 1.

Table 1: Desilication efficiency at Different pH

Black Liquor Characteristics				Desilication (%)
Before Desilication		After Desilication		
pH	SiO_2, %w/w	PH	SiO_2, %w/w	
12.5	3.03	10.5	2.8	17.5
		10.3	1.6	47.2
		10.2	0.8	73.6
		10.1	0.5	83.5
		10.0	0.40	86.8
		9.9	0.36	88.2

The results recorded in **Table 1** show that silica precipitation starts at a pH around 10.5 & around 88% desilication efficiency was achieved at a pH of 9.9. Results showed that residual silica content is almost same after pH level of 10.0. This indicates that carbonation of black liquor beyond pH 10.0 does not facilitate silica precipitation. The above results indicate that optimum pH range for precipitation of silica in wheat straw black liquor is 9.9 –10.0. Residual silica content in black liquor is 0.4 g/l at this pH range. The desilicated black liquor was filtered to separate precipitated silica. This black liquor is realkalized by adding 5.5gpl caustic to raise pH and RAA level and to maintain minimum RAA level above 4% required for LHT. The black liquor was characterized for various parameters important for chemical recovery point of view. Results are shown in table 2.

Table 2 : Chaacterization of original and desilicated black liquor

Parameters		**Control BL**	**Desilicated Re-alkalized BL**
Total Solids, %w/w.		11.2	11.3
pH		12.54	12.6
RAA, as NaOH	gpl	3.84	4.35
	%	3.44	4.92
SVR, ml/g		8	10
Silica as SiO2, %w/w.		3.03	0.36
Inorganic as NaOH, %w/w		31.59	33.82
Organics, %w/w.		68.41	66.18

From the results shown in Table 2, it may be observe that the physico-chemical & thermal properties of desilicated and realkalized black liquor were improved in respect of combustion behavior as reflected from increase in SVR which was improved from 8 ml/gm to 10 ml/ gm and silica level were reduced to 0.36 g/l from 3.03 g/l.

Liquor Heat Treatment of Desilicated Black liquor

Studies on Liquor heat treatment were carried out on Desilicated realkalized black liquor. Optimization of operational conditions like RAA, Temperature and Time were carried out.

Optimization of Residual Active Alkali (RAA)

Laboratories and pilot plant trials were conducted at different RAA levels keeping other process conditions (Retention time and temperature) constant. Liquor heat treatment was carried out at two temperatures on the same RAA values to reconfirm the impact of RAA on heat treatment. Results are shown in the table 3 & 4.

Table 3 : Optimization of Residual Active Alkali (RAA) at 175°C

RAA, %w/w as NaOH	**175°C (% reduction in Viscosity)**		
	50% solids	**55% solids**	**60% solids**
3.5	44.72	45.10	48.24
4.5	50.91	52.83	56.41
5.5	61.72	63.08	66.53
6.5	66.58	68.28	70.07

Table 4 : Optimization of Residual Active Alkali (RAA) at 185°C

RAA, %w/w as NaOH	**185°C (% reduction in Viscosity)**		
	50% solids	**55% solids**	**60% solids**
3.5	46.83	47.97	51.06
4.5	57.78	59.46	62.60
5.5	63.93	65.49	68.09
6.5	71.17	70.64	70.15

The above results go to indicate that a RAA level of around 5.5% is suitable for liquor heat treatment to achieve maximum benefit of viscosity reduction.

Optimization of Retention Time

Studies were conducted on different retention time keeping other process conditions (RAA and temperature) constant. Results are shown in the following table 5.

Table 5 : Optimization of Retention Time at 185°C

Time, minutes	% reduction in viscosity (RAA 5.5% / 185°)		
	55% solids	60% solids	65% solids
15	62.8	66.1	66.6
20	65.7	68.5	68.9
25	69.9	70.2	72.4

The studies conducted on optimization of retention time have shown that retention time of 20-25 minutes is optimum for liquor heat treatment for maximum viscosity reduction.

Optimization of Temperature

Lab and pilot plant trials were conducted on different temperature keeping other process conditions (RAA and RT) constant. Liquor heat treatment was carried out at three temperatures. Results are shown in the following table 6.

Table 6 : Optimization of Temperature (RAA5.5%)

Temperature, °C	% reduction in viscosity		
	50% solids	55% solids	60% solids
175	61.5	63.1	66.6
180	62.9	64.3	67.1
185	63.9	65.5	68.1

The studies conducted on optimization of temperature have shown that a temperature in the range of 175-180°C is suitable liquor heat treatment of wheat straw black liquor.

The above studies have shown that the following process conditions are optimum for Liquor Heat Treatment of wheat straw black liquor.

Residual Active Alkali : Minimum 5.5% Temperature, °C : 180 Retention Time, min : 20

Liquor Heat treatment of desilicated realkalized black liquor was carried out at optimized process conditions. Control black liquor, desilicated black liquor and Heat treated black liquors were analyzed for various parameters to observe the impact of Desilication coupled with LHT on black liquor properties. Results are shown in table 7 & 8.

Table 7 : Analysis of the Control, Desilicated and Heat Treated Black Liquor samples

Parameters		Control BL	Desilicated-Re-alkalized-Heat Treated BL
pH		12.54	12.55
RAA, as NaOH	gpl	3.84	5.71
	%	3.44	2.37
SVR, ml/g		8	15
Silica as SiO2, %w/w.		3.03	0.38
Inorganic as NaOH, %w/w		31.59	34.74
Organics, %w/w.		68.41	65.26

Table 8 : Viscosity of control and treated Black Liquor

Total Solids, %w/w.	Value. cps			
	Control BL (Without LHT)		Treated BL (After LHT)	
	100^0C	105^0C	100^0C	105^0C
50	350	295	111	93
55	885	718	195	155
60	2215	1735	342	259
65	5545	4200	600	432
70	-	-	1051	719

The above results go to indicate that wheat straw black liquor shows better physicochemical and burning behavior after desilication and heat treatment.

The reduction in viscosity and improved combustion behavior of the black liquor may be reflected due to depolymerization of the long chain Lignin Carbohydrate Molecules present in higher quantities in wheat straw the black liquor (14-20%) and in other agro based raw material. The higher xylan content in agro residue raw material leads to generation of higher LCC content in agro residue black liquor. Removal of silica also attributed to reduction in viscosity thus combined effect of LHT and desilication have resulted in higher reduction in viscosity.

The combustion behavior is also improved as shown by improved Swelling volume ratio of treated black liquor (15 ml/g) as against untreated black liquor (8 ml/g).

Observations

The following observations are made from the study conducted.

i. Liquor Heat Treatment coupled with desilication of wheat straw black liquor conducted at optimized conditions resulted in more than 75% reduction in viscosity.

ii. Treated liquor have shown better combustion behavior reflected by higher Swelling Volume Ratio (SVR) of treated black liquor (15 ml/g) as against untreated black liquor (8 ml/g).

iii. It is possible to achieve 5-6% higher concentration of treated black liquor due to lower viscosity and a concentration of more than 65% can be achieved as against 60% of untreated black liquor.

iv. Firing of black liquor at higher dry solids level will also reduces emissions from chemical recovery boiler.

v. Reduction in silica will help the agro residue based mills in installing full-fledged chemical recovery system

vi. In addition to above benefits, reduction in silica content will make lime sludge suitable for reburning and will improve dryness of lime sludge. This will reduce fresh lime requirement and less fuel will be required for lime mud reburning.

Conclusion

The development of Liquor heat treatment in combination with desilication of silica rich wheat straw black liquor and demonstration of the same at pilot plant level should help the Indian paper Industry employing wheat straw as raw material in achieving higher chemical recovery and thermal efficiency of chemical recovery operation.

References

1. Ibrahim, H, "Proceedings of The International Non-Wood Pulping and Papermaking " Beijing, Vol.II, p.877.(1988).
2. Panda, A., Indian Pulp & Paper, 16(6):701(1962).
3. Kulkarni, A.G., Kolambe, S.L.,Mathur, R.M.and Pant, R., Ippta, 21(1): 37(1984).