

AN INNOVATIVE APPROACH TO DEBOTTLENECK PULP MILL AND CHEMICAL RECOVERY IN AGRO BASED PAPER MILL



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Abstract

Indian pulp and paper industry is growing steadily through capacity expansion and technology modernization to improve quality of the paper and to address environmental issues. A number of mills have gone for marginal expansion of the pulp mill adopting oxygen delignification (ODL). These mills result with generation of additional black liquor. Many mills due to limited capacity of chemical recovery system could not process this additional black liquor in existing chemical recovery system thereby overloading it which leads to lower thermal and chemical recovery efficiency. In order to address this problem of processing of additional black liquor a process has been developed. The proposed process involves removal of lignin rich organic part from a portion of black liquor partially by carbonation followed by acidification. The lignin separated spent liquor after separation of lignin rich biomass is mixed with remaining black liquor and processed in chemical recovery system.

The studies have shown improved rheological, combustion and physico- chemical properties of the total black liquor. The separated lignin rich biomass has been utilized for production of value added by products which finds applications in rubber and ply-wood industry. The developed process also helps in improving economic and environmental status of the paper industry.

Introduction

The cooking chemicals are available in the form of dilute black liquor containing 85-90% water (10-15% dry solids in agro black liquor), along with lignin salts and degraded carbohydrates. This weak black liquor is a rich source of energy and inorganic cooking chemicals. Black liquor is processed in chemical recovery system to regenerate the inorganic chemicals (NaOH & Na_2S) used for the digestion of raw material and generating the energy in the form of steam by burning of organic part. The efficiency of chemical recovery system to a large extent, is influenced by the properties of black liquor. Chemical recovery is not only important for economic point of view as it is generating power and recycling cooking chemicals but it is essential for environmental point of view as black liquor poses very high COD and BOD load.

Chemical recovery is the most capital intensive single unit operation in a pulp mill. Due to high capital cost, installing a new chemical recovery for small mill is not viable. Marginal expansion of chemical recovery is not possible due to multi unit operation and nature of plant. Marginal expansion of pulp mill due to economic reasons and adoption of oxygen delignification for environmental point of view are common in pulp & paper mills. Additional black liquor is generated in pulp mill expansion and ODL. It is not possible to handle this additional black liquor in the existing chemical recovery system. Therefore the present research work is focused on this issue and is an unique attempt in this direction involving separation of lignin by carbonation followed by acidification so that part of the black liquor solids is diverted from chemical recovery loop and remaining is processed in the existing chemical recovery system. Thus the entire black liquor in pulp mill could be handled in existing chemical recovery system.

Method and Material

2.1- Collection of Black Liquor

Black Liquor was collected from an agro-based paper mill located in northern part of the country. The black liquor was characterized for various parameters of interest using standard TAPPI methods.

2.2- Optimization of the Lignin Removal Process from bagasse black liquor

A part of black liquor was subjected to lignin removal process (LRP). Lignin removal was carried out by carbonation followed by acidification. The process parameters were optimized in respect of pH & temperature. Lignin was filtered from carbonated and acidified black liquor and filtrate of the LRP was further characterized for different physio-chemical parameters using standard TAPPI methods.

2.3- Study on mixed black liquor (LRP Filtrate & Original Black Liquor)

The filtrate obtained from LRP was mixed to the original black liquor in different ratios of, 10: 90, 15: 85 & 20:80 (LRP filtrate : black liquor) on the basis of dry solids to study the effect of lignin removal on various properties of the blended black liquor. Standard TAPPI methods were used to analyze the black liquor & filtrate properties.

3.0 Result and Discussion

3.1 Characterization of Original Black Liquor

Black liquor collected from the mill was analyzed for various parameters important for its smooth processing in chemical recovery system. Results obtained are shown in tables 1 & 2.

Table 1 : Characterization of Original Black Liquor

S.No	Parameters	Value
1	Total Solids, %w/w.	11.2
2	pH	11.6
3	RAA, gpl as NaOH.	3.5
4	Carbon as C, %w/w.	33.3
5	Hydrogen as H, %w/w.	4.5
6	Nitrogen as N, %w/w.	0.80
7	Sulphur as S, %w/w.	0.15
8	Inorganic as NaOH, %w/w.	30.3
9	Organics, %w/w.	69.7
10	Chloride as NaCl, %w/w.	1.23
11	Silica as SiO ₂ , %w/w.	2.35
12	GCV, cal/g.	3340
13	SVR, ml/g.	10
14	Sodium as Na, %w/w.	14.4
15	Lignin, %w/w.	32.5

Table 2 : Viscosity of Original Black Liquor

Total Solids, %w.w	Viscosity, cps at 100°C
50	426
55	1002
60	2357
65	5545

3.2 Optimization of lignin removal process Conditions

pH and temperature are two major variable of Lignin removal process. The process was optimized in respect of pH and temperature. During the optimization process, lignin yield of the separated

liquor was taken as dependent variable whereas pH & temperature were taken as independent variables. Optimization experiments were carried out at different pH & temperatures. The results obtained are shown in figure 1.

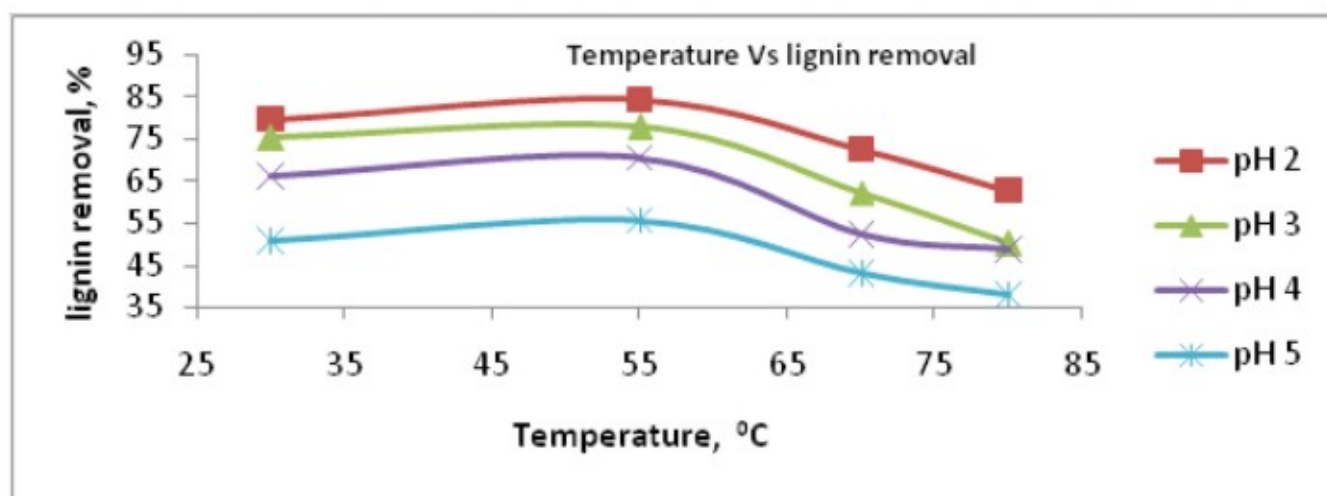


Figure -1: lignin removal percentage at different pH and Temperature

Optimization of pH

Figure 1 clearly indicates that as pH of the black liquor is lowered by acidification, lignin yield increases and get an maximum value at pH 2. This is due to the fact that at the lowest pH values hydrogen ions protonize the negatively charged lignin and neutralize the charges on the molecular surface which reduces the repulsive forces; eventually the precipitation of lignin occurs. Below 2 pH reduction does not increase substantial lignin yield whereas requirement of acid is quite high. Thus it can be concluded that pH 2 is optimum for achieving maximum lignin removal.

Optimization of temperature

Various experiments conducted between from 30°C to 80°C have shown that a temperature of 55°C is optimum for maximum lignin removal. With increase in temperature, the yield of lignin decreases as solubility of lignin increases with increase in temperature. Thus optimized level for pH and temperature can be considered as pH 2 and 55°C respectively for LRP.

3.3 Mixing of LRP Filtrate and Original Black Liquor

Efficiency and smooth operation of Chemical Recovery Boiler is dependent on physic chemical, thermal and rheological behavior of black liquor. Partial removal of lignin changes the characteristics of black liquor. If higher percentage of Lignin is removed from black liquor it will reduce organic content of the black liquor and it can adversely affect the functioning of chemical recovery boiler.

Thus optimization of the process is quite necessary. The treated black liquor should have properties in balanced conditions with original black liquor so that it can be processed in existing recovery boiler. Filtrate of LRP was mixed with the original black liquor in different ratios (10:90 to 20:80). All the calculations were conducted on dry solids basis. Optimization of mixing of the filtrate to original black liquor was done to obtain the conditions of blending which can serve the best for enhancing marginal capacity of recovery boiler. Control and mixed black liquors in different ratio were characterized for parameters of interest. The results of the experiment are given in the table 3 & 4.

Table 3 : Characterization of Original and Mixed Black Liquor

Parameters	Value				
	Original Black Liquor	LRP filtrate	Mixed B.L 90:10	Mixed B.L 85:15	Mixed B.L 80:20
Total Solids, %w/w.	11.2	9.6	10.97	10.88	10.81
pH	11.6	2.5	11.1	10.9	10.4
RAA, gpl as NaOH.	3.5	Nil	2.8	2.5	1.6
Carbon as C, %w/w.	33.35	19.62	32.7	32.3	31.4
Hydrogen as H, %w/w.	4.5	0.7	4.2	4.05	3.88
Nitrogen as N, %w/w.	0.80	1.0	0.9	0.91	0.94
Sulphur as S, %w/w.	0.15	5.4	0.66	0.81	1.15
Inorganic as NaOH, %w/w.	30.3	44.7	31.3	31.9	32.2
Organics, %w/w.	69.7	55.3	68.7	68.1	67.8
Chloride as NaCl, %w/w.	1.23	1.24	1.24	1.25	1.23
Silica as SiO ₂ , %w/w.	2.35	0.21	1.55	1.49	1.42
GCV, cal/g.	3340	1510	3210	3171	3052
SVR, ml/g.	10	-	10	10	9
Sodium as Na, %w/w.	14.4	14.1	14.3	14.2	14.2
Lignin, %w/w.	32.5	10.2	30.8	30.3	29.7

Analysis of original and mixed black liquor has shown marginal reduction in solids content, which is not substantial. RAA level has reduced substantially in case of 20% mixing of LRP filtrate whereas till 15% mixing it is the range of 2.5 to 3.0% which can be processed in recovery. Carbon and organic content of the original and the blended mixtures shows that there is no significant difference in these values... GCV shows a decreasing trend with increase in filtrate concentration in the blended black liquor. However it is not as low to support

with auxiliary fuel. A sharp downfall was observed at 20 % filtrate concentration.

Swelling volume Ratio (SVR) value which is a pointer towards burning behavior of black liquor has not changed till 15% LRP filtrate mixing however it decreases by 1 at 20%.

Viscosity is one of the key factors that affects the evaporation and burning of the black liquor in a recovery boiler. Viscosity of the control and treated black liquors at different total solids was measured. Results are shown in table 4.

Table 4 : Viscosity of Control and Blended Black Liquor at 100oC

Sample	Viscosity, cps at 100°C			
	50%w/w	55%w/w	60%w/w	65%w/w
Total Solids--				
Control BL	426	1002	2357	5545
10% blended BL	367	802	1580	3050
15% blended BL	360	769	1495	2903
20% blended BL	361	774	1504	2856

Viscometric analysis of mixed black liquor has shown a substantial decrease when compared with original black liquor. Lower viscosity is favorable for chemical recovery point of view. One of the favorable situations here is reduced viscosity even at low RAA levels. This is due to removal of partly high molecular weight lignin from black liquor. High molecular weight lignin is mainly responsible for high viscosity.

The above results go to indicate that up to 15% LRP filtrate mixing improves the black liquor properties and it can be easily process in conventional chemical recovery system.

4.0 Conclusion

Looking in to the results obtained from physico-chemical, thermal and viscometric analysis of treated black liquor it is observed that after mixing of lignin filtrate and original black liquor in various ratios, a ration of 15:85 is most suitable and the blended black liquor at this concentration exhibit better properties desired for its processing in chemical recovery system. Thus the proposed process has the potential to increase capacity of chemical recovery system by 15%. This will ensure that the pulp and paper mills can now increase their pulp production and also can adopt the oxygen delignification process which is becoming increasingly important in

modern pulp bleaching technology. Thus Lignin removal carried out by carbonation followed by acidification can be seen as an alternative that can be used to debottleneck an existing recovery boiler which is important from economic and environmental point of view.

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6.0 References

1. Gupta, A., Mathur, R.M. and Kulkarni, A.G. (2001). Non-process elements in non-wood black liquors: their effect on the operation and energy efficiency of chemical recovery systems. *Appita journal* 54 (6): 518-522.
2. Hammett, A.L., Youngs, R.L., Sun, X. and Chandra, M. (2001). Non-wood fiber as an alternative to wood fiber in China's pulp and paper industry. *Holzforsch* 55 (2): 219-224
3. Minu, K., Kurian Jiby, K. and Kishore, V.V.N. (2012). Isolation and purification of lignin and silica from the black liquor generated during the production of bioethanol from rice straw. *Biomass and Bioenergy* 39: 210-217.