Octa Journal of Environmental Research **Apr. – Jun., 2016**
International Peer-Reviewed Journal ISSN 2321 3655
Oct. Jour. Env. Res. Vol. 4(2): 110-116
Available online http://www.sciencebeingjournal.com

Research Article

Octa Journal of Environmental Research
(Oct. Jour. Env. Res.) ISSN: 2321-3655
Journal Homepage: http://www.sciencebeingjournal.com

SPS Scientific Planet Society

INCREMENTAL CAPACITY EXPANSION OF CONVENTIONAL CHEMICAL RECOVERY SYSTEM IN AN AGRO BASED PAPER MILL

Abhilasha Sharma, A. K. Dixit* and R. K. Jain
Chemical Recovery Division, Central Pulp and Paper Research Institute, Saharanpur-247001 UP, India
Corresponding Author's E-mail: dixit_ashwani@rediffmail.com
Received: 3rd June 2016 **Revised**: 19th June 2016 **Accepted**: 23rd June 2016

Abstract: Chemical recovery system is an integral part of pulp and paper units and the efficiency of chemical recovery play an important role in economics. With today's increasingly high energy and chemical costs and stringent environmental regulations, the need for improved recovery of chemicals from the pulp and paper making process has become a critical economic factor in the industry. It is essential that mills maximize steam and power production capacity, reduce re-circulating chemical dead loads and minimize chemical losses. Although earlier agro-based mills were not having recovery furnace due to high silica content of black liquor and smaller capacity, however now chemical recovery in agro-based mills have been made mandatory. Pulp and Paper mills have a desire to increase their pulp production or to adopt the oxygen delignification (ODL) from environmental point of view and also to improve their economy. In such cases, the recovery boiler is often one of the major bottleneck. To debottleneck the recovery boiler, lignin has been extracted from the black liquor, which decreases the load of the boiler in proportion to the lignin extraction. Separation of lignin will affect the properties of the black liquor and the recovery boiler operation. Thus in the present study, optimization of the lignin removal process (LRP) has been done along with the optimization of the mixing of LRP filtrate with the original black liquor to obtain the conditions which can serve the best for enhancing marginal capacity of recovery boiler. A key observation of the results shows that the mixing of the filtrate in the original black liquor in the ratio of 85:15 (black liquor: filtrate) is the most suitable one for its processing in chemical recovery system.
Keywords: Black Liquor (BL); Chemical Recovery; Lignin Removal Process (LRP); Marginal capacity expansion: Oxygen Delignification (ODL).
Postal Address: Chemical Recovery Division, Central Pulp and Paper Research Institute, Saharanpur (247001), Uttar Pradesh, India, Phone: +91 9412873634

INTRODUCTION

The demand and use of pulp and paper have marked the levels of civilization and development of the society. Till recently wood was the primary source of virgin fibre for making paper. However, the increased cost of pulp wood and its scarcity in many forest deficient countries have directed attention to the use of non-woods fibres in papermaking (Atchison, 1998; Hammett *et. al.*, 2001). Papermaking process involves pulping of lingo-cellulosic fibrous raw material under alkaline conditions. During pulping, the alkaline cooking chemicals react with lignin in the fibrous raw materials to form alkali soluble lignin salts like, alkali lignin and thio-lignin in the form of black liquor which is separated from cellulosic fibres (pulp) in the washing section (Smook, 1992). The spent chemicals are available in the form of dilute black liquor containing 85-90% water (10-18% dry solids), 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 and 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 from economic point of view for generating power and recycling cooking chemicals but also essential from environmental point of view as black liquor posses very high levels of 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 (Olausson, 2005; Williamson and Santyr, 1988; Orender, 1992). Further, marginal expansion of chemical recovery is not possible due to multi unit operation and nature of plant. Marginal expansion of pulp mill is essential due to economic reasons and for adopting oxygen delignification from environmental point of view but additional black liquor is generated in these expansion activities. It is not possible to handle this additional black liquor in the existing chemical recovery system. Therefore the present research work is focussed 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 (Davy *et al.*, 1998; Uloth *et al.*, 1991; Loufti *et al.*, 1991; Vakkilainen and Valimaki, 2009). Thus the marginal expansion of pulp mill or adoption of Oxygen delignification (ODL) could be a reality in a mill with no investment in chemical recovery system.

EXPERIMENTAL

Collection and Soda pulping of Bagasse Raw material: Bagasse was collected from an agro-based paper mill located in western Uttar Pradesh. Dry Depithing of the collected bagasse was conducted by using disc mill depither at CPPRI. Proximate chemical analysis of depithed bagasse was done for various physio-chemical properties adopting standard TAPPI methods. On the basis of the proximate analysis of raw material, bagasse was cooked in a pressurized oil heated series digester by soda pulping process using 17% NaOH chemical charge with a bath ratio of 1:5. Cooking temperature was 165^{o}C at top for 60 min. Black liquor from the cooked slurry was separated by centrifuging the pulp. The separated black liquor was further characterised for various parameters of interest using standard TAPPI methods.

Optimization of the Lignin Removal Process from bagasse black liquor: Black liquor was characterized for various parameters of interest. Lignin removal process was optimized in respect with pH and temperature. The suspensions were filtered using a Buchner-hopper and the obtained filtrate of the LRP was further characterized for different physio-chemical parameters using TAPPI methods.

Study after mixing of LRP Filtrate to Original BL: The filtrate obtained from LRP was mixed to the remaining (original) black liquor in different ratios of, 90: 10, 85: 15 and 80:20 (black liquor: filtrate) to study the effect of mixing on various properties of the blended black liquor. Standard TAPPI methods were used to analyse the black liquor and filtrate properties. The mixing was carried out on the basis of dry solids.

RESULTS AND DISCUSSION

Characterization of depithed bagasse and generation black liquor

Proximate chemical analysis of fibrous raw material gives a lead in accessing its suitability for papermaking. Proximate chemical analysis of depithed bagasse was carried out. The results are given in table 1.

Table 1: Characterization of Depithed Bagasse

S.No.	Parameters	Value
1.	Ash, w/w	1.82
2.	Silica, %w/w	1.06
3.	Lignin, %w/w	23.18
4.	Pentosan, %w/w	20.58
5	Holocellulose, %w/w	76.34
6.	∝- cellulose,%w/w	50.04
7.	β – cellulose,%w/w	11.18
8.	γ- cellulose,%w/w	15.12
9.	Soluble lignin,%w/w	1.08

Proximate chemical analysis of the depithed bagasse indicates that it has high percentages of holocellulose and alpha cellulose which show its suitability for papermaking. The results of the proximate analysis were similar to those obtained earlier from the proximate analysis of this non wood material (Hurter, 1988; Dixit *et al*., 2014). Hurter (1988) reported that bagasse has alpha cellulose in the range of 32-44%, lignin (19-24%), pentosan (27-32%), ash (1.5-5) and silica (0.7-3).

Pulping of Depithed Bagasse and Characterization of Black Liquor generated

Depithed bagasse was digested employing soda pulping conditions as prevailing in bagasse based mills. Black liquor was separated from pulp by washing. Separated black liquor was characterized for various physico-chemical parameters which are important for its processing in chemical recovery using standard TAPPI methods. The results are given in table 3. The analysis of black liquor shows that the organic percentage (69.92%) as well as carbon amount (33.35%) is quite high for producing a large amount of steam which is also confirmed by high gross calorific value (3476 cal/g) as noted in earlier studies (Jain *et al.,* 1990; Gupta *et al.,* 2001). The higher organic amount in the black liquor is also helpful for our study which is related to the separation of organic part from black liquor. The values of all the other parameters show a general trend for processing of black liquor in recovery boiler. The black liquor was also characterized for rheological behaviour. The results are shown in figure 1. Characterization of bagasse black liquor has shown that this black liquor could be processed in chemical recovery however for obtaining higher efficiency these properties needs some modifications.

Optimization of Lignin Removal Process Conditions

Lignin removal process was optimized in respect of pH and temperature. During the optimization process, removal of lignin from the bagasse black liquor was taken as dependent variable and different values of pH and temperature were taken as independent factors. Optimization experiments were carried out for different pH and temperatures. The results obtained are given in table 2. The observations are also summarized in figure 2.

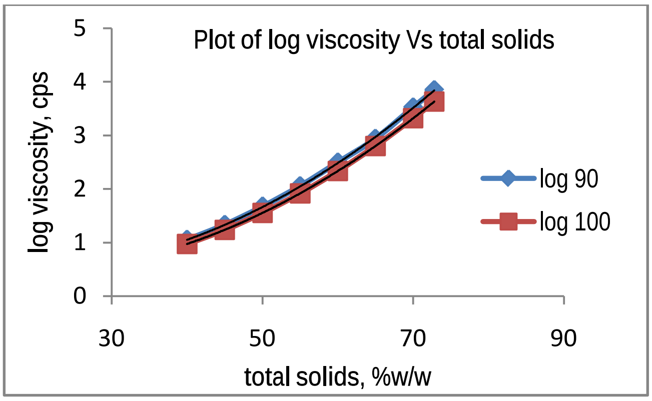

Figure 1. Viscosity of Bagasse Black liquor at two different temperatures

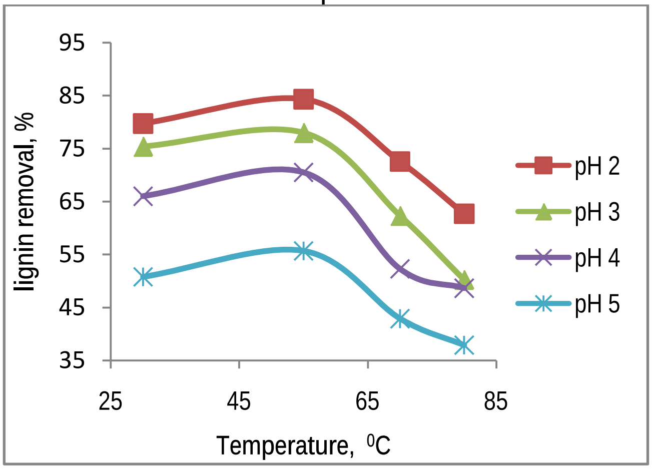

Figure 2. Impact of pH and Temperature on lignin removal

Optimization of Lignin Removal Process

Above results clearly indicate that as the pH of the black liquor is lowered by acidification, lignin removal increases to maximum 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. There was no substantial increase in weight of the precipitate from the black liquor below 2 pH. This might be because the further addition of acid led to increase only in the inorganic content of the separated lignin but had no effect in lignin separation. Various experiments were conducted between from 30°C to 80°C. Experiments at higher temperature (above 80°C) were also conducted but results show a very poor lignin removal with the formation of slurry which was hard to process further. Above results inferred that the maximum lignin removal of 84.36% was obtained at 55°C. With increase in temperature, lignin removal 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. According to Minu et al., 2012 maximum lignin removal in rice straw black liquor takes place at 3 pH and at 50°C while at temperatures above this the precipitated lignin weight was found constant. Ohman, 2006 proposed that at pH 9, about 70% of the lignin molecules precipitate by injecting CO_2 in the black liquor.

Mixing of the filtrate of LRP with original black liquor

As many pulp and paper mills are operating at or above their design capacities, pulp production is sometimes restricted by the limited amount of black liquor that can be burned in the recovery boiler. Removing some of the lignin from black liquor solids per metric ton of the pulp and the heating value of the solids, allowing increases in pulp production for a limiting load on the recovery boiler. Recovery boiler operation can be negatively affected if the lignin removal is too high or the mixing of LRP filtrate to original black liquor processes is not optimized. Thus optimization of the process is quite necessary which is tried in the present manuscript. The blended black liquor should be in balanced conditions with original black liquor to process in existing recovery boiler. In the present work, filtrate of LRP was mixed with the remaining (original) black liquor in different ratios. 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 blended black liquors were characterized for different physio-chemical parameters of interest. The results of the experiment are given in the table 3.

Table 2. Optimization of Lignin Removal process in respect of pH and Temperature

Temperature	% Lignin removal			
	2.0 pH	3.0 pH	4.0 pH	5.0 pH
30°C	79.75	75.4	66.01	50.78
55°C	84.36	78.0	70.51	55.69
70°C	72.6	62.34	52.29	42.90
80°C	62.73	50.24	48.65	37.89

Table 3. Analysis of LRP Filtrate, Control Black liquor and Blended Black liquor

Parameters	Original BL	LRP Filtrate	Mix BL(90: 10)	Mix BL(85: 15)	Mix BL (80:20)
Total Solids, %w/w.	9.67	7.40	9.44	9.32	9.216
pH	11.19	2.0	10.20	9.82	9.15
RAA, gpl as NaOH	2.96	Nil	2.46	2.12	1.49
Carbon as C, %w/w	33.35	19.62	31.97	31.29	30.60
Hydrogen as H, %w/w	4.58	0.66	4.18	3.99	3.79
Nitrogen as N, %w/w.	0.87	1.00	0.88	0.89	0.89
Inorganic as NaOH, %w/w	30.08	46.79	31.75	32.59	33.42
Organics, %w/w.	69.92	53.21	68.25	67.41	66.58
Chloride as NaCl, %w/w	0.23	0.24	0.23	0.23	0.23
Sulphate as Na_2SO_4, %w/w	0.52	34.75	3.94	5.65	7.37
Silica as SiO_2, %w/w.	1.73	0.26	1.58	1.51	1.43
GCV, cal/g	3476	1383	3305	3260	2815
SVR, ml/g	9	5	9	9	8
Sodium as Na, %w/w.	14.1	14.8	14.17	14.21	14.24
Potassium as K, %w/w	0.18	0.16	0.18	0.18	0.17
Calcium as Ca, %w/w	0.03	0.012	0.03	0.03	0.03
Lignin content, %w/w	35.43	4.10	32.30	30.72	29.16

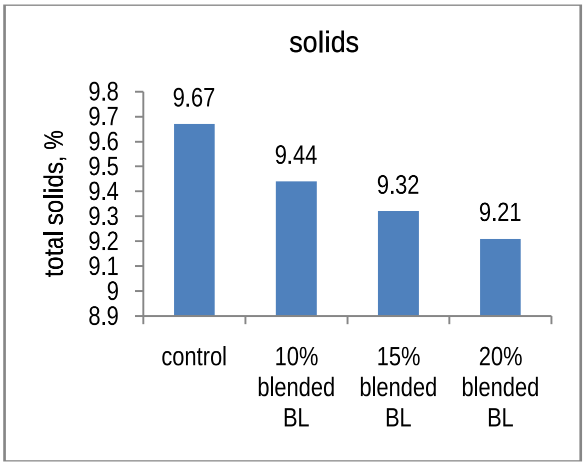

Figure 3. Total solids in Control BL and Blended BL

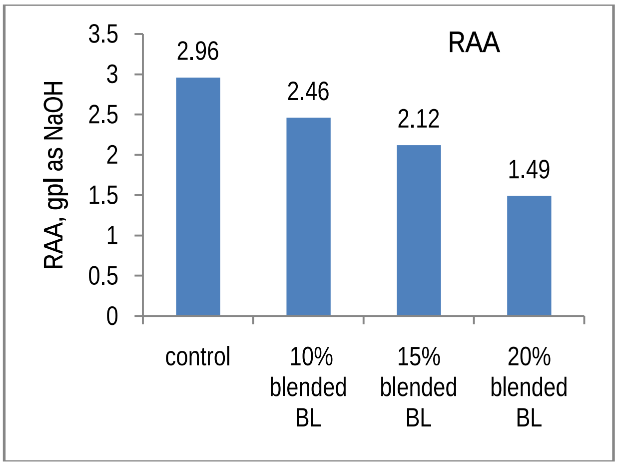

Figure 4. RAA of Control BL and Blended BL

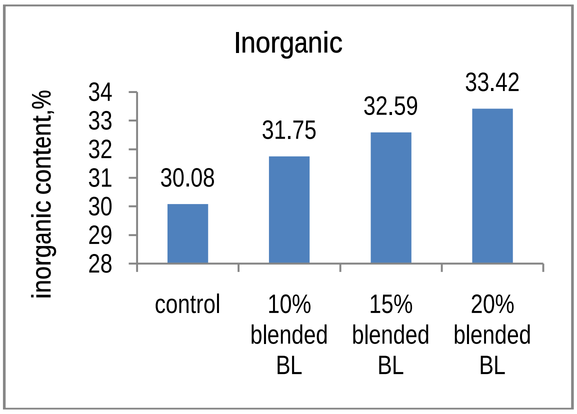

Figure 5. Inorganic content in Control BL and Blended BL

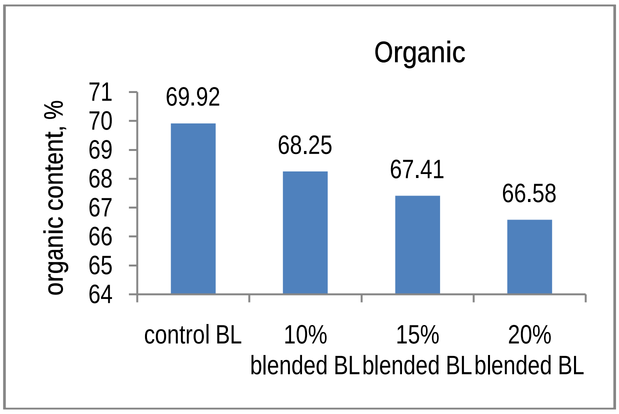

Figure 6. Organic content in Control BL and Blended BL

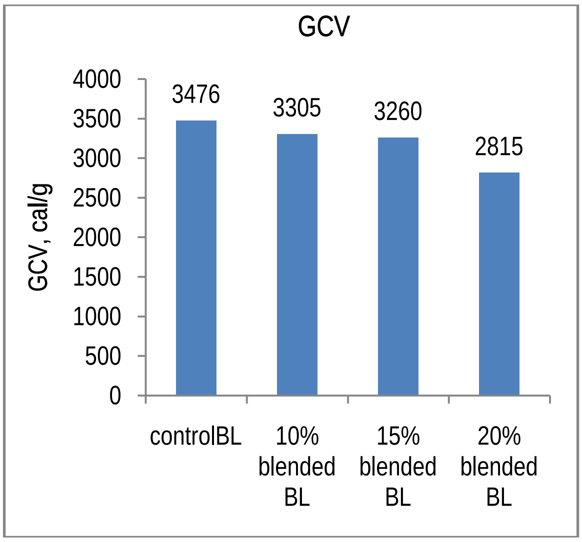

Figure 7. GCV of Control BL and Blended BL

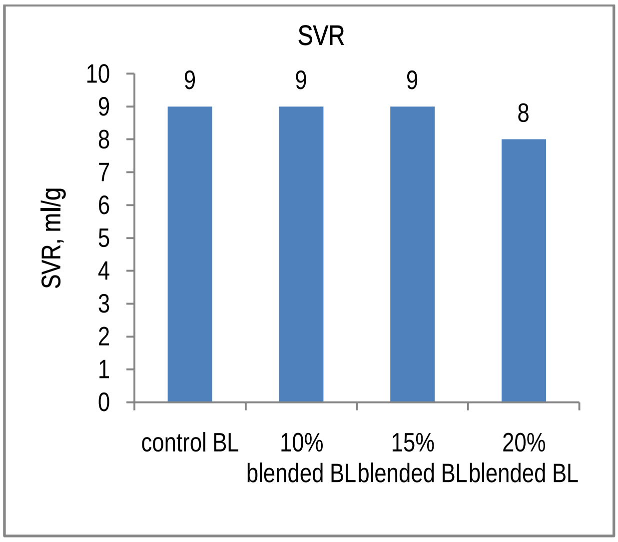

Figure 8. SVR of Control BL and Blended BL

Parameters which have key impact on the recovery process and are affected by filtrate mixing are plotted in the following graphs (figure 3 to 8). From the results, it is clear that solids of black liquor have reduced to some extent (Figure 3). RAA decreases with the increase in filtrate concentration in blended black liquor (Figure 4). RAA level was in favourable condition up to 15% filtrate concentration but after this, a sharp downfall in RAA level was observed in the black liquor. The organic content in the blended mixtures decreases with increase in LRP filtrate concentration in the blended black liquor while the inorganic content increases (Figure 5 and 6). This is due to the removal of organic content (lignin) from the black liquor during lignin removal process. Gross calorific value (GCV) is the amount of the energy that is released on burning one gram of the black liquor in the recovery boiler. GCV values (Figure 7) shows a decreasing trend with increase in filtrate concentration in the blended black liquor. But a sharp downfall was observed at 20 % filtrate concentration which will lead to the reduction in steam production in recovery furnace. Studies (Noopila *et al.,* 1991; Alen, 2000) show that the swelling volume ratio (SVR) which reflects the burning behaviour of the black liquor is proportional to the ratio of lignin to aliphatic acids in the liquor. Results clearly indicate that there is no change in the value of SVR upto 15 % filtrate concentration in the blended black liquor but at higher filtrate concentration (20%), value of SVR decreases which is not favourable for recovery process (Figure 8). 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 100^{o}C

Black liquor (BL)	Viscosity at different total solids (cps)				
	50, %w/w	55, %w/w	60,%w/w	65, %w/w	70, %w/w
Control BL	35.65	82.86	216.58	636.62	2103.75
10% blended BL	24.76	58.34	148.45	370.05	891.09
15% blended BL	36.27	71.72	148.81	324.05	740.51
20% blended BL	46.23	83.93	150.22	318.34	721.88

Viscometric analysis of the blended black liquors has shown a substantial decrease when compared with original black liquor. Lower viscosity is favourable for chemical recovery point of view. Decrease in viscosity is observed in all cases *i.e.* 10, 15 and 20% mixing. Previous research (Moosavifar *et al.,* 2006) also states that the effect of lignin separation on viscosity of softwood black liquor is more significant at high solids contents.

CONCLUSION

Looking in to the results obtained from physico-chemical, thermal and viscometric analysis it is observed that after mixing of lignin filtrate and original black liquor in various ratios, 15% is most suitable and the blended black liquor at this concentration exhibit better properties desired for its processing in chemical recovery system. 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. Oxygen delignification is environmentally and economically attractive in comparison to the commonly used bleaching chemicals (ClO_2). In order to minimize the use of chemicals in the bleach plant and allow more organic waste to be burned in the recovery boiler rather than these being released to the environment and also to produce high quality, totally chlorine-free pulp (TCF), mills will have to install oxygen delignification. Thus Lignin removal 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.

Acknowledgements: The authors want to gratefully acknowledge Dr. Tarun Dixit, Mr. A.S. Negi and Mr. Abhishek Jha for their valuable contribution to this work. We also thanks to the Department of Chemical Recovery Division, CPPRI for providing necessary laboratory facilities.

REFERENCES

Alen, R. (2000). Basic chemistry of wood delignification. *In:* Stenius, P. (Ed), *Forest Products Chemistry*, Fapet, Helsinki, Finland: 58-102.

Atchison, J.E. (1998). Update on global use of non-wood plant fibres and some prospects for their greater use in the United States. In: *Proceedings of the TAPPI North American Non-Wood Fiber Symposium*, Atlanta, GA, USA: 13-42.

Davy, M.F., Uloth, V.C. and Cloutier, J.N. (1998). Economic evaluation of black liquor treatment processes for incremental kraft pulp production. *Pulp Paper Can*. 99(2): 35-39.

Dixit, A.K., Dixit, T., Sharma, A. and Jain, R.K. (2014). Efficient Depithing of Bagasse for Reduction of Water Requirement in pulp Mill. International Journal of Engineering Research & Technology, ETWQQM-2014 Conference Proceedings.

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.

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.

Hurter, A.M. (1988). Utilization of annual plants and agricultural residues for the production of pulp and paper. *Proceedings of TAPPI Pulping Conference* 1988. New Orleans, LA, USA, Book 1: 139-160.

Jain, R.K., Gupta, A. and Kulkarni, A. G. (1990). New approach to recovery of chemicals from bagasse pulping liquors. *IPPTA* 2 (3): 1-7.

Loutfi, H., Blackwell, B. and Uloth, V. (1991). Lignin recovery from kraft black liquor: preliminary process design, *TAPPI,* 74 (1): 203-210.

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.

Moosavifar, A., Sandin, P. and Theliander, H. (2006). Viscosity and boiling point elevation of black liquor: consequences when lignin is extracted from the black liquor. *Nord. Pulp Pap. Res. J.21 (2): 180-188*

Noopila, T., Alen, R. and Hupa, M. (1991). Combustion properties of laboratory-made black liquors. *J. Pulp and Paper Sci.* 17 (4): 105.

Ohman, F. (2006). Precipitation and separation of lignin from kraft black liquor, PhD thesis. Department of Chemical and Biological Engineering. *Chalmers University of Technology.* Gothenburg, Sweden.

Olausson, L. (2005). Personal communication with general manager of technology and engineering Lars Olausson at Kvaener Power, Gothenburg, Sweden.

Orender, H.C. (1992). Recovery boiler upgrades, 25th Annual Pulp and Paper, Sao Paulo, Brazil, 23-27: 1007-1043.

Smook, J. A. (1992). Handbook for Pulp and Paper Technologists, 2nd Ed., Chaps. 7 and 10, Angus-Wilde, Vancouver.

Uloth, V., Richardson, B. and Hogikyan, R. (1991). Use of a recovery boiler computer simulation to evaluate some process alternatives to obtain incremental recovery capacity, Pulping Confrence, Orlando, Fl, USA, 3-7: 893-910.

Vakkilainen, E. and Valimaki, E. (2009). Effect of lignin separation to black liquor and recovery boiler operation. In: *Proceedings of TAPPI Eng. Pulp. and Environ. Conf*, Memphis, TN, USA: 1515-1533.

Williamson, D. and Santyr, G. M. (1988): Capacity upgrade of an existing chemical recovery boiler, TAPPI Engineering Conference, Chicago. USA: 381-388.

Source of Financial Support: None.
Conflict of Interest: None. Declared.