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RESEARCH ARTICLE

LIQUOR HEAT TREATMENT OF WHEAT STRAW BLACK LIQUOR TO FACILITATE RECOVERY PROCESS IN A PAPER MILL

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ABSTRACT

Recovery boiler combustion of black liquor to recover energy and cooking chemicals is becoming a necessary technique for non- wood pulping also. However, black liquor viscosity increases exponentially with solids content and therefore causes processing problems for paper industry by being a limited factor due to the high viscosity of non-wood based liquors. The present study highlights the work carried out on liquor heat treatment (LHT) to reduce viscosity and to improve the combustion behaviour of the wheat straw black liquor. Liquor heat treatment is one possible way to overcome the disadvantage of present recovery system. The process is based on the depolymerisation of larger molar mass organic components into lower mass components. This ultimately results in the lowering of viscosity of black liquor and reduction in polysaccharide content which shows up decreased energy consumption in pumping and also lesser scaling in strong liquor pipes. Also the sidewise increase in dry solid concentration raises the boiler capacity and efficiency. Studies were carried out to optimize the LHT process in respect of residual active alkali, treatment temperature and retention time. From the results it could be concluded that a temperature of 180^{0}C for 15 minutes at a RAA level of 5.5% (w/w as NaOH) was enough for LHT which results in 78% viscosity reduction as well as 55% increment in swelling of wheat straw black liquor.

INTRODUCTION

For a pulp mill operation to be cost-effective, the cooking chemicals that react with the raw material and subsequently contribute to the production of black liquor must be recovered (Smook, 1992). In order to regenerate these chemicals, black liquor is subjected to several environmentally deleterious and energy-intensive treatments such as evaporation and burning. But the high viscosity of the agro based black liquors is a major problem during these processes. The viscosity of the black liquor is determined by its composition. Black liquor is a complex colloidal aqueous solution composed of several components, including lignin, polysaccharides, and salts (Joanna E. Roberts *et al,* 1996). Polysaccharides like xylan are dissolved during the cook as long-chained molecules that increase the original viscosity level of black liquor. Research works in the past have demonstrated that both the lignin (Small *et al,* 1985) and polysaccharide (Soderhjelm, 1989) fractions may be responsible for the exponential increase in black liquor viscosity. The effect of lower viscosity shows up as decreased energy consumption in pumping and lesser scaling in strong liquor pipes (Ryham and Nikkanen, 1992) while strong or concentrated black liquor is a sticky, unpumpable liquid (Boone, 1991; Ramamurthy *et al,* 1992). Higher liquor viscosity consequently hinders process ability in terms of transport, storage and handling. High viscosity can lead to the formation of very large liquor droplets that are too heavy to burn well in the recovery boiler. Consequently, the large droplets that fall into the char bed in the recovery boiler cause the bed to grow. This can lead to increased thermal activity (thermal excursions or temperature spiking) that causes tube cracking and corrosion (McCabe *et al,* 2007).

The traditional method of controlling the liquor spray is by manipulating the firing temperature of the liquor. This is usually done manually and by visual observation of the bed shape. In this way, viscosity is managed indirectly and hence liquor sprayed at high solids concentrations (Porter *et al,* 2010). Unfortunately, since viscosity is an exponential function of solids concentration (Zaman *et al,* 1994) small variations in solids concentrations can cause large variations in viscosity even if the temperature is held constant and this makes temperature control schemes ineffective (Dutka *et al,* 2004).

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To control viscosity problem, methods such as oxidation (Milanova *et al*, 1990; Frederick *et al,* 1992) salting-in (Joanna E. Roberts *et al,* 1996) have been studied. In the oxidation process, black liquor is exposed to air to convert sulphides to thiosulfate (Milanova *et al,* 1990) thereby decreasing viscosity through a reduction in residual alkali concentration. However, this viscosity decrease is reversible; that is, addition of alkali following the oxidation step returns the liquor to its original viscosity.

The heat treatment of black liquor can be defined as a thermal treatment method where residual alkali reacts with dissolved polysaccharides and lignin. These reactions are very slow in typical evaporator temperatures so the black liquor is heated up to between 170 -180°C (i.e. 10^0C higher than cooking temperature). The treatment splits long chains and the effect is destruction of high molecular weight compounds and reduction of black liquor viscosity.

The greatest benefit of LHT is irreversible viscosity reduction that allows the evaporation of black liquor to higher dry solids and keeps the black liquor in a pumpable form even at atmospheric pressure. Raising the dry solids increases the boiler capacity and efficiency. High dry solids combustion improves the operation as lower flue gas amount means higher temperature at the furnace. A well known benefit of raising the dry solid level of black liquor is the reduction in sulphur dioxide emission. It has been observed that increasing the amount of shorter (that is, with a molecular weight of between 1500 and 3000) lignin chains increases swelling (Backman *et al,* 1996; Alen, 1997) of the black liquor during combustion. During the devolatilization, the black liquor droplets swell considerably.

The swelling is continuous from the onset of ignition until the devolatilization is complete (Hupa *et al,* 1987; Frederick *et al,* 1991; Milanova, 1988). For a particle to swell there must be gas generation inside the droplet and the surface must have plastic properties (Milanova, 1988). As discussed earlier, liquor heat treatment affects the polysaccharide content and so also the surface properties. It is suspected that the change in liquor swelling can be attributed to changes in polysaccharide and low molecular weight lignin content. A lot of research works have been carried out on heat treatment of Kraft black liquor while more study is still required for agro black liquors. The objective of present work is to study the impact of liquor heat treatment on rheological and combustion behaviour of wheat straw black liquor and to optimize the process in respect of RAA level, temperature and retention time.

MATERIALS AND METHODS

Semi concentrated wheat straw black liquor sample was collected from an agro based paper mill. The mill was adopting soda process for cooking using 17% (as NaOH) chemical charge. From the literature it was clear that LHT gives better results with semi concentrated black liquor (SCBL) than weak black liquor (WBL), so SCBL having total solids in the vicinity of 25% (w/w) was collected. The residual active alkali (RAA) was measured 5.0 % as NaOH (w/w) initially which was depleted to 3.5% as NaOH (w/w) after 48 hrs (when the study was started). NaOH was added to black liquor (3.5% RAA) for preparing the black liquors of higher RAA levels (4.5, 5.5 and 6.5). Prepared four black liquors (RAA 3.5, 4.5, 5.5 and 6.5) were used for the study. Liquor heat treatment of the black liquor was conducted in a batch digester at laboratory. Viscosity of the various black liquors was measured with the rheometer (MCR-100, Anton- Paar). Total solids, residual active alkali (RAA) and swelling volume ratio (SVR) were measured adopting standard TAPPI methods.

RESULTS

In the study four black liquors (used in the study) i e. SCBL of RAA 3.5%, SCBL of RAA 4.5%, SCBL of RAA 5.5% and SCBL of RAA 6.5% are abbreviated as SCBL-A, SCBL-B, SCBL-C and SCBL-D respectively. Each of the four black liquors was treated at three temperatures: 175^0C, 180^0C & 185^0C and a retention time of 10 minutes, 15 minutes & 20 minutes was given at every temperature.

Analysis of Control and Treated Black Liquors

Each of the four black liquors were analysed for residual active alkali and swelling volume ratio at every stage of treatment. The analysis results of control and treated black liquors are given in *Table 1.* Other parameters like silica, organic to inorganic ratio, chlorides, CHNS were also measured for treated and control black liquors but there was no drastic change for these values by treatment and so these results are not given.

Viscosity and Percentage Reduction in Viscosity of Black Liquors

Viscosity of control and all treated black liquors was measured; results are given in *Table 2.* From the viscosity results, given in *Table 2*, percentage reduction in viscosity at various treated conditions was calculated. Percentage reduction in viscosity of treated liquors is given in *Table 3.*

Table 1 Analysis of Control and Treated Black Liquors for RAA & swelling volume ratio

		SCBL-A								
		Treated								
		175^0C			180^0C			185^0C		
Parameter	Control	10 min.	15 min.	20 min.	10 min.	15 min.	20 min.	10 min.	15 min.	20 min.
RAA, % as NaOH	3.5	2.32	2.01	1.86	2.08	1.79	1.66	1.83	1.51	1.37
Swelling Volume Ratio, ml/g	6	8	8	8	8	9	9	9	9	9

		SCBL-B								
		Treated								
		175^0C			180^0C			185^0C		
Parameter	Control	10 min.	15 min.	20 min.	10 min.	15 min.	20 min.	10 min.	15 min.	20 min.
RAA, % as NaOH	4.5	2.49	2.20	2.06	2.23	2.00	1.79	2.09	1.82	1.65
Swelling Volume Ratio, ml/g	7	9	10	10	9	10	10	10	10	10

Parameter	Control	SCBL-C Treated 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
RAA, % as NaOH	5.5	2.55	2.30	2.16	2.39	2.06	1.90	2.20	1.89	1.77
Swelling Volume Ratio, ml/g	7	9	10	10	10	11	11	10	11	11

Parameter	Control	SCBL-D Treated 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
RAA, % as NaOH	6.5	2.60	2.39	2.23	2.48	2.15	2.02	2.34	1.99	1.85
Swelling Volume Ratio, ml/g	8	10	11	11	10	12	12	11	12	12

Table 2 Viscosity of control and treated black liquors at 100^{0}C

Total Solids, %w/w.	Control Black Liquor	Viscosity of SCBL-A at 100^{0}C, cp — Treated Black Liquor 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
55	398	209	206	205	204	201	200	202	199	198
60	1805	942	925	919	917	914	913	914	912	911
65	9717	4911	4827	4802	4765	4680	4662	4748	4669	4656

Total Solids, %w/w.	Control Black Liquor	Viscosity of SCBL-B at 100^{0}C, cp — Treated Black Liquor 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
55	289	124	122	121	121	118	118	120	118	117
60	986	403	394	391	389	379	376	388	377	372
65	5438	2014	1962	1945	1926	1867	1851	1917	1862	1847

Total Solids, %w/w.	Control Black Liquor	Viscosity of SCBL-C at 100^{0}C, cp — Treated Black Liquor 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
55	266	93	91	90	89	87	87	89	86	86
60	826	259	250	248	245	236	233	242	234	230
65	4215	1051	1009	992	969	924	908	954	907	889

Total Solids, %w/w.	Control Black Liquor	Viscosity of SCBL-D at 100^{0}C, cp — Treated Black Liquor 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
55	246	81	79	78	77	75	74	76	74	73
60	753	212	204	201	198	190	187	194	186	183
65	3983	822	779	762	738	693	675	716	669	650

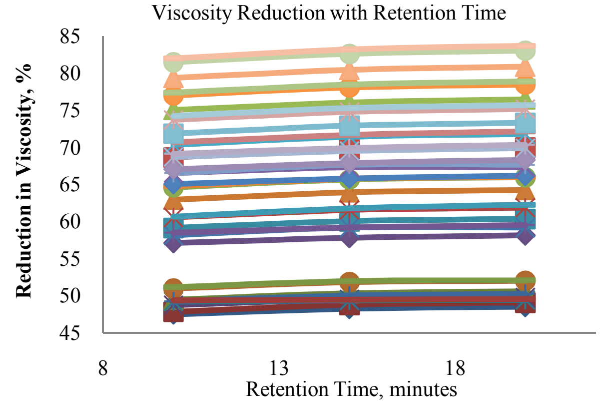

Fig 1 Percentage viscosity reduction with respect to retention time

Table 3 Percentage reduction in viscosity of various treated black liquors

Total Solids, %w/w.	Reduction in Viscosity of Treated SCBL-A, % — 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
55	47.49	48.24	48.49	48.74	49.50	49.75	49.25	50.00	50.25
60	47.81	48.75	49.05	49.20	49.36	49.42	49.36	49.47	49.53
65	49.46	50.32	50.58	50.96	51.84	52.02	51.14	51.95	52.08

Total Solids, %w/w.	Reduction in Viscosity of Treated SCBL-B, % — 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
55	57.09	57.78	58.13	58.13	59.17	59.17	58.48	59.17	59.52
60	59.13	60.04	60.34	60.55	61.56	61.87	60.65	61.76	62.27
65	62.96	63.92	64.23	64.58	65.67	65.96	64.75	65.76	66.03

Total Solids, %w/w.	Reduction in Viscosity of Treated SCBL-C, % — 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
55	65.04	65.79	66.17	66.54	67.29	67.29	66.54	67.67	67.67
60	68.64	69.73	69.97	70.34	71.43	71.79	70.70	71.67	72.15
65	75.06	76.06	76.47	77.01	78.08	78.46	77.37	78.48	78.91

Total Solids, %w/w.	Reduction in Viscosity of Treated SCBL-D, % — 175^{0}C 10 min.	15 min.	20 min.	180^{0}C 10 min.	15 min.	20 min.	185^{0}C 10 min.	15 min.	20 min.
55	67.07	67.89	68.29	68.70	69.51	69.92	69.11	69.92	70.32
60	71.85	72.91	73.31	73.71	74.77	75.17	74.24	75.30	75.70
65	79.36	80.44	80.87	81.47	82.60	83.05	82.02	83.20	83.68

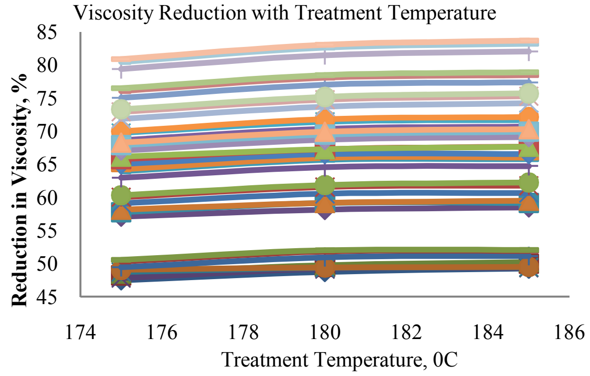

Fig 2 Percentage viscosity reduction with respect to treatment temperature

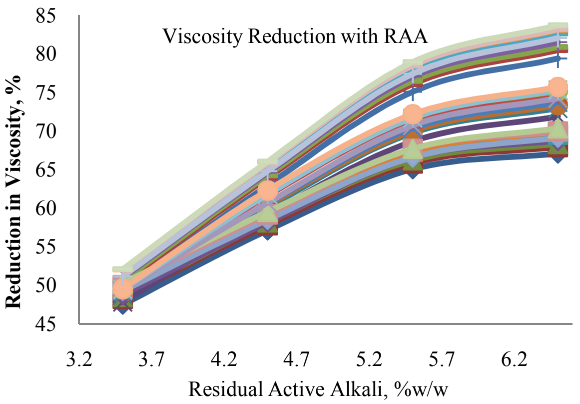

Fig 3 Percentage viscosity reduction with respect to RAA level

DISCUSSION

Results from *Table 1* indicate that the residual active alkali plays an important role in the liquor heat treatment. A decrease in residual active alkali was measured for all the treated black liquors which show that the residual active alkali was consumed by the polysaccharide content present in the black liquor. Though the residual active alkali decreased during heat treatment, it was enough for concentrating the black liquor to the higher solids than the control black liquor as no precipitation was observed during the evaporation of the black liquors and all treated black liquors could be processed smoothly for higher solid concentrations.

Swelling volume ratio is one of the most important parameters to understand combustion behaviour of the black liquor. From the results it is clear that the swelling volume ratio was increased for all treated black liquors which show an improvement in the combustion behaviour. Up to 55% increment in the swelling volume ratio was measured. Percentage viscosity reduction *(Table 3)* was plotted with respect to various adopted conditions. Different plots were used to optimize the process as explained below.

Optimization of LHT Process in respect of Time

Treatment was carried out at three retention times 10 minutes, 15 minutes and 20 minutes. Percentage viscosity reduction of all treated black liquors at different retention times is plotted in *Fig 1*. From *Fig 1*, it is clear that as the retention time increased from 10 to 20 minutes, viscosity reduction also increased. All the plots shown nearly a horizontal and linear behaviour which indicated that though the viscosity reduction increased with retention time, the effect of time was almost similar for all three time periods (i.e. for 10, 15 and 20 minutes). Further, from the *Fig 1*, it could be concluded that the rate of viscosity reduction was higher between 10 to 15 minutes. After 15 minutes retention time the viscosity reduction becomes almost constant and on the basis of these facts it was concluded that a retention time of 15 minutes was optimum level for treatment.

Optimization of LHT Process in respect of Temperature

Liquor heat treatment was started at 175^0C (10^0C higher than cooking temperature). Treatment was conducted at three temperatures i.e. 175^0C, 180^0C and 185^0C. Plots of percentage viscosity reduction with respect to treatment temperature are given in *Fig 2. Fig 2* appeared similar as *Fig 1* which indicates that percentage viscosity reduction showed a similar behaviour with respect to temperature as shown with retention time. Similarly as retention time, optimum treatment temperature could be optimizes as 180^0C.

Optimization of LHT Process Condition in respect of RAA level

Four black liquors SCBL-A, SCBL-B, SCBL-C and SCBL-D of different RAA levels 35%, 4.5%, 5.5% and 6.5% respectively were processed for liquor heat treatment. Percentage reduction in viscosity at different RAA levels is plotted in *Fig 3.* Plots shows that as we increased the RAA level, viscosity reduction increased. There was a sharp linear increment in viscosity reduction up to 5.5% RAA, while after this the rate of viscosity reduction decreased and the plots becomes horizontal. A viscosity reduction of 78% could be achieved at 5.5% RAA level. There was only 2% increment in viscosity reduction with further increment in RAA from 5.5% to 6.5%, thus from the results it could be concluded that 5.5% RAA level was an optimum level for liquor heat treatment.

CONCLUSION

From the study it could be concluded that temperature of 180^0C for 15 minutes at a RAA level of 5.5% (w/w as NaOH) was optimum for liquor heat treatment of wheat straw black liquor. With the liquor heat treatment, reduction of 78% in the black liquor viscosity could be achieved and the liquor could be concentrated to higher solids with lower pumping power. Combustion behaviour of the black liquor was improved with treatment as up to 55% increment in swelling volume ratio was noted after treatment.

References

1. Alen, R. (1997). Effect of black liquor composition to combustion properties (in Finnish, Mustalipeän koostumuksen vaikutus lipeän poltto-ominaisuuksiin), LIEKKI2- Yearly report, Part II. Turku, Finland: Åbo Akademi, Department of Chemical Engineering. 751-759.
2. Backman. R., Hupa, M., and Söderhjelm, L. (1996). Combustion properties of black liquor (in Finnish, Mustalipeän polttotekniset ominaisuudet), Report No. 96-9. Turku, Finland: Åbo Akademi University, Department of Chemical Engineering.
3. Boone, M. T. (1991). Recovery Enhancement Through Ultra High Solids, Tappi Kraft Recovery Operations Short Course, Tappi Press, Atlanta, p. 93.
4. Dutka, A. P., Basker, V. R. et al. (2004). Evaluation of a capillary-coriolis instrument for on-line viscosity and density measurements of kraft black liquor, Tappi Journal 3(3): 17-24.
5. Frederick, W. J., and Adams, T. (1992). Black Liquor Thermal and Transport Properties, 1992 Kraft Recovery Operations Short Course, Tappi Press, Atlanta, p. 97.
6. Frederick, W.J., Noopila, T.and Hupa, M. (1991). Combustion behavior of black liquor at high solids firing, Tappi J. 74 (12): 163-170.
7. Hupa, M., Solin, P., Hyöty, P. (March 1987). Combustion behaviour of black liquor droplets, JPPS 13 (2): J65 - J72.
8. Joanna E. Roberts, Khan Saad A. and Richard J. Spontaic (August 1996): Controlled black liquor viscosity reduction through salting-in, AIChE Journal, 42(8), 2319-2326.
9. McCabe, F. D., Mott, D. et al. (2007). Controlling black liquor "viscosity" to improve recovery boiler performance, International chemical recovery conference. Quebec, Canada, TAPPI/PAPTAC:427-432.
10. Milanova, E. (July 1988). Variables affecting the swelling of kraft black liquor solids, JPPS 14 (4): J95-J102.

11. Milanova, E., and Dorris, G. M. (1990). Effects of Residual Alkali Content on the Viscosity of Kraft Black Liquor, J. Pulp Paper Sci., 16, 594.
12. Porter, J., Sands, T. et al. (2010). Improving recovery boiler performance by controlling variability (new tools for an old problem), International chemical recovery conference.Virginia, USA, TAPPI/PAPTAC: 16pp.
13. Ramamurthy, P., Mujumdar, A. S., Van Heiningen, A.R.P. and Kubes, G. J. (1992). Concentration of Black Liquor to High Solids, Tappi J., 75, 195.
14. Ryham,R., and Nikkanen S. (1992). High Solids Firing in Recovery Boilers, Kraft Recovery Oper. Short Course, Tappi Press, Atlanta, 233-238.
15. Small, J.D., and Fricke, A. L. (1985). Thermal Stability of Kraft Black Liquor Viscosity at Elevated Temperatures, Ind. Eng. Chem. Prod. Res. Deu., 24, 608.
16. Smook, J. A. (1992). Handbook for Pulp and Paper Technologists, 2nd ed., Chaps. 7 and 10, Angus-Wilde, Vancouver.
17. Soderhjelm, L. (1989). Viscosity of Strong Black Liquor from Sulphate Mills, Int. Chem. Recouery Con8 Proc., Tappi Press, Atlanta, p. 95.
18. Zaman, A. A. and Fricke, A. L. (1994). Newtonian viscosity of high solids Kraft black liquors: effects of temperature and solids concentrations, Industrial and Engineering Chemistry Research 33(2): 428-435.

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