Improvement in Kraft Pulp Yield and Strength Properties of Paper by Black Liquor Pre-Treatment of Chips

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Black liquor pre-treatment of mixed hardwood chips followed by kraft pulping was carried out, and the properties of pulp produced were compared with the pulp produced after conventional kraft pulping without black liquor pre-treatment. Black liquor pre-treatment of chips was carried out using chips to liquor ratios of 1:2.5, 1:1:3.0, and 1:3.5; pre-treatment times of 30, 60, 90 minutes; and temperatures of 100, 110, 120 minutes. Black liquor generated during the conventional kraft pulping using 16% active alkali having 23.2% sulphidity, 90 minute cooking time, 1:3 chips to liquor ratio, and 160 °C cooking temperature was used for pre-treatment. After black liquor pre-treatment, liquor was drained and chips proceed for kraft pulping at using similar as well as reduced active alkali dosage and cooking temperature compared to kraft pulping carried out without using black liquor pre-treatment. Black liquor pre-treatment of mixed hardwood chips reduced shives content in pulp by 66%, active alkali demand during pulping by 1.5%, and H factor by 220. Black liquor pre-treatment of mixed hardwood chips followed by pulping at reduced temperature and active alkali improved unbleached screened pulp yield by 2.1%, viscosity by 1.8 cP, tensile index by 8.5%, tear index by 30.8%, and burst index by 35.7% compared to similar kappa number pulp produced without black liquor pre-treatment.

Key words: Black liquor pre-treatment; Pulping; Active alkali; Yield; Physical strength properties

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INTRODUCTION

Significant technological improvements have been employed in pulping of wood chips to reduce carbohydrate degradation, thereby improving the pulp yield. Use of black liquor or sulfide-containing liquor for impregnation of wood chips prior to pulping is one of the promising processes for improved kraft pulping.

Many research and industrial applications have shown that this modification can provide multiple benefits including higher pulp yield, better delignification selectivity, and lower production cost (Lönnberg *et al.* 1993; Svedman *et al.* 1995; Vikström *et al.* 1998). Impregnation of chips with weak black liquor improves air removal from the chips. Impregnation followed by cooking with white liquor gives uniform pulp quality, higher yield, and low shives content in pulp. Olm *et al.* (1996), studied on treatment of softwood with sulfide-containing liquor prior to a kraft cook. These authors reported that the pretreatment temperature results in an increase in the total sulfide absorption, thereby improving the pulp quality. Results of a plant-scale study carried out with black liquor impregnation of chips prior to pulping showed improvement in tear strength of paper by

10%, improvement in burst strength, reduction in beating energy, and improvement in bleachability of pulp (Höglund *et al.* 1994). Black liquor treatment of chips prior to pulping increased the concentration of hydrosulfide ions. The composition and concentration of the active pulping chemicals play an important role in pulping selectivity during kraft pulping. The main active components in kraft pulping liquor are hydroxide and hydrosulfide ions. Hydrosulfide ion accelerates the delignification and converts nonselective soda pulping process into a selective delignifying process. The sulphidity level at the beginning of bulk delignification governs the delignification efficiency (Sjöblom *et al.* 1983; Ban and Lucia 2003; Sixta and Rutkowska 2006; MacLeod 2007).

Green liquor (GL) pretreatment of wood chips has also showed potential to enhance quality of pulp and pulp yield. Hydrogen sulphide cooking with green liquor pretreatment in the presence of carbon dioxide or hydrogen sulphide gives a yield increase of 2 or 5 percentage points on wood, respectively, compared with the reference cook. The unbleached pulps have the same physical properties compared to reference pulp, except for the tear index at a given tensile index. No differences were observed in the beatability of the unbleached pulps (Olm *et al.* 1998). Ban *et al.* (2003) studied the green liquor (GL) pretreatment of softwood chips and the effect of such treatment on uncondensed phenolics and condensed hydroxyl groups. With the increase in GL charge the uncondensed phenolics and condensed hydroxyl groups decreased, but they increased with increasing pretreatment temperature (Ban *et al.* 2003). Lindström *et al.* (2004) studied the green liquor pretreatment of chips and compared the results with modified continuous cooking (MCC) process. Green liquor pretreatment of chips generated pulps of higher kappa than the MCC at similar *H* factors. The pulp yields and viscosities were also similar to those of the MCC process. Green liquor pretreatment using high total titratable alkali (TTA) produced higher tensile and burst index values relative the MCC pulps (Lindström *et al.* 2004).

Pre-treatment of wood chips using acidified water and acidic bleaching stage filtrate can considerably reduce the non-process elements content in the wood chips. Carbohydrate content and other wood constituents were not negatively affected by the applied acid pretreatment of wood chips (Santos *et al.* 2015). Study conducted with an aqueous pretreatment of chips at 50, 70, and 90 °C for 5 h showed that acid treatment contributed to better delignification (Sarto and Silva 2012).

In the present work the effect of black liquor treatment of mixed hardwood chips prior to pulping on unbleached pulp properties, bleachability, and mechanical properties was studied. The suggested process can be implemented in conventional batch types of liquor circulating digesters for improving the pulp yield, reducing shives content in pulp and improving physical strength properties of paper.

EXPERIMENTAL

For the study, mixed hardwood chips were collected from one of the unit of Ballarpur Industries Limited, situated in the northern part of India. All the experiments were carried out at Avantha Centre for Industrial Research & Development, Yamuna Nagar, India.

Mixed hardwood chips were initially treated with black liquor generated after control pulping (having sulphidity about 49 to 53 %). After pre-treatment the residual liquor was drained from the digester and chips were further processed for pulping experiments at reduced active alkali and cooking temperatures. Black liquor generated during conventional pulping process was used for black liquor pre-treatment of chips.

Pulping experiments were carried out in a lab autoclave digester consisting of six bombs each of 2.5 liters capacity rotating in an electrically heated polyethylene glycol bath. Pulping conditions including time, bath ratio, and sulphidity were maintained similar for all the experiments. At the end of the cooking, the bombs were removed and quenched in the water tank to depressurize. The digested material was dispersed with pulp disintegrator and washed with hot water to remove the black liquor and dissolved substances. After thorough washing, pulp was screened in a laboratory Somerville screen of 0.15 mm slot width. Pulps were evaluated for unscreened and screened yield, rejects content, kappa number, brightness, and viscosity as per standard test procedures.

- Moisture content was determined as per TAPPI test method T 210 cm-03
- Kappa number of unbleached pulp was determined as per TAPPI test method T 236 om-06
- Brightness of the pulp was determined as per TAPPI test method 525 om-06
- Viscosity of the pulp was determined as per TAPPI test method T 230 om-08
- PFI refining of pulps was carried out in PFI mill using TAPPI test method T 248 sp-00
- Freeness of pulp (Canadian standard method) was determined as per TAPPI test method T 227 om-04
- Handsheets of 60 gsm were made on sheet former as per TAPPI test method T 205 sp-02
- The physical strength properties of paper handsheets were determined as per TAPPI test method T 220 sp-01
- Thickness, tensile index, burst index, tear index, double fold, porosity and smoothness of paper hand sheets were tested using L&W Micrometer, L&W Tensile tester, L&W Bursting strength tester, L&W Tearing tester, MIT Folding endurance tester, L&W Air permeance tester and L&W Bendtsen roughness tester, respectively.
- Total solids of the black liquor was analyzed as per TAPPI test method T 650 om-09.
- Residual active alkali of black liquor was analyzed as per TAPPI test method T 625 cm-85.

All the experiments were performed in duplicate (triplicate in a few cases), and average values are reported herewith.

RESULTS AND DISCUSSION

Black Liquor Pre-treatment

Different conditions *viz.* bath ratio, time, and temperature were optimized for black liquor pre-treatment of chips, which was carried out using 1:2.5, 1:3.0, and 1:3.5 bath ratio and further cooked at 160 °C using 16% active alkali. Bath ratio 1:3.0 was found most advantageous as kappa number and rejects were lower and yield was higher

compared to 1:2.5 bath ratio and comparable with 1:3.5 ratio. Detailed results of the optimization of bath ratio during black liquor pre-treatment are given in Table 1.

Table 1. Optimization of Bath Ratio during Black Liquor Pre-treatment

Particular	Results			
Black liquor pre-treatment (Temperature – 110 °C, Time – 60 min)				
Bath ratio	Control	1:2.5	1:3.0	1:3.5
Initial free alkali (g/L)	--		5.6	
Initial total solids w/w (%)	--		20	
Post treatment free alkali (g/L)	--	1.5	1.6	1.8
Post treatment total solids, w/w (%)	--	22.2	21.8	21.6
Pulping (AA - 16 %, Temperature - 160 °C, Time - 90 min, Bath ratio - 1:3, Sulphidity - 23.2%)				
Unscreened pulp yield (%)	47.0	47.4	47.6	47.7
Rejects (%)	0.3	0.2	0.1	0.1
Screened pulp yield (%)	46.7	47.2	47.5	47.6
Kappa number	20.4	19.5	17.8	17.7
Brightness (% ISO)	29.7	30.9	33.1	33.3
Free alkali (g/L) as Na_2O	5.2	6.5	7.1	7.5
Total solids (%)	20.6	22.8	23.4	23.6

Similarly, pre-treatment temperature was optimized by giving treatment at 100, 110 and 120 °C, keeping other parameter constant. The pre-treatment temperature 110 °C was found optimum as kappa number and rejects are lower and yield was higher compared to 100 °C and comparable with that of 120 °C treatment temperature. Detailed results of optimization of black liquor pre-treatment temperature are given in Table 2.

Table 2. Optimization of Black Liquor Pre-treatment Temperature

Particular	Results			
Black liquor pre-treatment (Time – 60 min, Bath ratio – 1:3)				
Treatment temperature (min)	Control	100	110	120
Initial free alkali (g/L)	--		5.6	
Initial total solids w/w (%)	--		20	
Post treatment free alkali (g/L)	--	2.8	1.6	1.3
Post treatment total solids, w/w (%)	--	20.8	21.8	22.2
Pulping (AA - 16 %, Temperature - 160 °C, Time - 90 min, Bath ratio - 1:3, Sulphidity - 23.2 %)				
Unscreened pulp yield (%)	47.0	47.3	47.6	47.6
Rejects (%)	0.3	0.1	0.1	0.1
Screened pulp yield (%)	46.7	47.2	47.5	47.5
Kappa number	20.4	19.2	17.8	17.5
Brightness (% ISO)	29.7	32.6	33.1	33.4
Free alkali (g/L) as Na_2O	5.2	7.1	7.1	7.0
Total solids (%)	20.6	23.7	23.4	23.0

To optimize pre-treatment time, chips were treated for 30, 60, and 90 minutes keeping other parameter constant. Pre-treatment time of 60 minutes was found optimal as kappa number and rejects are lower and yield was higher compared to 30 min time and comparable with that of 90 min treatment time. Detailed results of optimization of black liquor pre-treatment time are given in Table 3.

Table 3. Optimization of Black Liquor Pre-treatment Time

Particular	Results			
Black liquor pre-treatment (Temperature – 110 °C, Bath ratio – 1:3)				
Treatment time (min)	Control	30	60	90
Initial free alkali (g/L)	--		5.6	
Initial total solids w/w (%)	--		20	
Post treatment free alkali (g/L)	--	3.4	1.6	1.5
Post treatment total solids, w/w (%)	--	21.1	21.8	21.9
Pulping (AA - 16 %, Temperature - 160 °C, Time - 90 min, Bath ratio - 1:3, Sulphidity - 23.2 %)				
Unscreened pulp yield (%)	47.0	47.2	47.6	47.8
Rejects (%)	0.3	0.3	0.1	0.1
Screened pulp yield (%)	46.7	46.9	47.5	47.7
Kappa number	20.4	19.3	17.8	17.6
Brightness (% ISO)	29.7	31.1	33.1	33.7
Free alkali (g/L) as Na_2O	5.2	6.9	7.1	7.3
Total solids (%)	20.6	23.1	23.4	23.7

Pulping at Reduced Temperature

To get maximum benefit of black liquor pre-treatment, pulping temperature was reduced to 158, 156, and 154 °C for the black liquor pre-treated chips. With the reduction in cooking temperature the unbleached pulp kappa numbers were reduced and residual active alkali in black liquor gets increased compared to control (Table 4).

Table 4. Black Liquor Pre-treatment Followed by Pulping at Reduced Temperature

Particular	Results				
	Control	Black liquor pre-treated			
Black liquor pre-treatment (Temperature – 110 °C, Time – 60 min, Bath ratio – 1:3)					
Initial free alkali (g/L)	--	5.6			
Initial total solids w/w (%)	--	20			
Post treatment free alkali (g/L)	--	1.6			
Post treatment total solids, w/w (%)	--	21.8			
Pulping (AA – 16 %, Cooking time – 90 min, Bath ratio – 1:3, Sulphidity – 23.2 %)					
Cooking temperature (°C)	160	160	158	156	154
H factor	760	760	640	540	460
Unscreened pulp yield (%)	47.0	47.6	48.2	48.8	49.4
Rejects (%)	0.3	0.1	0.2	0.5	1.5
Screened pulp yield (%)	46.7	47.5	48.0	48.3	47.9
Kappa number	20.4	17.8	18.7	20.1	23.7
Brightness (% ISO)	29.7	33.1	32.2	31.0	29.8
Viscosity (cP)	14.6	14.8	15.3	16.0	17.0
Free alkali (g/L) as Na_2O	5.2	7.1	7.3	7.6	8.3
Total solids (%)	20.6	23.4	23.2	22.9	22.2

Screened pulp yield and pulp viscosity were improved by 1.3 to 1.6% and 0.7 to 2.4 units, respectively with the pulping of black liquor pre-treated chips at lower temperatures compared to the control. Detailed results of black liquor pre-treatment followed by pulping at reduced temperature using similar active alkali (AA) are given in Table 4.

Effects of black liquor pre-treatment followed by pulping at reduced temperature using similar AA on unscreened and screened pulp yield and effect on unbleached pulp kappa number and viscosity are shown in graphical form in Figs. 1 and 2, respectively.

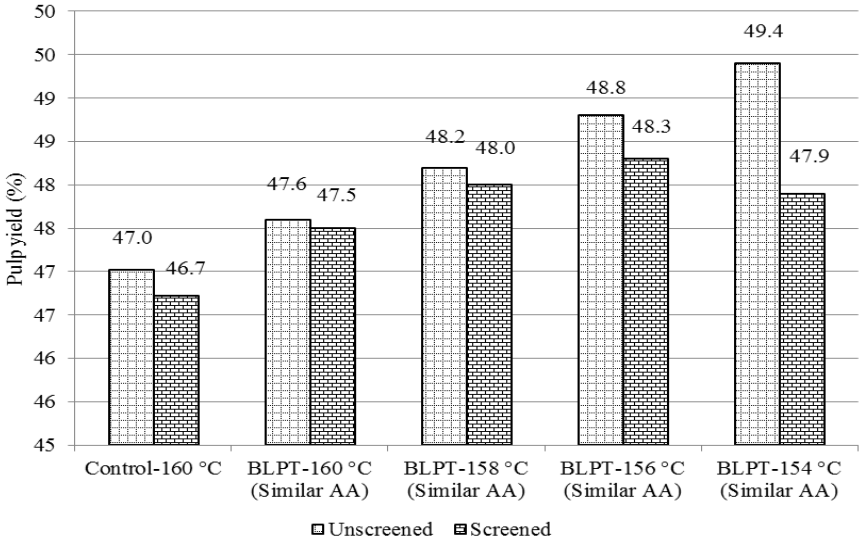

Fig. 1. Effect of black liquor pre-treatment (BLPT) followed by pulping at reduced temperature on unscreened and screened pulp yield

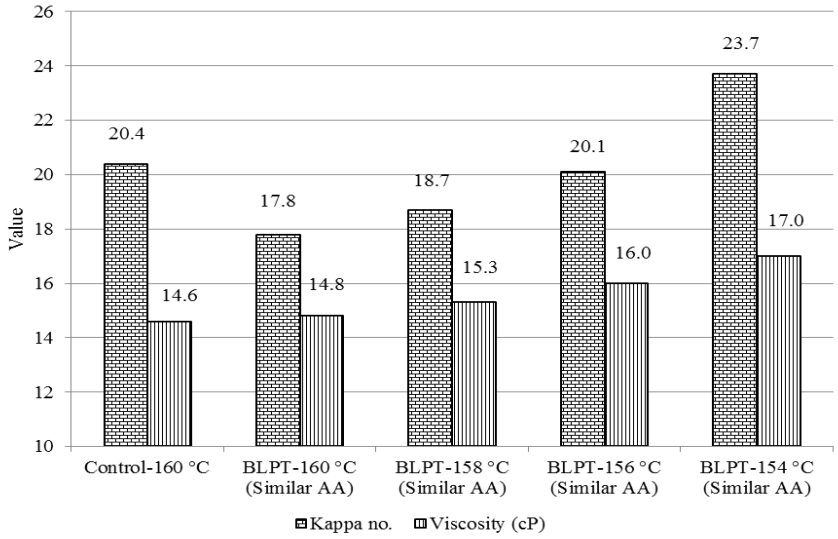

Fig. 2. Effect of black liquor pre-treatment (BLPT) followed by pulping at reduced temperature on unbleached pulp kappa number and viscosity

Pulping at Reduced Temperature and AA

To further maximize the benefit of black liquor pre-treatment, pulping was carried out at reduced temperature and AA, targeting to produce pulp of similar kappa number compared to control. With the reduction in cooking temperature and AA, screened pulp yield and pulp viscosity were significantly improved by 1.7 to 2.1% and 0.9 to 2.7 units, respectively with the pulping of black liquor pre-treated chips at lower temperatures and

AA compared to the control. Detailed results of black liquor pre-treatment followed by pulping at reduced temperature and AA are given in Table 5.

Table 5. Black Liquor Pre-treatment Followed by Pulping at Reduced Temperature and AA

Particular	Results				
	Control	Black liquor pre-treated			
Black liquor pre-treatment (Temperature – 110 °C, Time – 60 min, Bath ratio - 1:3)					
Initial free alkali (g/L)	--	5.6			
Initial total solids w/w (%)	--	20			
Post treatment free alkali (g/L)	--	1.6			
Post treatment total solids, w/w (%)	--	21.8			
Pulping (Cooking time – 90 min, Bath ratio – 1:3, Sulphidity – 23.2 %)					
Cooking temperature (°C)	160	160	158	156	154
H factor	760	760	640	540	460
Active alkali (%)	16.0	15.0	15.0	14.5	14.5
Unscreened pulp yield (%)	47.0	48.2	48.8	49.5	49.8
Rejects (%)	0.3	0.2	0.4	0.7	2.4
Screened pulp yield (%)	46.7	48.0	48.4	48.8	47.4
Kappa number	20.4	19.1	19.6	20.5	24.6
Brightness (% ISO)	29.7	31.3	32.8	30.3	29.2
Viscosity (cP)	14.6	15.0	15.5	16.4	17.3
Free alkali (g/L) as Na_2O	5.2	5.8	6.0	6.0	6.5
Total solids (%)	20.6	22.9	22.7	22.3	21.8

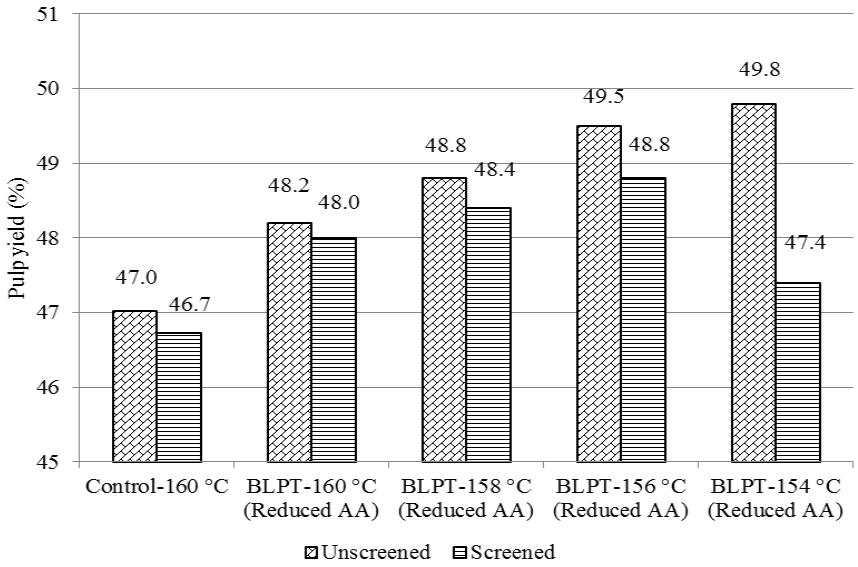

Fig. 3. Effect of black liquor pre-treatment (BLPT) followed by pulping at reduced temperature and AA on unscreened and screened pulp yield

The effects of black liquor pre-treatment followed by pulping at reduced temperature using similar AA on unscreened and screened pulp yield and effect on unbleached pulp kappa number and viscosity are shown in graphical form in Figs. 3 and 4, respectively.

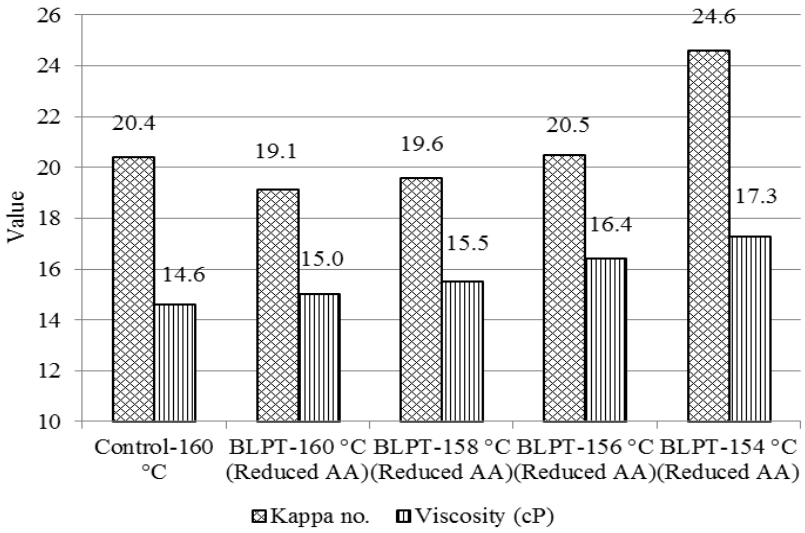

Fig. 4. Effect of black liquor pre-treatment (BLPT) followed by pulping at reduced temperature and AA on unbleached pulp kappa number and viscosity

Bleaching of Pulp

Pulps produced with and without black liquor pre-treatment of chips followed by pulping at reduced temperature and AA were bleached with $D_0E_{OP}D_1D_2$ sequence to brightness level of 88 to 89% ISO. Bleachability of the pulps obtained with black liquor pre-treatment of chips was marginally better with the control. Bleached pulp viscosity of pulp produced with black liquor pre-treatment of chips followed by pulping at reduced temperature and AA was improved by 1.3 units. In a plant trial study Höglund *et al.* (1994) also reported improvement in the bleachability of pulp with black liquor pre-treatment of chips. Detailed results of bleaching of similar kappa number pulps produced with and without black liquor pre-treatment are given in Table 6.

Physical Strength Properties

Physical strength properties of bleached pulps produced with and without black liquor pre-treatment of chips and cooked at 160 °C with 15 % AA were evaluated. There was improvement in the physical strength properties with the black liquor pre-treatment followed by pulping at reduced temperature and AA. Tensile, tear, and burst indices of BL pre-treated pulps were improved by 8.5, 30.8, and 35.7%, respectively, compared to the control. The improvement in physical strength properties specifically for tear and burst index was also reported by Höglund *et al.* (1994), though the pre-treatment conditions, pulping conditions, and nature of chips used in the plant scale study was different. Detailed results of physical strength properties of bleached pulps are given in Table 7. Effect of black liquor pre-treatment followed by pulping and bleaching on tear index, burst factor, and index and double fold of paper is shown in Figs. 6 and 7, respectively.

Table 6. Bleaching of Pulps Produced with and without Black Liquor Pre-treatment

Particular	Results			
	Control	Black liquor pre-treated		
Cooking temperature (°C)	160	160	158	156
Kappa number	20.4	19.1	19.6	20.5
D_O stage (K. factor- 0.24, Temperature – 60 °C, Retention time - 30 min)				
ClO_2 added (%)	1.86	1.74	1.79	1.87
End pH	2.8	2.7	2.6	2.7
Consumption (%)	98.3	98.0	97.8	98.3
E_{OP} stage (NaOH - 2.5 %, H_2O_2 - 0.5 %, Temp. – 80 °C, Time - 120 min)				
Final pH	10.8	10.9	10.7	10.8
Brightness (% ISO)	74.6	75.3	75.4	74.9
E_{OP} Kappa number	2.1	1.9	2.0	2.1
D_1 stage (ClO_2 added 0.9 %, Temperature – 75 °C, Retention time - 180 min)				
Final pH	3.7	3.8	3.6	3.8
Brightness (% ISO)	83.9	83.9	84.2	84.2
D_2stage (ClO_2 added 0.9 %, Temperature – 75 °C, Retention time - 180 min)				
Final pH	3.6	3.5	3.6	3.8
Brightness (% ISO)	88.5	89.0	89.0	88.9
CIE whiteness	76.2	77.9	77.1	76.7
Viscosity (cP)	10.8	11.2	11.5	12.1

The effects of black liquor pre-treatment followed by pulping and bleaching on pulp brightness, whiteness, and viscosity are shown in Fig. 5.

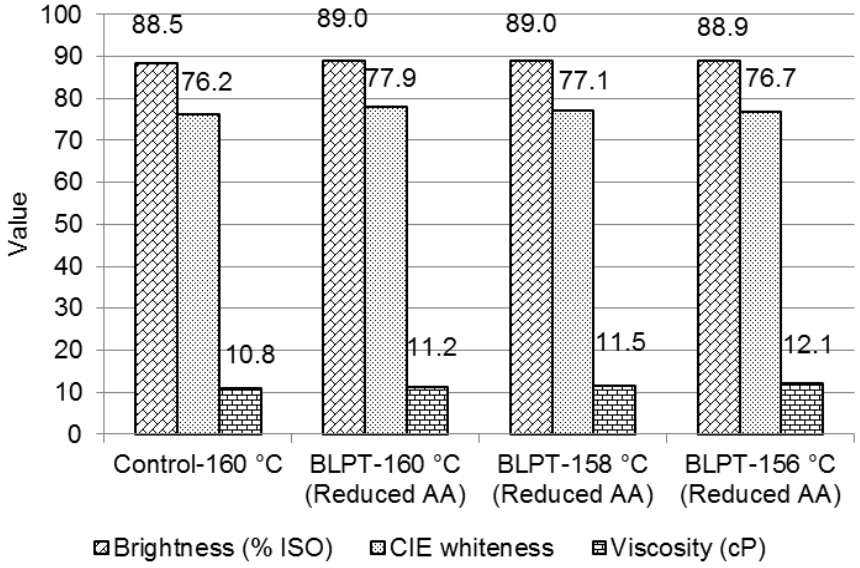

Fig. 5. Effect of black liquor pre-treatment (BLPT) followed by pulping and bleaching on pulp brightness, whiteness and viscosity

Table 7. Physical Strength Properties of Bleached Pulps

Particular	Results			
	Control	BL pre-treated		
Cooking temperature (°C)	160	160	158	156
ºSR	27.5	27.5	27.0	27.0
Grammage (g/m^2)	60.5	61.1	60.8	60.7
Bulk (cc/g)	1.29	1.32	1.31	1.29
Tensile index (N.m/g)	60.2	60.8	62.4	65.3
Burst index (kPa.m^2/g)	4.2	4.6	5.1	5.7
Tear index (mN.m^2/g)	6.5	7.2	8.1	8.5
Porosity (sec/100 ml)	6.2	8.4	8.4	7.1
Double fold (no.)	50	54	58	62
Smoothness (ml/min)	90	88	90	87

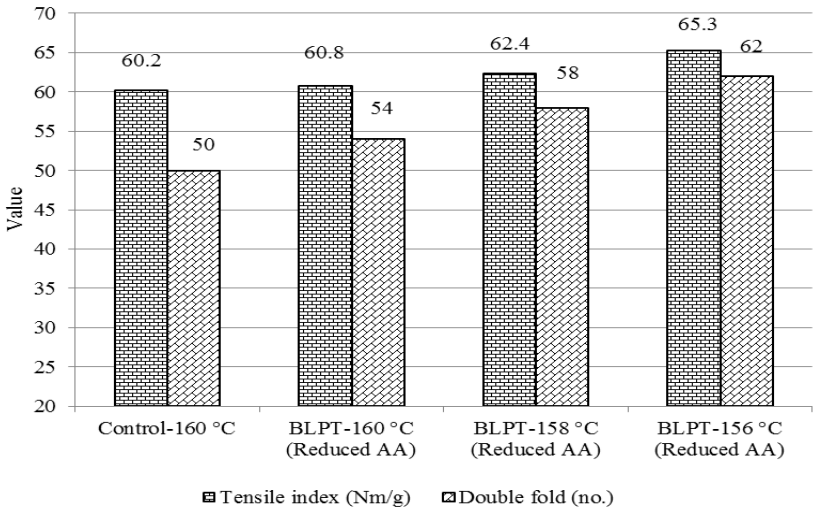

Fig. 6. Effect of black liquor pre-treatment (BLPT) followed by pulping and bleaching on tensile index and double fold of paper

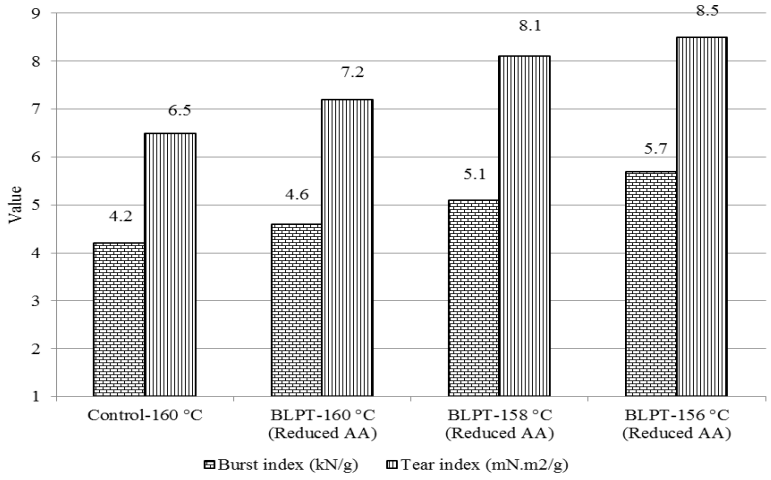

Fig. 7. Effect of black liquor pre-treatment (BLPT) followed by pulping and bleaching on tear index and burst factor of paper

CONCLUSIONS

With black liquor pre-treatment of chips followed by pulping at reduced temperature and active alkali, the following improvements were obtained at similar kappa number of pulp:

- Cooking temperature reduced by 4 °C
- Active alkali reduced by 1.5 %
- Viscosity improved by 1.8 cP
- Screened pulp yield improved by 2.1 %
- Tensile index improved by 8.5 %
- Tear index improved by 30.8 %
- Burst index improved by 35.7 %

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