

Efficacy of Some Carbohydrate Protectors During Pulping on Pulp Yield

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ABSTRACT

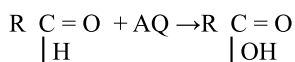
Efficacy of several chemicals viz. sodium borohydride, sodium hydrosulfite, HEDP (1-hydroxy ethylidene 1, 1-diphosphonic acid), ethylene di amine (EDA), hypophosphorus acid (HPA), sulphamic acid (SA) and urea as protector of carbohydrates during pulping of eucalyptus is presented in this paper.

By using sodium borohydride in pulping an increase of 1-2% in pulp yield and 1.7-4.4 unit reduction in pulp kappa was obtained; at same kappa number the pulp yield was improved by 2.3% with significant improvement in pulp viscosity. Use of sodium hydrosulfite during pulping also improves pulp yield by 0.6-1.0% with no significant difference in the pulp viscosity. Use of HEDP improves pulp yield by 0.4% with improved brightness of pulp. Use of Urea during pulping improves screened pulp yield by 0.6-1.0% and viscosity of pulp by 1.8-2.1 cp compared to control one. Black liquor properties like swelling volume ratio and viscosity also get improved with the use of urea.

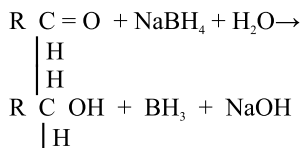
Introduction

Due to the increasing cost of raw materials and competitiveness in the paper market, it is desirable to increase the yield as well as quality of the product. The origin of yield loss is due to carbohydrate (hemicelluloses and cellulose) degradation during kraft cooking. Two mechanisms are known to degrade carbohydrates during pulping, peeling (which starts at low temperature and goes very fast upto 100°C) and alkaline hydrolysis (which starts around 140°C). Alkaline peeling of carbohydrates can be stopped either by oxidation or by reduction of end groups.

Several studies have been carried out worldwide in recent years on different types of chemicals/additives which show improvement in pulp yield and pulp quality. Polysulphide and anthraquinone stops the alkaline peeling reaction by oxidation of reactive aldehyde group end to less-reactive carboxylic group end (1, 2).



Sodium borohydride stops the alkaline peeling reaction by reducing the reactive aldehyde group end to less-reactive alcohol group end (3, 4).



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Surfactants are also used as an additive in kraft cooking to increase the liquor penetration into chips which improves uniformity of pulping. With the use of surfactants, increase in yield is obtained as a result of a decrease in screen rejects (5). Phosphonates (HEDP) are also used in kraft pulping as chelating agent; they improve pulp properties specifically initial brightness of pulp. Presence of amines in alkaline cooking liquors tends to protect polysaccharides against degradation and subsequent dissolution. In particular, it was shown that the cellulose is preferentially protected (6). In the present study efficacy of a few chemicals viz. sodium borohydride, sodium hydrosulfite, HEDP (1-hydroxy ethylidene 1, 1-diphosphonic acid), ethylene di amine (EDA), hypophosphorus acid (HPA), sulphamic acid (SA) and urea as protector of alkaline peeling reactions during pulping of eucalyptus is investigated.

Experimental

Studies were conducted on eucalyptus chips collected from a large integrated pulp and paper mill situated in northern India. Chips collected from the mill were air dried and kept in polythene bags to attain uniform moisture content. Moisture content of the chips was determined as per standard procedure prior to perform pulping experiments. Pulping experiments were carried out in lab autoclave digester consisting of six bombs each of 2.5 liters capacity rotating in an electrically heated polyethylene glycol bath. Pulping conditions like time, temperature, bath ratio and sulphidity were maintained similar for all the experiments. Chemical doses were selected so as to

get kappa number in the range of 18-22, which represents the current practice of Indian paper mills. At the end of the cooking, the bombs were removed and quenched in the water tank to depressurize. The digested wood chips were dispersed with pulp disintegrator and washed with hot water to remove the black liquor and dissolved substances. After thorough washing, pulp was screened in laboratory Somerville screen of 0.15 mm slot width. Pulps were evaluated for unscreened and screened yield, rejects content, kappa number, brightness and viscosity. Black liquor generated was tested for swelling volume ratio (7), viscosity (8) and total solids as per Tappi test methods.

The dosage of different carbohydrate protectors used during pulping was in the range of 1.0 - 10.0 kg per ton of OD raw material. The chemicals were dissolved first in water, added in the kraft cooking liquor and mixed thoroughly before adding it to the chips.

Analytical Procedures

- *Moisture content*: was determined as per Tappi Test Method T 210 cm-03.
- *Kappa no. of unbleached pulp*: was determined as per Tappi Test Method T 236 om-99.
- *Brightness of the pulp*: was determined as per ISO 2470.
- *Viscosity of the pulp*: was determined as per Tappi Test Method T 230 om-04.

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

Results and Discussion

Efficacy of NaBH₄ in pulping

Different dosages of sodium

Table 1: Impact of sodium borohydride on pulping

Parameter	1	2	3	4	5	6
Sodium borohydride (%)	0.00	0.10	0.20	0.50	0.75	1.00
Kappa no.	20.8	19.1	17.2	17.0	16.7	16.4
Unscreened pulp yield (%)	47.5	48.1	48.7	48.7	49.0	49.0
Reject (%)	0.63	0.30	0.1	0.05	traces	traces
Screened pulp yield (%)	46.9	47.8 (+0.9)	48.6 (+1.7)	48.7 (+1.8)	49.0 (+2.1)	49.0 (+2.1)
Viscosity (cp)	13.4	12.5	12.0	11.9	11.8	11.6
Brightness (%ISO)	29	29.0	30.7	30.5	31	31.3
Free alkali (g/l) as Na ₂ O at 20% solids	6.0	6.3	6.9	7.6	7.6	7.9
Black liquor solids (%)	21.2	21.1	20.8	19.6	20.0	20.1

AA dose: 17.5%, sulphidity: 23.5%, cooking temp. : 162°C, cooking time: 120 min.

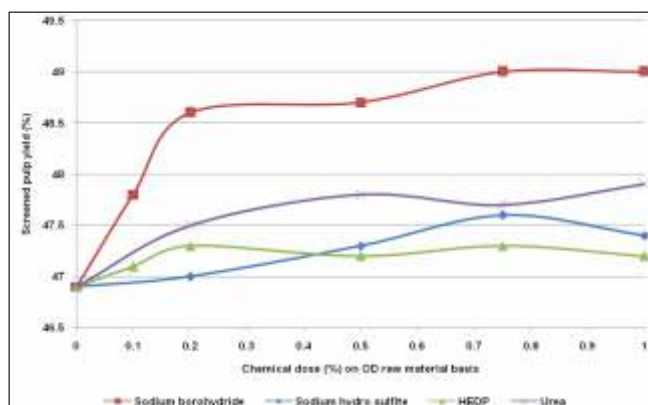
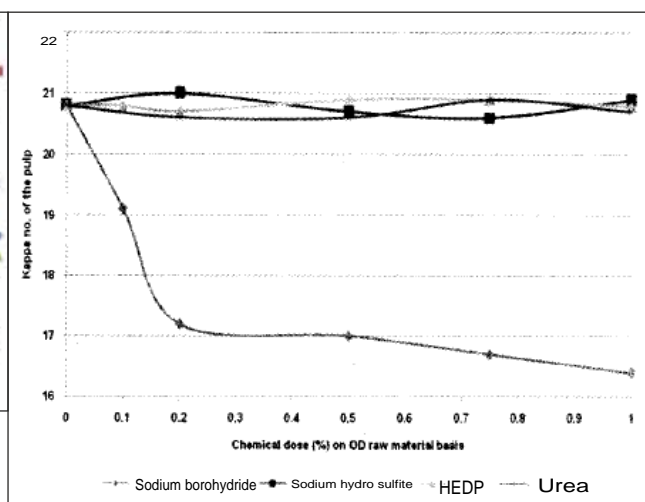
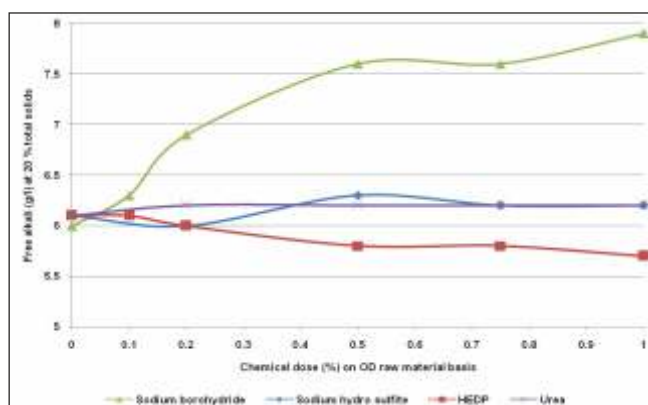
Table 2: Impact of sodium borohydride on pulping at reduced AA dosages

Parameter	1	2	3	4
Active alkali as Na ₂ O (%)	17.5	17.5	16.5	16.0
NaBH ₄ added (%)	0.0	0.2	0.2	0.2
Kappa no.	20.8	17.9	20.3	21.1
Unscreened pulp Yield (%)	47.5	48.6	49.2	49.7
Reject (%)	0.63	0.24	0.53	0.50
Screened pulp yield (%)	46.9	48.4 (+1.5)	48.9 (+2.0)	49.2 (+2.3)
Viscosity (cp)	13.4	14.9	15.7	16.4
Brightness (%ISO)	29.0	29.3	28.7	29.4
Free alkali (g/l) as Na ₂ O	6.4	7.1	6.1	5.9
Free alkali (g/l) as Na ₂ O (at 20% solids)	6.1	6.8	6.2	6.1
Black liquor solids (%)	21.1	20.8	19.5	19.4

Sulphidity: 23.5%, cooking temp. : 162°C, cooking time: 120 min.

borohydride were used viz. 0.1, 0.2, 0.5, 0.75 and 1.0% with cooking liquor during pulping. Result shows that with the increase of NaBH₄ dosage kappa number of pulp gets reduced from 20.8 to 16.4 whereas, screened pulp yield increased from 46.9 to 49.0%. Screen rejects also reduced from 0.63% to traces; free alkali in black liquor and unbleached pulp brightness increased to 7.9 from 6.0 g/l and 31.3 from 29.0% respectively. Detailed pulping results are given in Table 1.

As the pulp kappa number reduced substantially and free alkali increased with the use of NaBH₄, pulping experiments were conducted at reduced AA dosage of 16.5 and 16.0%. Results show that with the use of 0.2% sodium borohydride at reduced AA dose, pulp yield improved by 2.3% with significant improvement in pulp viscosity. Detailed pulping results are given in Table 2. Sodium borohydride shows the best results compared to other chemicals in terms of improvement in pulp yield, reduction in kappa number of pulp and reduction in AA demand as shown in the Figure 1, 2 and 3.

Figure 1: Effect of additives on pulp yield**Figure 2: Effect of additives on kappa number of pulp****Figure 3: Effect of additives on residual active alkali**

Efficacy of Sodium hydrosulphite in pulping

Efficacy of sodium hydrosulphite was assessed as carbohydrate protector during pulping which is less expensive reducing agent compared to NaBH₄. With the use of sodium hydrosulphite unbleached pulp yield increased from 46.9 to 47.4% with improvement in unbleached pulp brightness by 1.6%. Reduction potential (rp) of sodium hydrosulphite is less (-0.66 v)

Table 3: Impact of sodium hydrosulfite on pulping

Parameter	1	2	3	4	5
Sodium hydro sulfite added (%)	0.0	0.2	0.5	0.75	1.0
Kappa no.	20.8	21.0	20.7	20.6	20.9
Unscreened pulp Yield (%)	47.5	47.6	47.6	47.8	47.7
Reject (%)	0.63	0.56	0.30	0.24	0.33
Screened pulp Yield (%)	46.9	47.0 (+0.1)	47.3 (+0.4)	47.6 (+0.7)	47.4 (+0.5)
Unbleached pulp viscosity (cp)	13.4	--	13.6	--	13.3
Brightness (%ISO)	29.0	29.5	29.2	29.7	30.6
Free alkali (g/l) as Na ₂ O (at 20% solids)	6.1	6.0	6.3	6.2	6.2
Black liquor solids (%)	21.1	21.0	21.1	21.3	21.6

AA dose: 17.5%, sulphidity: 23.5%, cooking temp. : 162°C, cooking time: 120 min.

Table 4: Impact of HEDP on pulping

Parameter	1	2	3	4	5	6
HEDP added (%)	0.0	0.1	0.20	0.5	0.75	1.00
Kappa no.	20.8	20.8	20.7	20.9	20.9	20.8
Unscreened pulp Yield (%)	47.5	47.2	47.3	47.2	47.3	47.2
Reject (%)	0.63	0.10	0.04	0.05	0.02	0.05
Screened pulp Yield (%)	46.9	47.1 (+0.2)	47.3 (+0.4)	47.2 (+0.3)	47.3 (+0.4)	47.2 (+0.3)
Viscosity (cp)	13.4	--	--	11.8	--	--
Brightness (%ISO)	29.0	29.0	30.9	31.0	31.6	30.9
Free alkali (g/l) as Na ₂ O	6.4	6.4	6.3	6.1	6.1	6.1
Free alkali (g/l) as Na ₂ O at 20% solids	6.1	6.1	6.0	5.8	5.8	5.7
Black liquor solids (%)	21.1	21.2	21.4	21.5	21.4	21.9

AA dose: 17.5%, sulphidity: 23.5%, cooking temp. : 162°C, cooking time: 120 min.

Table 5: Impact of urea on pulping

Parameter	1	2	3	5	6
Urea added (%)	0.0	0.2	0.5	0.75	1.0
Kappa number	20.8	20.6	20.6	20.9	20.7
Yield (%)	47.5	47.6	47.9	47.9	48.2
Reject (%)	0.60	0.10	0.10	0.20	0.30
Screened pulp Yield (%)	46.9	47.5 (+0.6)	47.8 (+0.9)	47.7 (+0.9)	47.9 (+1.0)
Viscosity (cp)	13.4	--	15.4	15.5	15.4
Brightness (%ISO)	29.0	30.2	29.9	29.8	28.9
Free alkali (g/l) as Na ₂ O	6.4	6.6	6.7	6.7	6.8
Free alkali (g/l) as Na ₂ O (at 20% solids)	6.1	6.2	6.2	6.2	6.2
Black liquor solids (%)	21.1	21.4	21.7	21.8	22.1
Swelling Volume Ratio (ml/g)	86.7	--	92.1	93.2	--
Viscosity at 52% solids (cp)	105.2	--	72.4	--	--

AA dose: 17.5%, sulphidity: 23.5%, cooking temp. : 162°C, cooking time: 120 min.

Table 6: Impact of ethylene diamine, hypo phosphorus acid and sulphamic acid on pulping

Parameter	Control	EDA	HPA	SA
Chemical dose (%)	0.0	0.5	0.5	0.5
Kappa no.	20.8	21.0	20.0	20.2
Yield (%)	47.5	47.4	47.3	47.2
Reject (%)	0.63	0.33	0.25	0.08
Screened pulp Yield (%)	46.9	47.1 (+0.2)	47.1 (+0.2)	47.1 (+0.3)
Viscosity (cp)	13.4	13.3	13.5	12.8
Brightness (%ISO)	29.0	28.8	29.7	28.7
Free alkali (g/l) as Na ₂ O	6.4	6.4	6.0	5.8
Free alkali (g/l) as Na ₂ O at 20% solids	6.1	6.0	5.9	5.4

AA dose: 17.5%, sulphidity: 23.5%, cooking temp. : 162°C, cooking time: 120 min.

compared to reduction potential of sodium borohydride (-1.24 v) this may be the reason behind the less efficacy of sodium hydrosulphite to protect carbohydrate degradation compared to sodium borohydride. Detailed pulping results are given in Table 3.

Efficacy of HEDP in pulping

Phosphonates are generally used to prevent scale build-up in water treatment. They are also used in peroxide bleaching stage as chelating agent. Results show that use of HEDP in pulping improves pulp yield from 46.9 to 47.3%, reduces screen rejects from 0.63 to 0.02% with significant improvement in pulp brightness. The reason behind improved initial pulp brightness may due to reduction in chromophore structure formation in lignin and reduction in metal content in the fiber as HEDP acts as chelating agent (9). Detailed pulping results are given in Table 4. To improve unbleached pulp brightness HEDP is the best compared to other chemicals as shown in Figure 4.

Efficacy of Urea in pulping

Urea in kraft pulping did not have any effect on the kappa number but increased the unbleached pulp yield, viscosity of the pulp and free alkali in the black liquor. Unbleached pulp yield increased to 47.9% from 46.9%, unbleached pulp viscosity increased to 15.5 from 13.4 cp with the use of urea. It appears that urea addition leads to some polysaccharide preservation by aldol condensation involving the aldehyde moieties in reducing end groups. Black liquor properties like viscosity and swelling volume ratio improve by using urea in pulping. Black liquor viscosity at 52% solids reduced to 72.4 cp with 0.5% urea compared to 105.2 cp (control). Detailed pulping results are given in Table 5.

Efficacy of EDA, HPA and SA in pulping

Efficacy of few other chelating agents and reducing agents viz. ethylene diamine (EDA), hypo phosphorus acid (HPA) and sulphamic acid (SA) were also assessed by using it in kraft pulping along with cooking chemicals in small quantity. Result indicates that use of EDA, HPA and SA during pulping does not gives significant changes in pulp yield and quality. Detailed pulping results are given in Table 6.

Figure 4: Effect of additives on unbleached pulp brightness

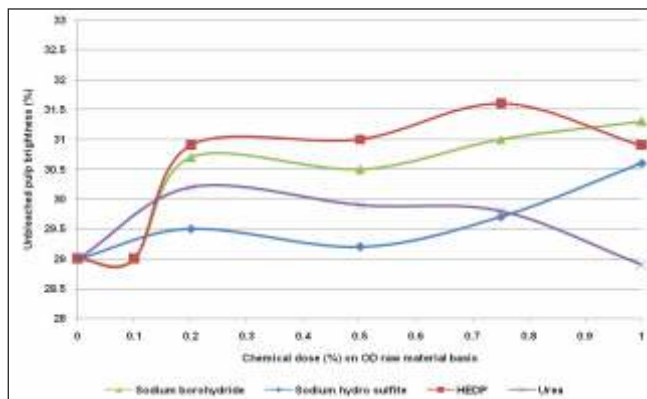


Figure 5: Comparison of pulp yield with different additives

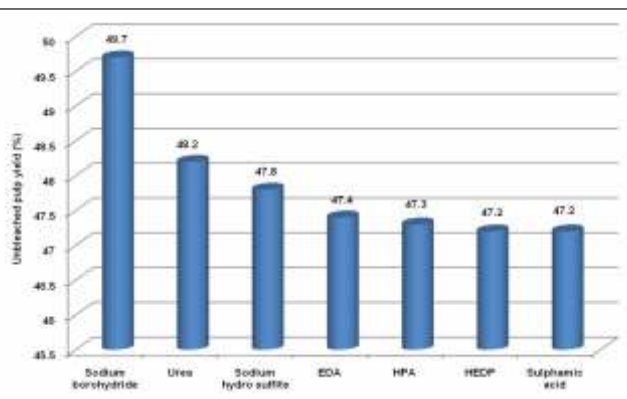
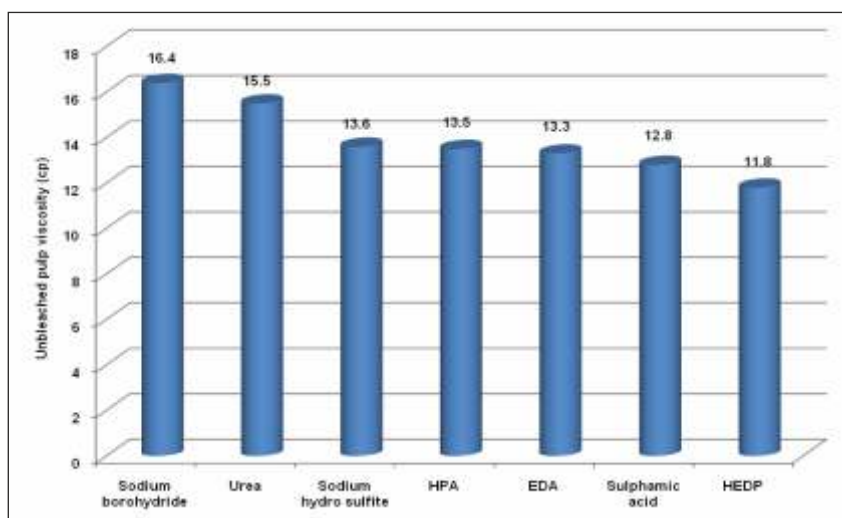


Figure 6: Comparison of viscosity of pulp with different additives



Conclusion

Efficacy of reducing agents in pulping as carbohydrate protector depends on the reduction potential. Sodium borohydride which has highest reduction potential (rp of -1.24 v) provides maximum efficiency as pulping additive followed by sodium hydrosulphite (rp of -0.66 v) and hypo phosphorus acid (rp of -0.50 v).

Amongst the chelating agents ethylene diamine and HEDP both are more effective in improvement of initial pulp brightness rather than carbohydrate protector.

Urea is an effective pulping additive which improves pulp yield and pulp

quality.

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