Oxygen Delignification: An Effective Back-end Modification To Reduce Pollution Load And Improve Mechanical Strength Properties Prior To Bleaching

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ABSTRACT

Most of the Indian pulp and paper industry bleaches the pulp by conventional bleaching sequence (CEHH). The final discharge of the mill contributes to high COD load and AOX which is highly toxic in nature. The introduction of molecular O_2 before bleaching and reinforcement of alkali extraction stage with O_2 and H_2O_2 (E_{OP}) in OC(Eop)HH bleaching sequence reduces the COD load by 40.58%, suspended solids by 24.74%, dissolved solids by 36.53%, total solids by 35.94%, AOX by 42.86% and chlorides by 34.69% than that of C(Ep)HH bleaching sequence with improvement in mechanical strength properties. The operating cost of OC(Eop)HH bleaching sequence is only Rs. 1275.00 per tonne of pulp more including the cost of bleaching chemicals compared to CEpHH bleaching sequence.

Key words: O_2 delignification, Bleaching, Effluent characteristics, Kraft pulping, Paper

Introduction

In India 181 mills are agro-based and 28 mills are wood based. The kappa number of wood based mills vary from 14-25 and kappa number of agro-based mills vary from 18-30. The chlorine consumption of agro-based and wood based mills is 130-200 and 60-100 kg/T of pulp. The AOX range in final discharge of agro based mills with and without chemical recovery process is 7-11 and 14.2-21.5 mg/L. Where, AOX in final discharge of wood based mills is 0.60-9 mg/L. It was found out that the C-stage was generally the first point in which 2,3,7,8-TCDD, 2,3,7,8-TCDF and 1,2,7,8-TCDF congeners were always present[1-3]. The E-stage filtrate was found to have the highest concentrations of dioxins[4] known as changing the blood chemistry and causing liver damage, skin disorders, lung lesions and tumor types at numerous sites within the body, liver and thyroid included[5-7].

The stringent discharge standards of pollution control board compel the pulp and paper industry to improve their discharge limit within the range. Since last two decades, bleaching of pulp has become an issue of great concern primarily because of the environmental hazards caused by release of adsorable organic halides and due to increasing public awareness. This shifted spotlight on bio-bleach agents that can work in combination with chemical bleaching.

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Most of the mills in India are using CEH, CEHH and CHH bleaching sequences. The present study aims at controlling effluent discharge standards like, COD, suspended solids, dissolved solids, total solids, AOX, colour and chloride and effect on paper properties by putting extended delignification stage before conventional bleaching sequence. In oxygen delignification stage, approximately 50 % lignin left after cooking stage can be removed[8]. Since the lignin remaining in the pulp after oxygen delignification is low and chlorination becomes less intensive. The level of AOX, TOCl, chlorinated dioxins, chlorophenols, chlorinated organo compounds and chloroform in pulp bleaching effluents can considerably be decreased by oxygen delignification stage than that of conventional bleaching sequence[9,10].

Materials and methods

Kraft pulping and extended delignification

Wood chips of *P. deltoids* and *E. tereticornis* mixed in the ratio of 90:10 were collected from Star Paper Mills Ltd., located in the foothills of Shavalik hills of district Saharanpur of northern India. The accepted chips of size having dimensions length 25cm, width10cm and thickness 6cm were digested in WEVERK electrically heated rotary digester of 0.02 m^3 capacity having four bombs of one liter capacity each. The chips of *P. deltoids* and *E. tereticornis* were cooked at 16 % active alkali (as Na_2O), sulphidity 20%, liquor to wood ratio 2.8:1, digester pressure 6.5 kg/cm^2 and maximum cooking time at 162 ^{0}C 75 min. After completion of cooking, the pulps were washed on a laboratory flat stationary screen having 300 mesh wire bottom for the removal of residual cooking chemicals. The pulp was disintegrated and screened through WEVERK vibratory flat screen with 0.15 mm slits and the screened pulp was washed, pressed and crumbled. The pulp was further delignified with molecular O_2 dose of 1.8% (O_2 pressure 7.5 kg/cm^2), consistency 11 %, initial pH 11.8, maximum reaction temperature 100 ^{0}C for 30 min in presence of carbohydrate stabilizer Epsom salt (0.1% $MgSO_4$). Both the pulps were analyzed for kappa number (T 236 cm-85), brightness (T 452 om-02) and viscosity (T 230 om-04) as per Tappi Standard Test Methods: 2007. The results are reported in Tables 1 and 2 and compared in Table 3.

Pulp bleaching

The O_2 delignified and kraft pulps were bleached by C(Ep)HH and C(Eop)HH bleaching sequences and beaten at 40 ^{0}SR. Laboratory hand sheets of 60 g/m^2 were prepared according to Tappi T 221 cm-99 and tested for various physical strength properties, like tear index (T 414 om-98), tensile index (T 494 om-01), burst index (T 403 om-97), double fold (T 423 cm-98) and bulk density (grammage (T 410 om-02) divided by thickness (T 411 om-05). The combined effluent generated at each stage of C(Eop)HH and C(Ep)HH bleaching sequences were analyzed for AOX[11], COD (IS 3025 : Part 58 : 2006), suspended solids (IS 3025 : Part 17 : 1984), dissolved solids (IS 3025 : Part 16 : 1984), total solids (IS 3025 : Part 15 : 1984) and chlorides (IS 3025 : Part

32 : 1988) as per BIS specifications. The results of bleaching sequences are reported in Tables 4 and compared in Table 5. The results of C(Ep)HH and OC(Eop)HH bleaching sequences were validated by taking a plant trial at Star Paper Mills Ltd., Saharanpur and comparison of both the bleaching sequences in terms of cost is summarized as in Table 6.

Statistical analysis

Data collected were subjected to analysis of variance (ANOVA, $P < 0.05$) for each cooking and bleaching experiments separately using appropriate statistical software. Sources of variation were screened pulp yield, kappa number, pulp viscosity and mechanical strength properties like tear, tensile and burst indices and double folds. This approach provides a more accurate picture of standard error.

Results and discussion

Table 1 shows the results of kraft pulping of mixed chips of *P. deltoides* and *E. tereticornis* blended in the ratio of 90:10. An optimum screened pulp yield of 47.90 % of kappa number 19.6 and brightness 30.1 % (^{0}PV) is obtained at active alkali 16%, sulphidity 20%,

Table 1- Cooking conditions and results of mixed pulping of *P. deltoids* and *E. tereticornis* blended in the ratio of 90:10

Sl no	Parameters	Results
1	Unbleached pulp yield, %	49.75
2	Screened pulp yield, %	47.90
3	Screen Rejects, %	1.85
4	Residual alkali, g/L	0.23
5	Kappa Number	19.6
6	Unbleached pulp brightness. ^{0}PV	30.1
7	Viscosity, cps	28.0

Cooking conditions: Active alkali = 16 % (as Na_2O), sulphidity = 20 %, liquor to wood ratio = 2.8:1, digester pressure = 6.5 kg/cm^2, time taken to raise temp from ambient to 162 ^{0}C = 120 min and time at temp at 162 ^{0}C = 75 min.

time at temperature 162 ^{0}C, maximum pulping time 75 min, digester pressure 6.75 kg/cm^2 and liquor to wood ratio 3:1. The differences in screened pulp yield and kappa number for different cooking experiments were not statistically significant (ANOVA, $P < 0.05$).

Table 2 reveals the conditions and results of O_2 delignification of mixed chips of *P. deltoides* and *E. tereticornis*. Extended delignification of unbleached kraft pulp of kappa number 19.6 is carried out with 18 kg/T of oxygen. The extended delignification with molecular O_2 is carried out at 100 ^{0}C, consistency 11%, NaOH 2% reaction time 30 min and O_2 pressure 7.5 kg/cm^2. 0.1% $MgSO_4$(Epsom salt) is also added during O_2 delignification to protect carbohydrates and to mask the

Table 2- Conditions and results of O_2 delignification

Sl. No.	Particulars	Results
1	Unbleached pulp kappa number	19.6
2	Pulp brightness, %(ISO)	30.1
3	Pulp viscosity, cps	28
4	Pulp consistency, %	11
5	O_2 applied, kg/T	18
6	NaOH applied, kg/T	20
7	Temperature, ^{0}C	100
8	Reaction time, min	30
9	O_2 pressure, kg/cm^2	7.5
10	End pH	10.8
11	Kappa number	8.8
12	Pulp brightness, %(ISO)	45.2
13	Pulp viscosity, cps	22
14	Kappa number reduction,%	55.10
15	Brightness gain,%	33.4
16	Viscosity loss, %	23.57
17	Pulp shrinkage	2.4

activities of transition metals which causes the hemolytic cleavage of O_2[12]. Oxygen delignification causes reduction in kappa number and viscosity by 55.10 and 21.42 % respectively whereas; pulp brightness improves about 50.17% with pulp shrinkage of 2.4%. A major portion of lignin is removed by oxygen delignification before the start of actual bleaching operation. The dissolved lignin during oxygen delignification is taken to recovery section. Since the lignin remaining in the pulp after oxygen delignification is low and chlorination becomes less intensive.

Table 3 reveals the comparison of mechanical strength properties of unbleached and O_2 delignified pulp and comparison of effluent generated during pulp washings of kraft pulping and pulp washings O_2 deliginification.

Table 3- Comparison of mechanical strength properties of unbleached and O_2 delignified pulp and comparison of effluent generated during kraft pulping and O_2 deliginification

Sl. No.	Particulars	Unbleached krtaft pulp	O_2 delignified pulp	% difference
1	Initial beating level, ^{0}SR	16	17	—
2	Final beating level, ^{0}SR	30	30	—
3	Beating time, min	25	22	—
4	Bulk density, cm^3/g	1.44	1.42	—1.39
5	Burst index, kPam^2/g	3.53	3.63	+2.83
6	Tear factor, mNm^2/g	7.94	7.64	—3.78
7	Double fold, no.	56	42	—25
8	Tensile index, Nm/g	52.35	50.65	—3.25
9	COD, mg/L	1200	800	—33.3
10	Suspended solids, mg/L	800	600	—25.0

There is a reduction in bulk density of paper by 1.39% after O_2 delignification. The reason is removal of lignin increases the flexibility of fibers and fibers collapse readily into ribbons and provide maximum surface contact area for bonding which results an increase in apparent density of paper. All the mechanical strength properties like burst index, tear index, tensile index and double fold decreases or increase marginally after O_2 deliginification compared to kraft pulp. It is important to note that O_2 deliginification decreases COD load and suspended solids by 33.3 and 25.0% respectively which contribute towards pollution load of effluent.

Table 4 reveals the experimental conditions and results of C(Ep)HH and OC(Eop)HH bleaching of mixed pulps of *P. deltoides* and *E. tereticornis*. C(Ep)HH and OC(Eop)HH bleaching sequences produce a pulp brightness of 84.2 and 87.6% (ISO) respectively. OC(Eop)HH bleaching sequence shows a gain in pulp viscosity by 28.57% over C(Ep)HH bleaching sequence and total solids in effluent of OC(Eop)HH increase by 3.6% than that of C(Ep)HH bleaching sequence due to introduction of O_2 prior to bleaching.

Table 5 reveals the comparison of mechanical strength properties and combined effluent of C(Ep)HH and OC(Eop)HH bleached pulp of *P. deltoides* and *E. tereticornis*. All the mechanical strength properties of OC(Eop)HH bleached pulp like tear index (+4.08), tensile index (+2.97) and double fold (+11.43) improve compared to mechanical strength properties of C(Ep)HH bleached pulp. The OC(Eop)HH bleaching sequence decreases the COD load by 23.90%, suspended solids by 24.74%, dissolved solids by 35.94%, total solids by 35.94%, AOX by 42.86% and chlorides by 34.69% than that of C(Ep)HH bleaching sequence. Therefore, OC(Eop)HH bleaching sequence is not only helpful to improve mechanical strength and brightness of pulp but mitigate the pollution load of effluent generated during bleaching.

Table 6 shows the comparison of cost between C(Ep)HH and OC(Eop)HH bleaching sequences. The total operating cost of CEpHH and OC(Eop)HH bleaching sequences are Rs 3874.50 per tonne of pulp and Rs. 5149.50 per tonne of pulp respectively. The operating cost of OC(Eop)HH bleaching sequence is Rs 1275.00 per tonne of pulp more compared to

Table 4-Experimental conditions and results C(Ep)HH and OC(Eop)HH bleaching

Sl. No.	Particulars	C(Ep)HH	OC(Eop)HH
1	Unbleached pulp permanganate number	19.6	—
2	O_2 delignified kappa number	—	8.8
3	Chlorination stage		
	Molecular Cl_2 applied, % (O. D. pulp basis)	3.0	2.0
	Temperature, ^{0}C	Ambient	Ambient
	Reaction time, min	30	30
	Consistency, %	3.0	3.0
	pH	2.5	2.4
4	Extraction stage		
	NaOH applied, %(O. D. pulp basis)	3.5	3.0
	H_2O_2 applied, %(O. D. pulp basis)	0.5	0.5
	O_2 pressure, kg/cm^2	—	3.5
	Temperature, ^{0}C	75	75
	Reaction time, min	70	70
	Consistency, %	11.5	11.8
	pH	11.6	11.7
5	Hypochlorite stage (H_1)		
	$Ca(OCl)_2$ %(O. D. pulp basis)	1.5	1.0
	Temperature, ^{0}C	45	45
	Reaction time, min	120	120
	Consistency, %	10.5	10.6
	pH	11.2	11.3
6	Hypochlorite stage (H_1)		
	$Ca(OCl)_2$ %(O. D. pulp basis)	1.0	1.0
	Temperature, ^{0}C	45	45
	Reaction time, min	120	120
	Consistency, %	10.4	10.3
	pH	11.6	11.4
7.	Brightness, % (ISO)	84.2	87.6
8.	Viscosity, cps	7	9
9	Total solid gain in black liquor, %	—	+3.6

Table 5-Comparison of mechanical strength properties and combined effluent of C(Ep)HH and OC(Eop)HH bleached pulp.

Sl. No.	Particulars	C(Ep)HH	OC(Eop)HH	% difference
1	Initial freeness, ^{0}SR	18	18	—
2	Final freeness, ^{0}SR	40	40	—
3	Tear factor, mNm^2/g	4.9	5.10	+4.08
4	Burst index, kPam^2/g	3.14	3.14	Nil
5	Tensile index, Nm/g	48.46	49.90	+2.97
6	Double fold, no.	35	31	11.43
7	Brightness, % (ISO)	84.2	87.6	+3.4
8	Viscosity, cps	7	9	+28.57
9	COD, mg/L	4539	2697	—40.58
10	COD load, kg/T	0.151	0.121	—23.90
11	Suspended solids, mg/L	1265	952	—24.74
12	Dissolved solids, %	24.002	15.235	—36.53
13	Total solids, %	25.267	16.187	—35.94
14	AOX, kg/T	4.2	2.4	—42.86
	$Cl^{—}$, mg/L	9800	6400	—34.69

Table 6-Costing of C(Ep)HH and OC(Eop)HH bleaching sequences.

Sl. No.	Particulars	Bleached pulp cost					
		CEpHH Sequence			OCEopHH Sequence		
		Consumption, kg/T	Rate, Rs/kg	Bleaching cost, Rs/T	Consumption, kg/T	Rate, Rs/kg	Bleaching cost, Rs/T
1	Oxygen	?	?	?	20*	8	160
2	Chlorine	56	10	560	42	10	420
3	Alkali	35	38	1330	55#	38	2090
4	H_2O_2	12	45	540	12	45	540
5	Cl_2 as hypo	12	45	540	12	45	540
6	Power	163*	4	652	223*	4	892
7	L.P. steam	500	0.4	200	500	0.4	200
8	M.P. steam	?	?	?	400	0.6	240
9	Water	35^e	15	52.5	45^e	1.5	67.5
Total			Rs. 3874.5			Rs 5149.50	

* 16 kg/T in ODL and 4 kg/T in Eop stage making total 20 kg/T
\# 20 kg/T in ODL and 35 kg/T in Eop stage making total 55 kg/T
figure in kwh/T
^{e} figure in m^3/T

CEpHH bleaching sequence.

Conclusions

Oxygen delignification is helpful to mitigate pollution load after pulp bleaching since the lignin remaining in the pulp after oxygen delignification is low and chlorination becomes less intensive. The level of absorbable organic halides (AOX), COD, suspended solids, dissolved solids, total solids and chlorides in pulp bleaching effluents are considerably be decreased by oxygen delignification stage than that of conventional bleaching sequence. OC(Eop)HH bleaching sequence shows an improvement in mechanical strength properties and reduction in pollution load when compared with C(Ep)HH bleaching sequence and the enhancement in operating cost of Rs 1275.00 per tonne of pulp in cost of OC(Eop)HH bleaching sequence has been increased which is justified if it is looked from the environment point of views.

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