Bleaching of Oxygen-Delignified Bamboo-Hard Wood Pulp using Catalyst, Chlorine Dioxide and Conventional sequences

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ABSTRACT: *The catalytic effect of molybdate in alkaline hydrogen peroxide bleaching of oxygen delignified bamboo and hard wood pulps has been confirmed vis a vis optical properties. 21 different bleaching systems have been studied including CEH, CEpH, CEHED and CEpHED sequences in presence of a new catalysts. The oxygen delignification has been carried out at temperatures of 100 and 120⁰C on laboratory as well as mill pulps (12-17% AA charge). COD and colour of effluent generated from the first few systems, have been determined. Properties such as kappa no., viscosity, strength properties (burst, tear, breaking length and double fold) have been determined along with the optical properties (brightness and PC no.). FS factors of the bleached pulp have also been reported. The results have been used to confirm the effect of a new catalyst in improving the optical properites of bleached pulp compared to the conventional bleaching processes.*

INTRODUCTION

It was reported recently on the new finding at PAPRI (1) that molybdate can be employed in alkaline peroxide bleaching to impart superior optical properties. A similar study was carried out previously by Eckert et.al. (2) with H_2O_2 in acid media using oxygen lignified soft wood pulps. Role of metallic elements namely Ca, Fe, Cu, Mn, Mg and Si in the bleaching processes using peroxide has been shown to be of significance by many authors (3-6). The concentration of these trace metals reported in pulp, is mentioned in Table 1A.

The elements can be estimated in spectrophotometry (7), in atomic absorption spectrometry, induced plasma emission spectrocopy, or in X-ray spectrometry. The concentration is variable according to the source of raw material and bleaching processes adopted.

The role of these trace metals is attributed mainly on--

- delignification rate
- degradation of cellulose
- peeling effect
- decomposition of H_2O_2
- chelating effect
- stabilisation of the system
- buffer action

These have considerable effect on the bleached pulp namely on--

- Brightness and
- PC Number.

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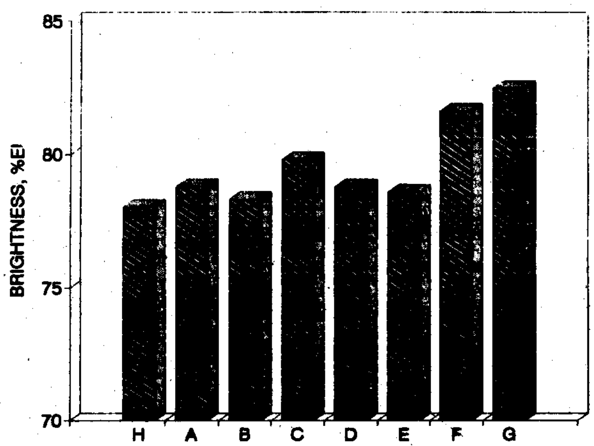

Fig.-1: Brightness of pulp in CEH sequence
(H = Without O2 delignification
A-G = With O2 delignification)

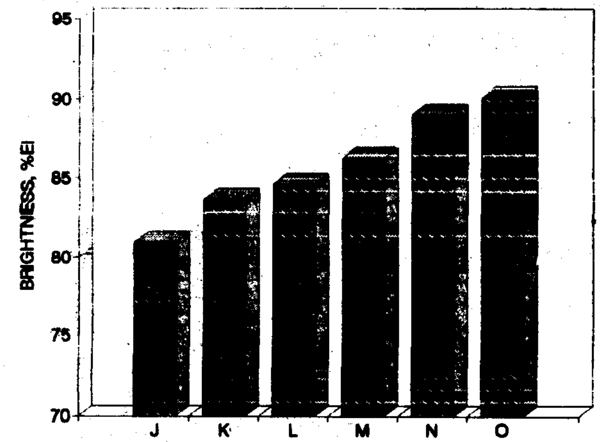

Fig.-2: Brightness of pulp
J = CEH sequence
K = CEpH sequence
L = CEp(cat)H sequence
M = CEHED sequence
N = CEpHED sequence
O = CEp(cat)HED sequence

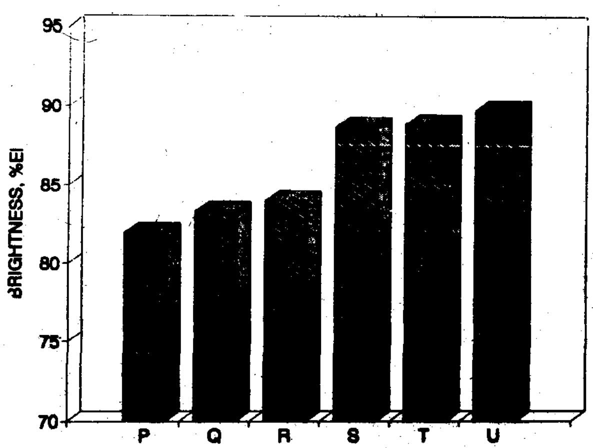

Fig.-3: Brightness of pulp
P = CEH sequence
Q = CEpH sequence
R = CEp(cat)H sequence
S = CEHED sequence
T = CEpHED sequence
U = CEp(cat)HED sequence

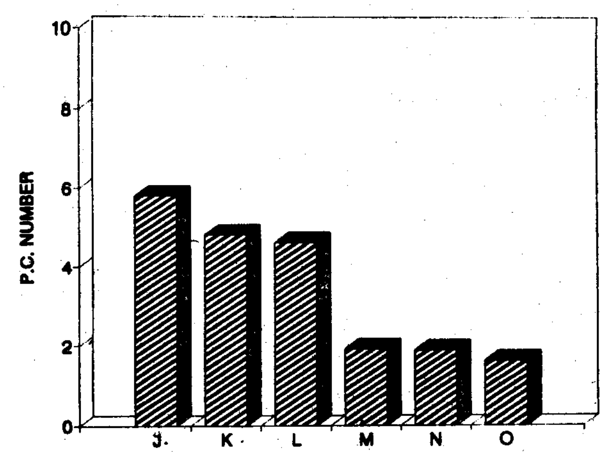

Fig.-4: P.C. Number of pulp
J = CEH sequence
K = CEpH sequence
L = CEp(cat)H sequence
M = CEHED sequence
N = CEpHED sequence
O = CEp(cat)HED sequence

The metals are invariably present in the raw material itself and if it is in excess, it is needed to eliminate but in some cases, the pulp becomes deficient of some of these metals also. The exact requirement of these metals for attaining optimum optical properties, is not specified. It is reported in case of cotton linter that the iron has beneficial effect (9) in some respect but excess is reported to be detrimental to the pulp vis a vis optical properties. $MgCO_3$, $MgSO_4$ and Na_2SiO_3 are added from external source to have beneficial effect. In the present work, molybdenum metal in form of Na_2MoO_4 has been added and it was reported recently (1) that a brightness gain of ~2% El with PC No. reduction of ~3.5 could be achieved on using oxygen delignified pulp. In order to compare the bleaching properties with other known systems, results of various other sequences have also been reported.

EXPERIMENTAL

Cooking

Bamboo and bamboo-hard wood mixed chips were collected from the nearby mill and the accepted chips (-32, +3 mm) were cooked in a 15 litre capacity laboratory rotary digester. The constant cooking conditions are:

Time to temperature 165°C - 2 hrs.

Time at temperature 165°C - 1½ hrs.

In case of bamboo AA charge is varied from 12 to 17% while for bamboo hard wood it is 11 to 17%.

Oxygen delignification

The unbleached pulp is treated with oxygen from cylinder in the rotary digester. After attaining the required temperature, oxygen is injected to desired level. The treatments made are as follows--

Oxygen pressure = 2 kg/cm²

Temperatures = 100 and 120°C

Retention time = 1 hr.

NaOH = 2 and 2.5% on O.D. pulp basis.

Bleaching

The sequences adopted are mentioned in Table 1 along with some other experimental conditions. The sequences followed are--

CEH

CEpH

CEp(cat)H

CEHED

CEpHED

CEp(cat)HED.

Properties

The optical properties (brightness and P.C.No.) have only been determined along with F.S. factor and strength properties for few systems following to standard Tappi methods.

Effluent analysis

COD and colour of the effluent generated from CEH sequence have only been determined.

Results and Discussion

As results of 21 different bleaching systems have been reported, the sets are classified in Table 1 from A to U. The first four (A-D) systems contain bamboo alone using CEH sequence while E to U systems have bamboo + hard wood mixed pulp (E-G laboratory pulp and H to U from the mill). The active alkali charge in A to G (excepting D) was 11-14% while in H to U systems, AA charge taken is 17%. The oxygen pressure during delignification in all systems (excepting the blank) is 2 kg/cm². The temperatures for O_2 delignification was 120°C for A to O and then 100°C from P to U. H_2O_2 has been applied in K, L, N, O, Q, R, T and U systems while ClO_2 was confined to M, N, O, S, T and U; the molybdate catalyst being in L, O, R and U systems. These combinations have been chosen to find out the improvement, possible to be obtained with respect to--

- CEH sequence which is applied in most of Indian paper mills.
- CEpH applied in few mills, and
- CEpHED in 2 or 3 mills in the country.

Table-1.

Systems used for experiments

Set	Raw material	A.A charge (%)	O_2 Kg/cm²	Temperature °C	Bleaching sequence
A	Bamboo	12	2	120	CEH
B	Bamboo	13	2	120	CEH
C	Bamboo	14	2	120	CEH
D	Bamboo	17	Nil	--	CEH
E	Bamboo+ Hardwood	11	2	120	CEH
F	Hardwood	12	2	120	CEH
G	Hardwood	14	2	120	CEH
H	Hardwood	17	Nil	--	CEH
I	Hardwood	17	Nil	--	--
J	Hardwood	17	2	120	CEH
K	Hardwood	17	2	120	CEpH
L	Hardwood	17	2	120	CEp(cat)H
M	Hardwood	17	2	120	CEHED
N	Hardwood	17	2	120	CEpHED
O	Hardwood	17	2	120	CEp(cat)HED
P	Hardwood	17	2	100	CEH
Q	Hardwood	17	2	100	CEpH
R	Hardwood	17	2	100	CEp(cat)H
S	Hardwood	17	2	100	CEHED
T	Hardwood	17	2	100	CEpHED
U	Hardwood	17	2	100	CEp(cat)HED

Table-1A.

Trace metal content in pulp (ppm)

Pulp	Fe	Mn	Cu	Ref
Block Spruce (SGW)	11.7	79.7	11.1	4
Pinus Radiata (TMP)	5.99	32.05	4.2	5
Norway Spruce (TMP)	82.3	102.3	20.6	6
Unbleached Soft Wood Kraft Mill Pulp	15.0	153.0	1.0	8
Unbleached Soft Wood Kraft Lab Pulp	33.0	135.0	17.0	8

The effect of catalyst is also compared to the above systems.

Results of oxygen delignification with bamboo pulp (A-D) prepared in laboratory using AA charge of 12, 13, 14 and 17% are given in Table 2. The total yield obtained is 50-64%, the highest being at 12% AA which is normal because of minimum degradation of cellulose and presence of lignin. Kappa number has been found to vary from 25.4 to as high as 50.1, the lowest being in D and C systems (25.4 and 27.8 respectively). The viscosity values also decrease with increase in AA charge (33.4 to 23 cps).

In the oxygen delignification of A, B and C systems, 2% of NaOH has been added with constant O_2 pressure of 2 kg/cm². It is interesting to note that the kappa number can be reduced to 18.7 with a viscosity

Table-2.

Pulping and oxygen delignification with bamboo

Particulars	A	B	C	D
PULPING:				
Active alkali charge, %	12	13	14	17
Total yield, %	63.67	58.48	49.95	53.40
Kappa no.	50.1	45.8	27.8	25.4
Viscosity, cP	33.4	28.1	22.8	23.0
OXYGEN DELIGNIFICATION				
Alkali dose, %	2	2	2	--
Alkali consumed, %	1.78	1.20	1.03	--
O_2 pressure, Kg/cm^2	2.0	2.0	2.0	--
Kappa no.	27.1	28.1	18.7	--
Viscosity, cP	17.9	18.7	12.5	--

Table-3.

Bleaching characteristics of the oxygen delignified pulp from bamboo

Particulars	A	B	C	D
Kappa no.	27.1	28.1	18.7	25.4
Total Cl_2 added, %	11.0	10.7	8.0	10.2
Cl_2 consumed,	9.90	10.27	6.68	8.33
NaOH added, %	2.3	2.4	1.7	2.0
Brightness, % El	78.8	78.3	79.8	78.8
P.C. No.	11.8	11.6	10.5	13.0
Viscosity, (0.5M CED) cP	8.8	7.2	6.0	7.7

value of 12.5 from an initial kappa no. of 27.8. The percentage reductions in kappa no. are as follows--

System	% reduction
A	46
B	38.6
C	32.7

These results show that the percentage reduction in kappa no. in oxygen delignification is more significant for pulp having higher initial kappa no. It can also be inferred from these results that lower the initial kappa no., more difficult it is to delignify with oxygen. The kinetic model for oxygen delignification (8) is given by the equation--

$$\frac{K_O - K_F^2}{K - K_F} = 1 + (8000e^{\frac{-5850}{T}})C_O^2.t \quad .....(1)$$

Where K_O= Initial kappa no. (39.1 in the example)

K = Final kappa no.

K_F = "Floor" kappa no. in a particular process for pine karft anticipated to be 8.5.

T = Temperature, ^{0}K

C_O = Initial alkali concentration, g/l

t = Bleaching time, min.

A relationship between lignin content and kappa number is given as--

(Lignin) = 0.15 X kappa no. .....(2)

The delignification limit is reported to be maximum 50% without any significant effect on cellulose degradation (8, 10).

The optical properties for A-D systems are given in Table 3. The brightness values are more or less same

Table-4.

Results of effluent from oxygen delignification of bamboo (in Kg/t)

Bleaching Stage	A		B		C		D	
	COD	Colour	COD	Colour	COD	Colour	COD	Colour
Chlorination	25.7	**0.08**	20.5	1.28	22.1	0.02	26.7	1.13
Extraction	16.0	**61.2**	30.9	70.2	25.6	50.3	16.8	88.0
Hypo	6.8	**0.02**	9.7	0.22	8.3	0.008	7.7	0.25

Table-5.

Strength properties (40° SR) of oxygen delignified pulp from bamboo

Particulars	A	B	C	D
Bulk, cc/g	1.41	1.41	1.41	1.44
Burst factor,	39.13	28.9	25.2	34.3
Tear factor,	49.43	50.2	32.9	44.3
Breaking length, m.	5500	4750	5070	5000
Double fold, no.	15	11	6	11

Table-6.

Pulping and oxygen delignification with bamboo-hard wood

Particulars	E	F	G	H
PULPING:				
Active alkali charge, %	11	12	14	17
Residual active alkali at 18° TW gpl	4.34	3.87	--	12.40
Total yield, %	57.84	56.95	55.37	46.42
Kappa no.	54.0	37.1	31.4	22.0
Viscosity, cP	35.3	28.1	24.6	13.3
OXYGEN DELIGNIFICATION				
Alkali added,, %	2.0	2.0	2.0	--
O_2 pressure, Kg/cm^2	2.0	2.0	2.0	--
$MgSO_4$ as Mg^{+2}	0.05	0.05	0.05	--
Kappa no.	21.0	13.0	14.0	--
Viscosity, cP	17.4	9.3	12.2	--

in A, B and D (78-79) which is ~80 in C. The later has also the least PC no. of 10.5 compared to 12-13 in other systems. This system - C has also low kappa no. requiring least chemical during bleaching but viscosity is low (6 cps).

The results of effluent from the oxygen delignification are given in Table 4 for A-D systems. The colour due to oxygen delignification decreases from 88 kg/ton (D) in blank to 50.3 in C which is 43%. The COD value also is found to be lowered by 23% due to oxygen delignification in CEH sequence.

The strength properties of A-D are shown in Table 5. The burst factor, tear factor, breaking length and double fold values of system A are highest of all, where 12% of AA was employed.

In case of bamboo-hard wood pulp (Table 6) the AA charges in E, F, G and H are 11, 12, 14 and 17%

Table-7.

Bleaching characteristics of bamboo-hard wood pulp after oxygen delignification

Particulars	E	F	G	H
Kappa no.	21.0	13.0	14.0	22.0
Total Cl_2 added, %	8.4	5.25	5.3	8.75
Cl_2 consumed,	7.58	4.68	4.64	7.66
NaOH added, %	1.75	1.10	1.20	1.80
Brightness, % El	78.6	81.6	82.5	78.0
P.C. No.	13.1	10.2	9.3	12.6
Viscosity, (0.5M CED) cP	7.2	5.8	6.7	7.4

Table-8.

Results of effluent from oxygen delignification of bamboo-hard wood (in Kg/t)

Bleaching Stage	E		F		G		H	
	COD	Colour	COD	Colour	COD	Colour	COD	Colour
Chlorination	14.1	0.29	13.7	0.36	--	0.36	16.3	0.36
Extraction	12.6	20.7	6.7	15.3	14.1	36.0	18.9	46.8
Hypo	9.6	0.20	2.9	0.15	7.9	0.25	16.0	0.25

Table-9.

Physical strength properties (40° SR) of oxygen delignified pulp from bamboo-hard wood

Particulars	E	F	G	H
Bulk, cc/g	1.57	1.45	1.53	1.55
Burst factor,	29.4	39.2	26.9	27.8
Tear factor,	54.2	64.1	44.0	44.5
Breaking length, m.	4695	5325	4025	4150
Double fold, no.	11	27	8	8

respectively. The yield at lowest AA charge of 11% is 58% compared to 46% at 17% of AA. The kappa no. reduction in E-G systems are--

System	% reduction
E	61
F	65
G	55

The percentage reduction in kappa no. in the mixed pulp is thus higher than bamboo pulp. The viscosity values of the oxygen delignified pulp are also higher in view of the higher lignin content as shown in equation (2).

The brightness and PC no. values of E - H systems, tabulated (Table 7) indicate that a brightness of 82.5 with PC no. of 9.3 can be achieved. The results of COD and colour values in (Table 8) show that both colour and COD are reduced due to oxygen delignification. The pulp having 12% of AA charge (F) is found to have higher strength properties than the other systems (Table 9). The increase in breaking length from 4150 m in blank (H) to 5325 m in F; tear factor from 44.5 to 64.1, burst factor from 27.8 to 39.2 and double fold from 8 to 27 are quite remarkable.

Table-10.

Kappa number after oxygen delignification

Particulars		I	J-O	P-U
NaOH dose	%	2.5	2.5	2.5
O_2 pressure	Kg/cm^2	--	2.0	2.0
Maximum temperature,	°C	120	120	100
Retention time at maximum temperature,	mts	60	60	60
Kappa no.		16.5	8.8	10.8

Initial kappa no. = 21

Table-11.

Bleaching characteristics of bamboo-hard wood pulp after oxygen delignification at 120°C

Particulars		J (CEH)	K (CEpH)	L CEp(cat)H)	M (CEHED)	N (CEpHED)	O (CEp(cat)HED)
Kappa no.		8.8	8.8	8.8	8.8	8.8	8.8
Total chlorine added,	%	3.5	3.5	3.5	4.2	4.2	4.2
Chlorine consumed,	%	2.4	2.24	2.34	3.2	3.02	3.12
NaOH added,	%	0.8	0.8	0.8	1.1	1.1	1.1
Final brightness,	%El	81.0	83.7	84.6	86.2	89.0	90.0
P.C. Number		5.8	4.8	4.6	1.9	1.87	1.6
Drop in F.S. factor (with respect to J)	%	--	2.80	--	16.86	15.48	17.93

Table-12.

Bleaching characteristics of bamboo-hard wood pulp after oxygen delignification at 100°C

Particulars		P (CEH)	Q (CEpH)	R CEp(cat)H)	S (CEHED)	T (CEpHED)	U (CEp(cat)HED)
Kappa no.		10.8	10.8	10.8	10.8	10.8	10.8
Total chlorine added,	%	4.3	4.3	4.3	5.0	5.0	5.0
Chlorine consumed,	%	3.56	3.38	3.28	4.35	4.17	4.07
NaOH added,	%	0.9	0.9	0.9	1.25	1.25	1.25
Final brightness,	%El	82.0	83.4	84.1	88.8	89.0	90.0
P.C. Number		5.2	5.0	4.2	3.8	2.6	2.0
Drop in F.S. factor (with respect to P)	%	--	8.2	12.3	24.1	26.8	24.3

In order to attain still lower kappa no. with mixed mill pulp (17% AA), the NaOH concentration was increased from 2 to 2.5% in I to U systems (Table 10) where the reductions in kappa no. are--

System	% reduction
J-O	58
P-U	49

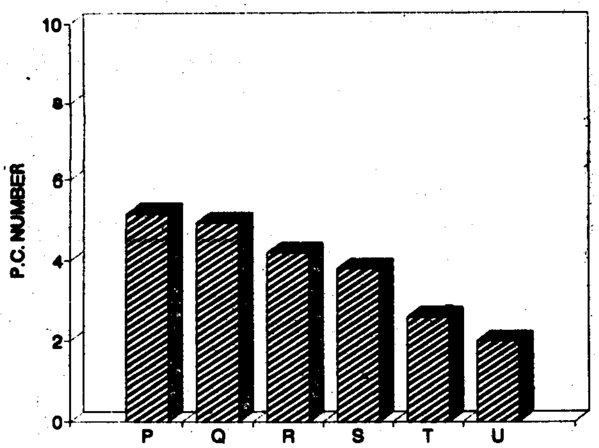

Fig.-5: P.C. Number of pulp
P = CEH sequence
Q = CEpH sequence
R = CEp(cat)H sequence
S = CEHE sequence
T = CEpHED sequence
U = CEp(cat)HED sequence

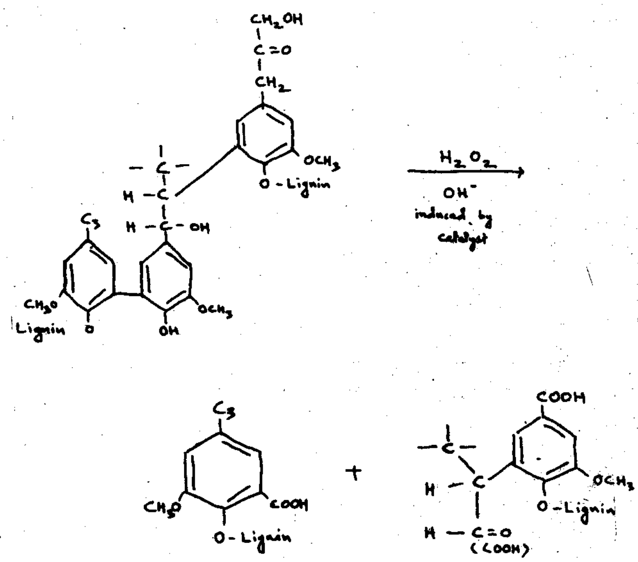

Fig.-6: Peroxide - Lignin Reactions In Bleaching

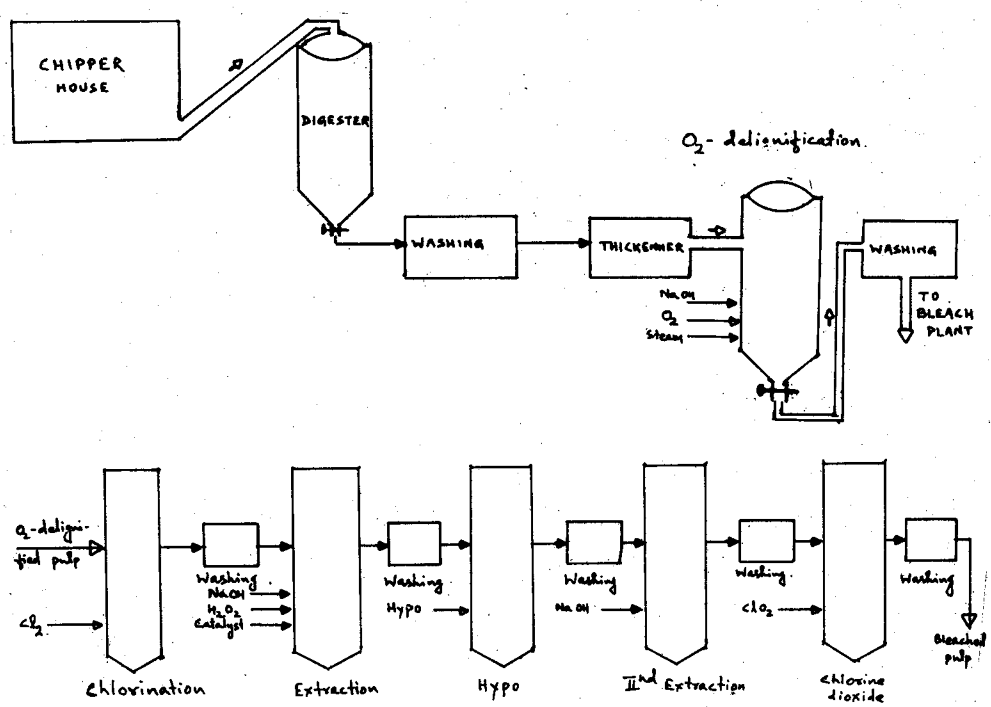

Fig.-7: Flow diagram Showing Oxygen deliguification process with CEpH/CEp(cat)H/ CEp(cat)HED

These values are quite appreciable compared to 21% reduction without oxygen treatment, showing thereby the contribution of oxygen treatment in removal of lignin.

The bleaching charcteristics of bamboo-hard wood pulp having kappa no. of 8.8 are given in Table 11 for J to O systems. It can be seen that the brightness value increases with decrease in PC no. in the following order--

CEp(cat)HED, CEpHED, CEHED, CEp(cat)H, CEpH and CEH; the brightness values being 90, 89, 86.2, 84.6, 83.7 and 81% El. PC no. of 1.6 is achievable in O system. The supremacy of catalyst-containing systems namely L compared to J and K and O compared to N, and M can be seen. Finally, the effect of this catalyst is valid both in CEH and CEHED sequences in case of oxygen delignified pulp.

The same systems have been taken (P-U) at 100°C with pulp of 10.8 kappa no. (Table 12). It can be seen that here also brightness of 90% El can be achieved on using catalyst in CEpHED sequence. The effect of catalyst is applicable at 100°C also in both CEH and CEHED systems. Results of FS factor show drop of ~24% in case of later compared to 12% in the former.

A critical examination of kappa no. reduction will show that oxygen delignification can help reducing the kappa no. to 50% or more. However, the question of cellulose degradation is to be examined when it is higher than 50%. With reduction of FS factor by ~20%, the kappa no. reduction can be 60-65% assuming that the reduction in FS factor is mostly due to cellulose degradation. The effect of catalyst in improvement of optical properties was explained previously (1).

It was reported recently (11) that metals such as Al, Ca, Cr, Mn and Fe in groundwood pulp play important role in single and two stage peroxide bleaching process of Eucalyptus regnans. (The metal can originate from wood or process linings.) A brightness increase of 73% ISO has been reported by these authors (11). The role of metal ion in the brightness improvement is linked essentially with the peroxide decomposition and chelating effect.

H_2O_2 dissociates following to the equation--

$$H_2O_2 + H_2O \Leftrightarrow H_3O^+ + O_2H^-$$

The bleaching effect of H_2O_2 is attributed to the oxidative action of the perhydroxyl ion (O_2H^-). The rate of reaction apparently increases in presence of the catalyst. This effects the degradation of lignin to the colourless acidic compounds and thus there is gain in brightness as shown in Fig. 6.

The flow diagram of oxygen delignification in combination with various bleaching sequences discussed is given in Fig. 7. It has been estimated that compared to the cost born for brightness improvement by other processes, the use of catalyst can be economically quite viable.

CONCLUSIONS

Decrease in kappa number due to oxygen delignification requiring lesser chemicals in the bleaching process is one of the major advantages. The reduction in COD, colour and chloroorganic compounds in the effluent generated after oxygen treatment, is also quite important for pollution abatement. Comparision of the brightness values obtained previously from pulp without oxygen treatment (1) and the present data using oxygen delignified pulp, shows that the final brightness obtained here is more than previously obtained. Oxygen delignification thus ensures production of bleached pulp with a brightness of ~90% El with PC no. of ~1-2 when molybdate catalyst is used with ClO_2. In CEH sequence also, oxygen delignification increases the pulp brightness.

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