Delignification of Kraft Pulp with Oxygen-Chlorine Combinations

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INTRODUCTION

Environmental considerations provided the ultimate incentive to develop oxygen bleaching as an alternative to acid chlorination and alkaline extraction. During the last two decades an impressive body of knowledge has been accumulated regarding oxygen bleaching of softwoods/hardwoods. However, oxygen delignification of non-wood raw materials like bamboo has been largely overlooked. In the present investigations the kinetics of oxygen bleaching of bamboo kraft pulp have been studied to assess the adoptibility of bamboo pulp to this technique. Besides, investigations on: (i) kinetics of each stage of CEHD bleaching sequence, which is commonly employed for pulp bleaching in India, (ii) properties of pulp obtained upon bleaching with CEH & ODEH sequences and (iii) analysis and characterisation of effluents have been made and reported here, (C=Chlorination, E=Alkali extraction, H = Calcium hypochlorite treatment, D = Chlorine dioxide treatment, O=Oxygen).

Kinetics of Delignification with Alkaline Oxygen

In the alkaline delignification process the rate of delignification can be represented as a function of the concentration of delignifying agent, lignin concentration, alkali concentration and temperature. In the present study oxygen concentration has been kept constant at 8.1 kg./cm^2, the level already found optimum and the variables studied are alkali, with three different alkali charges of 1.5%, 2.0% and 2.5%, and temperature, namely, 90°C, 110°C and 130°C.

The kinetics of the delignification reaction was studied with respect to:

(i) decrease in Klason lignin concentrations,

(Klason lignin was determined as per TAPPI standard T12m-59)

(ii) decrease in Kappa no.,

(Kappa no. was determined as per TAPPI standard T236m-60)

(iii) dissolution of Pentosans and,

(Pentosans were determined as per TAPPI standard T19-m-20)

(iv) change in Lignin/Carbohydrate ratio.

The results obtained are given in Table 1 to 3.

It is observed that delignification of bamboo kraft pulp with respect to lignin concentration followed a pseudo zero order kinetics. The rate expression can be expressed as:-

$$-\frac{dL}{dt} = k_o C^a$$

Where L is lignin concentration, k_o is zero order rate constained, C is the concentration of alkali and 'a' is the order of reaction with respect to alkali. The value of 'a' being highly dependent on reaction condition (alkali concentration and temperature).

Delignification reaction in terms of decrease in Kappa no. also followed zero order kinetics; the process, in fact, followed two pseudo zero order kinetics characterised by initial rapid stage followed by a slow process. The rapid phase acts for about 30 min. at all the condition of reaction under this report. It is also observed that the decrease in Kappa no. in the rapid phase is both alkali and temperature dependent. In the slower phase it is seen that the rate of decrease in Kappa no. is independent of

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Table-1

Delignification of Bamboo kraft pulp with oxygen at 90°C

Conditions of delignification
Oxygen pressure : 8 kg./cm²
Alkali Conc. : 1.5%, 2% and 2.5% NaOH on O.D. pulp basis.
Pulp Consistency : 15%

Alkali Conc., % on O.D. pulp	Time at 90°C (min)	Pulp yield % on raw material	Kappa no.	Pentosan % on O.D. pulp	Pentosan % on O.D. raw material	Lignin % on O.D. pulp	Lignin % on O.D. raw material (L)	L / 100-L
	30	40.32	26.3	16.78	6.76	5.56	2.24	.023
1.5	60	38.45	24.2	16.46	6.33	5.65	2.17	.022
	90	38.40	23.2	15.27	5.86	4.90	1.88	.019
	30	40.46	22.4	16.63	6.82	4.80	1.94	.020
2.0	60	38.37	21.1	16.44	6.31	3.80	1.46	.015
	90	38.26	19.7	14.90	5.70	2.61	1.00	.010
	30	39.62	19.8	17.05	6.75	4.70	1.86	.019
2.5	60	38.60	18.4	17.07	6.50	3.63	1.40	.014
	90	38.06	16.9	14.84	5.65	2.55	0.97	.010
Unbleached Pulp		41.00	35.0	18.29	7.50	5.86	2.40	.025

Table-2

Delignification of Bamboo kraft pulp with oxygen at 110°C

Conditions of delignification
Oxygen pressure : 8 kg./cm²
Alkali Conc. : 1.5%, 2% and 2.5% NaOH on O.D. pulp basis.
Pulp Consistency : 15%

Alkali Conc., % on O.D. pulp	Time at 110°C (min)	Pulp yield % on raw material	Kappa no.	Pentosan % on O.D. pulp	Pentosan % on O.D. raw material	Lignin % on O.D. pulp	Lignin % on O.D. raw material (L)	L / 100-L
	30	39.64	13.2	16.55	6.56	4.66	1.85	.019
1.5	60	36.03	10.9	17.60	6.34	3.44	1.24	.013
	90	36.64	8.9	17.03	6.24	1.82	0.67	.010
	30	39.44	12.9	16.48	6.50	4.03	1.65	.017
2.0	60	36.60	10.6	17.21	6.30	2.46	0.90	.010
	90	36.38	8.5	17.07	6.21	0.43	0.16	.002
	30	39.70	12.0	15.87	6.30	4.04	1.60	.016
2.5	60	36.48	9.9	16.85	6.15	1.94	0.75	.008
	90	36.35	7.9	16.51	6.00	0.29	0.11	.001
Unbleached Pulp		41.00	35.0	18.29	7.50	5.86	2.40	.025

Table-3

Delignification of Bamboo kraft pulp with oxygen at 130°C

Conditions of delignification
Oxygen pressure : 8 kg./cm²
Alkali Conc. : 1.5%, 2% and 2.5% NaOH on O.D. pulp basis.
Pulp Consistency : 15%

Alkali Conc., % on O.D. pulp	Time at 130°C (min)	Pulp yield % on raw material	Kappa no.	Pentosan % on O.D. pulp	Pentosan % on O.D. raw material	Lignin % on O.D. pulp	Lignin % on O.D. raw material (L)	L / 100-L
	30	39.68	10.9	18.02	7.15	4.10	1.63	.017
1.5	60	36.64	9.3	17.92	6.56	2.39	0.88	.009
	90	36.60	7.6	17.49	6.40	0.33	0.12	.001
	30	39.00	10.0	17.69	6.90	4.12	1.61	.016
2.0	60	36.61	8.2	17.49	6.40	2.29	0.84	.010
	90	36.59	6.0	16.40	6.00	0.19	0.07	.001
	30	39.02	8.4	17.41	6.80	4.02	1.57	.016
2.5	60	36.62	6.8	17.07	6.25	2.18	0.80	.008
	90	36.58	5.5	16.40	5.80	0.08	0.03	.000
Unbleached Pulp		41.00	35.0	18.29	7.50	5.86	2.40	.025

initial alkali charge at a given temperature.

The rate equation for delignification with respect to Kappa no. is given as:-

$$\frac{-\,d\,\text{Kappa no.}}{dt} = k_0(r).C + k_0(s)$$

Where the first term on the right hand side represents the rapid phase and the second term represents the slower phase. C is the concentration of alkali.

The kinetics of oxygen rection with respect to pentosans dissolutions was also found to be of zero order and the rate expression can be written as:-

$$\frac{-\,d[P]}{dt} = k_0\, C^a$$

Where C is the concentration of alkali and 'a' is the order of reaction which appears to be dependent on reaction conditions, particularly on temperature beyond 110°C.

The zero order rate expression for the changes in the lignin to carbohydrate ratio during the delignification reaction can be given as:-

$$\frac{-\,d[L/(100-L)]}{dt} = k_0C$$

Where C is the concentration of alkali.

Kinetics of Each Stage of Delignification with CEHD Sequence

Bamboo kraft pulp having Kappa no. 35 was bleached under the condition as follows:-

i. Chlorine stage-Cl_2 7.0%, Consistency 3.0%. Temp. 30°C, Time 60 min.

ii. Extraction stage-NaOH 3.0%, consistency 10.0%, Temp. 70°C, Time 90 min.

iii. Hypochlorite stage-Available Cl_2 5%, consistency 3.0%, Temp. 30°C, Time 120 min., pH 10.0.

iv. Chlorine dioxide with two different consistency of 10% and 5% at reaction temp. of 75°C and 55°C.

And the reaction kinetics were studied for each stage. The kinetics of chlorination hypochlorite and chlorine dioxide stages was followed by estimating residual available chlorine iodometrically.

The results obtained are given in Table-4 to 8.

Table-4

Reaction of chlorine with bamboo kraft pulp

Reaction Temp. (°C)	Consistency (%)	Chlorine (%)	Retention Time (Min.)	Residual Chlorine (%)	1 / %Residual Chlorine
			10	1.00	1.00
40	3.0	7.0			
			20	0.61	1.65
			30	0.48	2.10
			40	0.39	2.60
			50	0.32	3.10
			60	0.28	3.60
			10	1.67	0.6
			20	1.11	0.9
			30	0.91	1.1
30	3.0	7.0			
			40	0.77	1.3
			50	0.67	1.5
			60	0.59	1.7
			10	3.33	0.33
			20	1.11	0.9
			30	0.91	1.1
30	3.0	7.0			
			40	0.77	1.3
			50	0.67	1.5
			60	0.59	1.7
			10	3.33	0.3
			20	2.50	0.4
			30	2.00	0.5
20	3.0	7.0			
			40	1.67	0.6
			50	1.67	0.6

Table-5

Change in Kappa numbers of pulps chlorinated under varied conditions

Reaction Temp. (°C)	Available chlorine % on O.D. pulp	Consistency % on O.D. pulp	Chlorine consumed % on O.D. pulp	Kappa no.
			4.0	9.0
2.0	7.0	3.0		
			5.0	8.0
			6.0	6.0
			7.0	5.0
			4.0	8.7
			5.0	8.0
*2.0	7.0	3.0		
			6.0	6.1
			7.0	5.0

Table-6

Consumption of caustic soda at 70°C

Reaction Temp.(°C)	Consistency (%)	Retention Time(min.)	Consumption of caustic soda (%)
		0	3.00
		10	2.67
70	3	20	1.83
		30	1.82
		40	1.81
		50	1.80
		60	1.80

Table-7

Decrease in hypochlorite concentration with time

Reaction Temp. (°C)	Consistency (%)	Available Chloride (%)	Reaction Time (Min.)	Residual Chlorine (%)	Log (% Residual chloride
			0	5.00	0.700
			10	4.30	0.633
30	3	5			
			20	4.15	0.615
			30	3.98	0.600
			40	3.85	0.585
			50	3.71	0.570
			60	3.51	0.545

Table-8

Decrease of chlorine dioxide with time

Reaction Temp.(°C)	Consistency (%)	Retention Time(min.)	Residual ClO (%)
		0	1.0
75	10		
		10	0.51
		30	0.40
		60	0.31
		0	1.0
		10	0.50
75	5		
		30	0.31
		60	0.25
		0	1.0
55	10		
		10	0.24
		30	0.15
		60	0.10

At the chlorination stage the reaction is marked by an initial rapid phase followed by a slow reaction period. The rapid phase continues upto 3-4 minutes from the start of the reaction and consumes about 70% of applied chlorine, whereas the remainder is

consumed gradually with a much slower rate. The rate law equation can be given as:-

$$-\frac{dC}{dt} = k_1 C_f + k_2 Cs^2$$

Where, C denotes the concentration of available chlorine, C_f the concentration of available chlorine during rapid phase and Cs the concentratrion of available Chlorine in the slow phase of the reaction.

From the study of the change in Kappa no. of pulps chlorinated under varied conditions corroborates the fact that a first-order law is followed by a second-order law.

In the extraction stage it is found that the kinetics of caustic soda consumption follows a zero-order reaction upto first 20 min. of extraction period, beyond which no further consumption of caustic soda is observed. Consumption of caustic soda follows the following rate law:-

$$-\frac{d[NaOH]}{dt} \quad k_o$$

Where k_o is the velocity constant. The value of ko is found to be 6.0×10^{-2}.

In the hypochlorite stage, the decrease of hypochlorite concentration with time is found to be of first order reaction kinetics upto a lapse of 5 min. from the start of the reaction under the conditions of investigations which is then followed by the latter slow consumption of hypochlorite following a first-order kinetics.

Bleaching in the chlorine dioxide stage is again divided into an initial rapid reaction period followed by a subsequent slow reaction period. The rapid phase is found to be more influenced by temperature and consistency as compared to slow reaction period. The reaction order is found to be dependent on reaction conditions and time elapsed from when bleaching started.

Physical and Optical Properties of Bleached Pulp Fibres

The test pulp specimen were taken from unbleached bamboo kraft as well as from the partially and fully bleached pulps under following different bleaching sequences:-

i. Partially bleached pulp through alkaline-oxygen treatment; under constant oxygen pressure of 8.1 kg/cm., at three different temp. of 90°C, 110°C and 130°C with different alkali charges of 1.5%, 2.0% and 2.5%.

ii. Fully bleached pulp through CEH sequence, using 7% Cl_2 with 3% consistency at 20°C at the chlorine phase, 3% NaOH soln. with 5% consistency at 70°C for 60 min. in the extraction phase and 5% available chlorine with 3% consistency at pH10 and temp. 30°C at the hypochlorite stage.

iii. Fully bleached pulp through ODEH sequence.

Pulps cooked with alkaline-oxygen with 2.5% alkali at 130°C for 90 min. having Kappa no. 6.1 was subjected to DEH(D=Chlorine dioxide, E=extraction and H=hypochlorite) treatment under different conditions. The results obtained are given in Table-9.

In the partially bleached pulp through alkaline-oxygen treatment it is observed that there is marginal improvement in the tensile index property with the change in alkali concentration. The tensile index remains almost unchanged when the temp. is raised from 90°C to 110°C, but when it is raised to 130°C the index decreases appreciably.

Increase in brightness of oxygenated pulp sheets with the decrease in Kappa no. consists of two phase process-initial rapid phase and the latter slower one.

Printibility test shows that standard hand sheet of oxygenated pulp fibres give 'Good' to 'Excellent' results.

It is observed that except for the brightness of pulp sheets bleached through CEH sequence, the other physical properties of the hand sheets made from oxygenated pulps are very well comparable to those properties of the hand sheets obtained through CEH sequence.

When the physical and optical properties of the pulps, bleached through ODEH sequence are compared with the corresponding values of pulps

Table-9

Physical and Optical Properties of Bleached Pulp Fibres

Conditions of bleaching			Tensile index (Nm./g.)	Tear index ($mNm^2/g.$)	Burst index ($k.Pa.m.^2/g.$)	Brightness (Elrepho 200 A) (%)
Unbleached Kraft Pulp			86.39	11.43	5.83	18.10
			Oxygenated pulp			
Temp. 90°C	a1.5%	t 90 min.	76.99	12.25	5.24	21.30
	a2.0%	t 60 min.	84.92	11.00	6.05	25.95
	a2.0%	t 90 min.	77.66	12.01	5.30	26.62
	a2.5%	t 30 min.	84.71	10.30	6.07	26.65
	a2.5%	t 90 min.	83.92	10.91	5.75	25.29
Temp. 110°C	a1.5%	t 90 min.	80.03	11.96	5.59	36.20
	a2.0%	t 60 min.	84.41	10.20	5.87	40.75
	a2.5%	t 60 min.	84.86	11.20	5.62	47.45
	a2.5%	t 90 min.	83.91	11.69	6.07	42.29
Temp. 130°C	a1.5%	t 90 min.	73.77	12.94	5.34	38.05
	a2.0%	t 60 min.	69.66	15.85	4.77	46.87
	a2.5%	t 30 min.	84.01	14.69	5.13	40.73
	a2.5%	t 60 min.	73.03	11.88	5.86	38.92
	a2.5%	t 90 min.	65.6	15.03	4.52	50.91

(Note a is alkali percent and t is time of reaction)

		Pulp bleached through CEH sequence			
Chlorination phase (Ch.7%, Temp. 20°C and consistency 3%)	t 20 min.	59.29	7.75	3.39	47.0
	t 40 min.	55.88	5.31	3.09	47.5
	t 60 min.	70.77	3.40	3.34	49.5
EXTRACTION PHASE (one hr. Chlorinated pulp extracted with 3% caustic soda soln., and consistency 5% at 70°C temp.)	t 20 min.	71.22	3.43	3.33	47.0
	t 40 min.	72.00	3.43	3.32	47.0
	t 60 min.	71.12	3.42	3.39	46.8
HYPOCHLORITE PHASE (extracted pulp of 90 min. treated with hypochlorite; 5% available chlorine at pH 10, 30°C	t 20 min.	72.13	3.85	3.93	63.0
	t 40 min.	73.45	4.15	4.15	72.0
	t 60 min.	72.00	5.00	4.16	73.0
		Pulp bleached through ODEH sequence			
D 1.0%, E 2.0% & H 0.5%		59.66	6.98	3.41	78.0
D 1.5%, E 2.0% & H 1.0%		64.97	6.69	3.70	80.0
D 1.0%, E 2.0% & H 1.0%		73.20	10.04	4.65	68.0

(Note:- D- Chlorine dioxide, E- Extraction with alkali and H- hypochlorite)

obtained through CEH sequence, it is seen that ODEH sequence produce stronger pulp having higher tensile index and burst index values as well as higher brightness.

Characterisation and Analyses of Effluents

The effluent from the oxygen stage bleaching was analysed for dry solids, residual alkali and molecular weight distribution of lignin degraded products. Also the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were determined from the effluents from ODEH sequence as well as from CEH sequence and the data obtained were compared. The results are given in Table-10.

It is seen that the dry solids content and residual alkali percent are very low and the same

Table-10

COD and BOD in the effluents

Sequence of bleaching		Bleaching condition				COD kg./t.	BOD kg./t.
ODEH		D	1.0%, E	2.0%, H	0.5%	10.34	9.00
		D	1.5%, E	2.0%, H	1.0%	10.36	9.10
		D	1.0%, E	2.0%, H	1.0%	10.37	9.00
CEH	(i)	Cl	7%,	consistency	3%,	23.00	20.00
		temp. 20°C, reaction time 60 min.					
	(ii)	E 3% NaOH soln., consistency 5% temp. 70°C, reaction time 60 min.					
	(iii)	H 5% available chlorine, pH 10, consistency 3%, temp. 30°C, reaction time 60 min.					

have to be recycled in the bath ratio to have higher concentration of dry solids content and residual alkali so that those can be recovered economically.

In the molecular weight distribution of lignin degradation products it is seen that at lower temp. of 90°C the ratio of the high molecular weight to low molecular weight is less than unity indicating that there are high proportion of low molecular weight lignin degraded products. But the situation has reversed at higher temperature of 110°C and 130°C where the high molecular weight derivatives are in higher proportion. This may be due to condensation of the lignin degraded products into higher molecular weight compounds.

It is seen that the BOD and COD have reduced to almost half when bleaching of pulp is changed from conventional CEH sequence to ODEH sequence.

CONCLUSION

Introduction of oxygen in the bleaching sequence can give brighter pulp without any loss of physical property but considerably reducing pollution load in the effluents.