Oxygen Delignification of Unbleached Hardwood Pulp - A Bench Scale Study at SPB

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ABSTRACT: Conventionally, unbleached kraft pulp is bleached with elemental chlorine and chlorine compounds. The chloride ions generated from chlorine and chlorine compounds react with lignin, and appear in bleach plant effluent as "organochlorine" resulting in increased pollution load to the stream.

Due to various reasons, cost of chlorine is increasing steeply in recent times.

Considering the escalating cost of chlorine, its adverse environmental effect and the industry's commitment to society in the reduction of pollutants to the environment, it is imperative to restrict the use of chlorine to the maximum possible extent in the bleaching process.

This is possible by delignification of unbleached pulp entering the bleach plant.

As the extent of delignification of raw material during pulping process has its own limitations, the most suitable eco-friendly method of achieving this goal is extended delignification prior to bleaching using molecular oxygen.

Extended delignification of brown stock washed pulp by molecular oxygen in the presence of caustic soda has the following advantages-

- *higher bleaching process efficiency*
- *lower chlorine consumption*
- *higher black liquor solids to chemical recovery system*

With above mentioned back drop, bench scale studies were carried out to optimise the conditions in oxygen delignification stage at medium consistency (10%) level with unbleached hardwood pulp from the final stage of brown stock washer. Studies were carried out to evaluate the effect of sequestering agents during oxygen delignification. The pulp obtained from optimised condition of oxygen delignification stage was bleached by C/H sequence and compared with conventional (C/EH/H) bleached pulp (without oxygen delignification) with respect to pulp and effluent characteristics and bleach chemical consumption.

The study revealed that, there is considerable reduction in total chlorine consumption by introducing oxygen delignification stage prior to bleaching.

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INTRODUCTION

Environmental protection is the utmost priority of the industry. In an integrated chemical pulp and paper mill, the bleach plant constitutes the major source of pollutant emissions in the mill effluent. In order to reduce the pollution load of the effluent, steps to be taken are to reduce colour, chemical oxygen demand, biochemical oxygen demand and total dissolved solids from it.

Most of the Indian Paper mills are adopting pulp bleaching sequence with chlorine as gas and other chlorine compounds. The chlorine atoms applied in some form of bleaching chemical will end up as chloride ions, while the remaining chlorine atoms are covalently bound to carbon atoms in the pulp, which is known as "organochlorine" (1). This organochlorine comes out through filtrate from the bleaching process, and is measured as adsorbable organic halide (AOX), chlorinated dioxins and furans etc. From a study of a Canadian team, it has been found out that, chloro organic compounds are present even in the effluent of non-bleach kraft mills due to the use of PVC/FRP lining of pipes and use of polymeric sealants in the process.

However, with the purpose of reducing the environmental pollution impact from paper mills regarding effluent as well as the usage of chlorine containing compounds, several measures have to be taken to modify the pulping and bleaching techniques.

The amount of chlorine consumption during bleaching process depends on the kappa number of pulp (which is a measure of lignin content in pulp) entering the bleach plant. Reduction in the usage of this pollutant (chlorine) in bleaching process can be achieved by reducing the lignin content of incoming pulp to bleach plant. It has been reported that (2,3), the oxygen delignification stage reduces the lignin input to the bleach plant by 40 - 50%, thereby effecting a substantial reduction in the generation of chloro - organics and/ or savings in chemical costs can be realised.

The development of oxygen delignification/ bleaching is felt imperative in the light of environmental, economic, and emergy related considerations (4,5,6). It is reported that (7), substantial reduction in bleach plant effluent (AOX, BOD, colour etc.) can be realised by oxygen delignification of the unbleached pulp in alkaline medium.

Delignification of brown stock washer pulp with molecular oxygen in the presence of caustic soda is conceived as a non-polluting step in which effluents free of chlorides, could be recycled to the recovery system by which the sodium and heat values can be recovered. At the same time, the organic matter which accounts for much of the effluent colour, is burnt in the recovery furnace.

Considering the above benefits in respect of environmental aspects, oxygen delignification experiments were carried out with hardwood pulp (of kappa number 25) in R&D laboratory.

In the present study, several parameters such as alkali dose, oxygen pressure and reaction time, were optimised during oxygen delignification stage in respect of kappa number reduction and brightness improvement of pulp. The pulp obtained from optimised oxygen delignification, was bleached with C/H bleaching sequence and compared with the pulp obtained from C/E_H/H and C/E/H/H bleaching sequences were also studied.

Fundamental aspects involved in oxygen delignification stage

i. Oxygen delignification is a function of alkali charge (8).

ii. Alkali is consumed by acids generated in the oxidation.

iii. Delignification in an oxygen - alkali system is the result of alkali promoted oxidative and hydrolytic processes.

iv. Carbohydrate degradation limits reaction temperature and alkali charge (8).

v. Oxygen pressure and ionic strength are of minor importance (8).

Like chlorine, oxygen undergoes one electron transfer oxidative processes, but also is reduced to hydrogen peroxide which selectively oxidizes the chromophoric structures. In a sense, oxygen bleaching entails reaction characteristics for both acid chlorination and peroxide bleaching (9).

As a result, a substantial amount of lignin is being removed from pulp and improvement in brightness of pulp is being achieved during oxygen delignification stage.

The main challenge in bleaching with oxygen is to generate just enough hydroxyl radicals to maintain acceptable rates of oxidative processes (auto-oxidation) without initiating excessive damage to carbohydrates.

CONSISTENCY ASPECTS

From several earlier studies (10,11,12), it has been reported that, the medium consistency system during oxygen delignification offers following advantages over the high consistency system--

i. low steam requirement due to efficient use of blow heat;

ii. flexibility in layout and use of simpler equipments;

iii. less corrosion due to lower consistency;

iv. more lignin removal with less carbohydrate degradation;

v. lower quality of explosive vapours and gases;

In view of above mentioned advantages and process feasibility, the present oxygen delignification study is carried out at medium consistency level (10% consistency) of pulp.

LOCATION OF OXYGEN EXTRACTION STAGE

Since reduction in consumption of chlorine as gas as well as avoiding pollution load to stream are the two main objectives, the location of extended delignification stage with molecular oxygen is best suitable between 3rd and 4th stage in brown stock washing system.

EXPERIMENTAL

For this study, unbleached hardwood pulp of 25 kappa number was taken. The physical strength properties of unbleached pulp were evaluated for control purpose and details are presented in table-1.

Table-1.

Unbleached hardwood pulp properties (Control)

Particulars	Unit	Test value
Kappa number of pulp	no	25
Brightness of pulp (TB)	%	22
Initial freeness of pulp	°SR	17
PFI revolutions	no	1300
Final freeness of pulp	°SR	40
Burst factor	-	36
Tear factor	-	104
Breaking length	m	6600
Wet zero span breaking length	m	12,100
Pulp viscosity (1% Cupram, solution at 20°C)	cps	20

Optimisation of conditions in oxygen delignification stage were carried out in C C L digester by varying oxygen pressure (6,8 & 10 kg/cm²), alkali dose (1.5%, 2% and 2.5% on OD pulp), and retention time at 100°C (30 and 60 minutes). Pulp consistency (10%) and reaction temperature (100°C) were kept constant. The optimisation study was done with respect to reduction in pulp kappa number. The optimised results are presented in table-2.

Table-2.

Oxygen delignification of hardwood pulp (at optimised conditions)

Unbleached pulp kappa number : 25.0
Unbleached pulp brightness (TB), % : 22.0

Particulars	Unit	Test value
Caustic dose (on O.D. pulp basis)	%	2.0
Oxygen pressure	kg/cm²	10.0
Reaction temperature	°C	100
Reduction time	min.	60
Pulp consistency	%	10.0
Final pH	-	10.2
Kappa number of pulp	no	13.0
Reduction in kappa number	%	48.0
Brightness of pulp (TB)	%	39.0

The effect of sequestering agents were studied with Magnesium sulphate and sulphuric acid. In this study, the conditions in oxygen delignification stage were maintained at oxygen pressure of 10 kg/ cm², alkali dose of 2.5% and retention time of 30 minutes. Magnesium sulphate was added to pulp at the dosage of 0.1% and then pulp was taken for oxygen treatment. The effect of sulphuric acid was studied by adding 1.5% dose of concentrated sulphuric acid on O.D. unbleached pulp to attain 3.0 pH, at the pulp consistency of 5% for 60 minutes and at ambient temperature. After acid treatment the pulp was washed thoroughly and then the pulp was taken for oxygen treatment. The kappa number, brightness, viscosity and wet zero span breaking length were determined for the pulp obtained without using sequestering agent and by treating with magnesium sulphate and sulphuric acid separately. The results are tabulated in table-3.

Table-3.

Test results of oxygen delignification of pulp with and without sequestering agents

Particulars	Unit	Control	1	2	3
Oxygen pressure	kg/cm²	-	10	10	10
Caustic dose	%	-	2.5	2.5	2.5
Pulp consistency	%	-	10	10	10
Reaction temperature	°C	-	100	100	100
Reduction time	min.	-	30	30	30
Final pH	-	-	11.10	11.3	11.3
Kappa number of pulp	no	25.0	12.9	14.0	14.0
Brightness of pulp (TB)	%	22.0	39.0	38.0	38.0
Wet zero span breaking length	m	12,100	11,200	11,600	11,500
Viscosity of pulp	cps	20.0	17.9	18.7	18.8

1. **Without sequestering agent**
2. **Pretreated with $MgSO_4$ at 0.1% dose, 10% consistency, for 3-4 minutes.**
3. **Pretreated with H_2SO_4 at 1.5% dose to attain 3.0 pH, 5% consistency, 60 minutes retention time at ambient temperature, after treatment, the pulp washed thoroughly.**

The pulp obtained from optimised oxygen delignification stage was bleached with C/H sequence to attain the pulp brightness of 80 ± 1%. For comparative study the unbleached pulp was bleached in C/E_H/H and C/E/H/H sequences separately to attain the same brightness level of 80 ± 1%. The bleaching date of all the three bleaching processes are presented in table-4.

Table-4.

Bleaching data of hardwood pulp

Particulars	Unit	E_O/C/H	C/E_H/H	C/E/H/H
Kappa number of pulp	no	13*	25	25
Chlorine consumed				
as gas	%	3.15	5.7	5.7
as hypo	%	1.56	3.2	2.4
Total caustic applied	%	2.8**	1.5	2.1
Brightness of bleached pulp (TB)	%	81	81	80
Bleached pulp yield	%	94.5	95.7	96.1
Post colour number of pulp	no	3.1	4.6	3.4
Viscosity of bleached pulp (1% Cupram solution at 20°C)	cps	12.2	10.4	11.5

* after E_O stage
** including E_O stage
*** unbleached pulp viscosity is 20 cps

The physical strength properties of bleached pulp obtained from E_O/C/H, C/E_H/H, C/E/H/H bleaching sequences were evaluated separately and presented in table-5.

Table-5.

Physical strength properties of hardwood pulps

Particulars	Unit	Unbleached (control)	E_O/C/H	C/E_H/H	C/E/H/H
Initial freeness of pulp	°SR	17	19	19	19
PFI revolutions	no	1300	1100	1100	1100
Final freeness of	°SR	40	39	41	40
Burst factor	-	36	38	35	34
Tear factor	-	104	100	96	96
Breaking length	m	6600	5800	5900	5900
Wet zero span breaking lenght	m	12,100	10,900	10,100	10,300

The effluent obtained from each stage of E_O/C/H, C/E_H/H and C/E/H/H bleaching sequences were studied separately with respect to pH, total solids, colour, chemical oxygen demand and biochemical oxygen demand. The findings of the effluent characteristics are given in table-6.

Table-6.

Effluent characteristics at each stages of bleaching sequence

Particulars	Unit	E_O/C/H			C/E_H/H			C/E/H/H			
		E_O stage	C stage	H stage	C stage	EH stage	H stage	C stage	E stage	H stage	H stage
pH of extracted water	-	10.2	1.9	7.8	1.9	7.6	7.6	1.9	9.11	8.4	8.2
Total solids	gpl	6.1	1.6	6.4	1.1	7.7	1.5	1.1	1.7	9.4	2.1
Residual alkali	gpl	0.9	-	-	-	-	-	-	-	-	-
Colour	P.C.U.	10375	130	700	190	470	50	190	4100	472	40
COD	ppm	5090	320	1080	454	1950	250	454	1900	636	230
BOD_5	ppm	410	90	270	150	425	75	150	395	220	14

The reduction in colour, BOD and COD of the effluent obtained through oxygen bleaching over to C/E_H/H and C/E/H/H bleaching sequences were calculated in kilograms per ton of pulp used for bleaching and tabulated in table-7

Table-7.

Removal of colour, BOD_5 and COD content using oxygen delignification stage

(C/E_H/H - bleaching sequence.)

Stage	Colour kgs/ton	COD kgs/ton	BOD kgs/ton
C	6.1	14.7	4.9
E_H	4.2	17.6	3.8
H	0.5	2.3	0.7
	10.8	34.6	9.4

(C/E/H/H - bleaching sequence.)

Stage	Colour kgs/ton	COD kgs/ton	BOD kgs/ton
C	6.1	14.7	4.9
E	36.9	17.1	3.6
H	4.3	5.7	2.0
H	0.4	2.1	0.7
	47.7	39.6	11.2

Table - (Continued)

(E_O/C/H - bleaching sequence.)

Stage	Colour kgs/ton	COD kgs/ton	BOD kgs/ton
E_O	Recycled	Recycled	Recycled
C	4.2	10.3	2.9
H	6.3	9.7	2.4
	10.5	20.0	5.3
	3	42	44
	78	50	53

% reduction over C/E_H/H sequence
% reduction over C/E/H/H sequence

RESULTS AND DISCUSSIONS

A. Optimisation of process conditions in oxygen delignification stage-

Results of optimisation studies indicated that, at the oxygen pressure of 10 kg/cm², maximum reduction in kappa number of pulp (Fig 1, 2 & 3) and the improvement of brightness of pulp is attained (Table-2). At this level of oxygen pressure, The alkali dose of 2.5% on O.D. pulp and retention time of one hour is resulting in maximum reduction in kappa number of pulp (50.4%). Since, the kappa number of pulp obtained from the alkali dose of 2.0% and 2.5% for the retention time of one hour is not having significant difference, the conditions of 10 kg/cm² oxygen pressure. alkali dose of 2.0%, reaction temperature of 100°C and retention time of 60 minutes are taken as optimised conditions for the oxygen delignification stage, with a view to conserve alkali dosage.

Fig 1 Alkali Dosage Vs Kappa No. of pulp

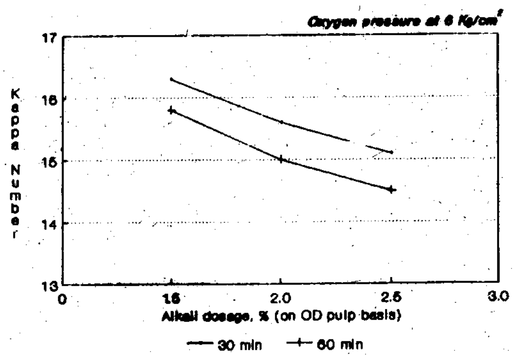


Fig 2 Alkali Dosage Vs Kappa No. of pulp

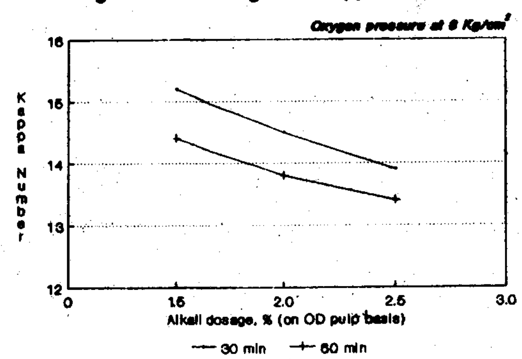
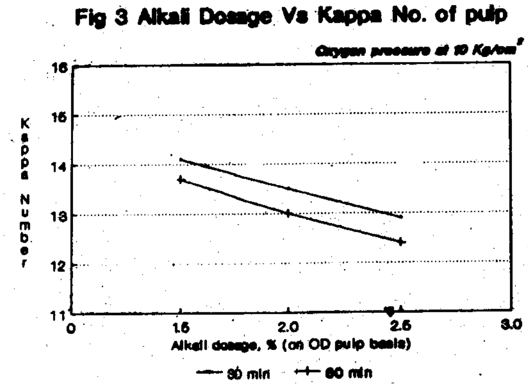


Fig 3 Alkali Dosage Vs Kappa No. of pulp



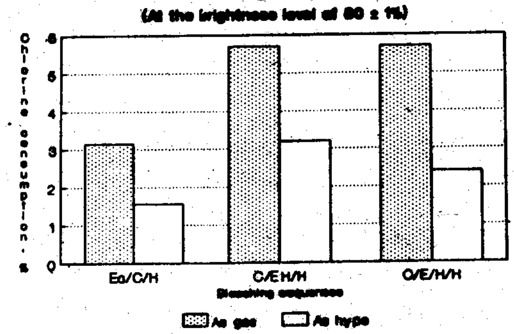
B. Effect of sequestering agents

By pretreating the unbleached pulp with sequestering agent such as either magnesium sulphate or sulphuric acid, there is some improvement in viscosity and wet zero span breaking length of oxygen delignified pulp (Table-3). But with the treatment of magnesium sulphate or sulphuric acid prior to oxygen delignification stage, decreases the delignification rate, as shown by the increase in kappa number and decrease in brightness of oxygen treated pulp. since, in these mild conditions of oxygen delignification stage there is no significant improvement in viscosity of pulp by the treatment of sequestering agent, the present oxygen delignification experiments were carried out without pretreating the unbleached pulp with sequestering agent.

C. Bleaching chemical consumption

As the pulp obtained after oxygen delignification stage is having the kappa number of 13, compared to original unbleached pulp kappa number of 25, it is obvious that, the requirement of bleach chemical will be much lesser in case of oxygen delignified pulp compared to the conventional bleaching sequences such as C/E_H/H and C/E/H/H at the same brightness level (Fig.4).

Fig 4. Chlorine consumption in various bleaching sequences
(At the brightness level of 80 ± 1%)



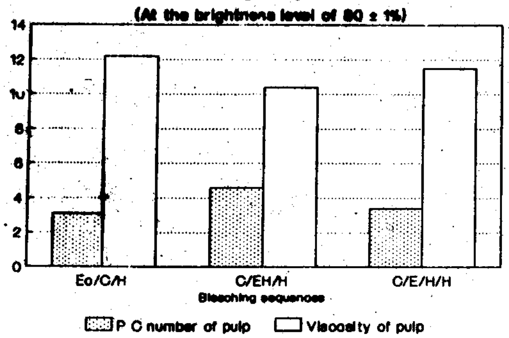
To achieve the same brightness level of 80 ± 1%, there is a substantial reduction (45%) in the consumption of chlorine as gas, due to extended delignification with molecular oxygen. Chlorine consumption as hypo is also showed considerable reduction compared to conventional bleaching sequences (Table.4).

The total alkali consumption in E_0/C/H, C/E_H/H and C/E/H/H bleaching sequences are 2.8% (including E_0 stage), 1.5%, 2.1% respectively. The higher consumption of caustic in `E_0' stage will not cause any appreciable cost burden since the extracted liquor is sent to recovery for reclaiming the chemicals.

D. Pulp quality

The bleached pulp obtained from E_0/C/H sequence is superior in respect of post colour number and viscosity of pulp to that of C/E_H/H and C/E/H/H bleached pulp (Table. 4, Fig. 5). The strength properties of bleached pulp optained from E_0/C/H, C/E_H/H and C/E/H/H bleaching sequences are comparable (Table. 5).

Fig 5. Bleached pulp quality of various bleaching sequences
(At the brightness level of 80 ± 1%)



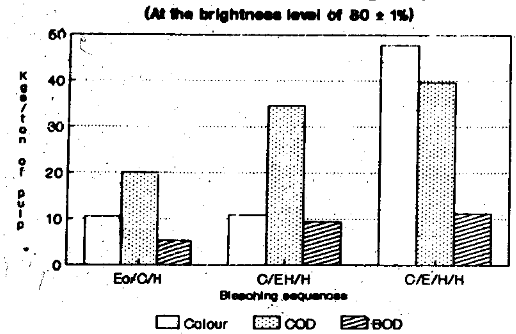
E. Pollution abatement

The reduction in pollution load for a bleach plant preceded by an oxygen stage has been documented in many publications. Table. 6 shows typical effluent properties of each stage of E_0/C/H, C/E_H/H and C/E/H/H bleaching sequences.

The superiority of introducing `$E_0$' stage lies in the fact that, the extracted liquor characterised by high colour, BOD, COD and dissolved solids can be sent back to soda recovery, where it becomes a source of energy as well as chemicals (instead of polluting the stream) unlike in case of conventional `E' stage where the effluent goes to the stream causing pollution.

The colour, COD and BOD aspects of the effluents of C/E_H/H, C/E/H/H and E_0/C/H bleaching processes in kilograms per ton of even dry pulp bleached are presented in table-7 and figure-6. There are significant reductions in pollution loading through oxygen bleaching as compared to the conventional bleaching processes (C/E_H/H and C/E/H/H). With E_0/C/H bleaching sequence, a reduction of 42% in COD, 44% in BOD can be obtained over C/E_H/H bleaching sequence. In respect of colour of the effluent there is a marginal reduction is achieved over C/E_H/H bleaching. A reduction of 78% in colour, 50% in COD and 53% in BOD can be achieved through E_0/C/H bleaching process over C/E/H/H bleaching sequence.

Fig 6. Total pollution load in the effluent of various bleaching sequences
(At the brightness level of 80 ± 1%)



The reduction in pollution load of E_0/C/H bleaching sequence is due to the reduction in kappa number of pulp in the oxygen stage (i.e., prior to chlorine bleaching stage). A oxygen stage can also be of benefit in the reduction of chlorinated organics such as phenolics and chloroform. These are potentially hazardous because of their toxic and carcinogenic nature. With an oxygen stage upstream of the bleach plant, the total amount of chlorinated organic compounds formed will be decreased considerably, typically in proportion to the drop in kappa number.

CONCLUSIONS

The oxygen-alkali delignification before chlorination in E_0/C/H bleaching sequence offers a definite advantage over the conventional bleaching sequences (C/E_H/H and C/E/H/H) in respect of lower elemental chlorine consumption, lower total bleach chemical consumption, improved pulp quality.

The most important advantage can be obtained by introduction of molecular oxygen prior to bleaching sequence is the reduction of substantial amount of pollution loads from bleachery effluents, as the filtrate obtained from E_o stage (uncontaminated by chloride ion) can be routed back to the recovery furnace for chemical recovery. Moreover, when oxygen delignification will be introduced in between brown stock washers i.e., prior to brown stock screening, the toxicity of the screen room effluent and pitch deposition on the screen room equipment can be reduced substantially.

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