

# Modified Oxygen Pretreatment of Unbleached Pulp of Indigenous Raw Material For Better Bleachability

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## ABSTRACT

The oxygen pretreatment of unbleached pulp of fibrous raw material used for papermaking is world wide well established technology for reduction of pulp kappa number. In context of Indian paper industry, the indigenous raw material like bagasse, wheat straw, eucalyptus and bamboo has responded well at laboratory scale. Though there are only few mills ( based on hardwood, bamboo and bagasse) which has installed the oxygen pretreatment technology in their fiber line.

The kappa number reduction after oxygen pretreatment for pulp of different indigenous raw materials ranges between 40-60%, The reduction of unbleached pulp kappa number further lead to low bleach chemical demand and lower effluent generation during bleaching, depending on the quality of raw material and types of lignin. But it is observed that normally industrial oxygen treatment operate around 20% below their delignification potential i.e. compared to what can be obtained in laboratory experiments.

The efficiency of oxygen treatment technology is of great concern considering the scale of operation in Indian Paper Mills and high cost of technology. Literature reveals number of studies carried out to enhance the efficiency of oxygen treatment technology. It includes the treatment of oxygen along with some additional chemical, change in treatment conditions etc.

To meet out norms set by government for paper mill effluent discharge, Indian paper mills are looking for the modern technological options, which are cost effective and support their scale of operation. In the present study, the work is carried out on oxygen treatment and modified oxygen treatment (treatment along with peroxide) of pulp of Indian raw materials as bagasse, wheat straw, eucalyptus and bamboo. A comparison of characteristics of unbleached pulp, oxygen treated pulp and modified oxygen treated pulp followed by DEpD bleaching was carried out.

The study results in substantial drop in unbleached pulp kappa number after modified oxygen treatment, viz. 80, 76,62,63% compared to oxygen treatment viz.53,62, 47 and 55% respectively for bagasse, wheat straw, eucalyptus and bamboo. There was not any appreciable difference in pulp intrinsic strength after modified oxygen treatment and it has been preserved during the treatment (962, 823, 569 and 734 cc/g) compared to oxygen treated pulp (816, 863,544 and 750 cc/g) respectively for bagasse, wheat straw, eucalyptus and bamboo pulp. There is significant gain in brightness after modified oxygen treatment viz. 54, 66, 51 and 46 % ISO compared to oxygen treatment viz.38, 48, 41, 37 % ISO respectively for bagasse, wheat straw, eucalyptus and bamboo . The impact of better delignification and better initial brightness is also observed in DEpD bleached pulp brightness. There is 1-4 point gain in DEpD bleached pulp brightness for modified oxygen treated pulp as 88,87,85 and 86.5 % ISO compared to oxygen treated pulp 85, 85.4, 83 and 83.5 % ISO respectively for bagasse, wheat straw, eucalyptus and bamboo .

## INTRODUCTION

The paper Industry in India is in the process of undergoing technological changes to increase productivity, improve product quality and meet CREP (Corporate responsibility for environment protection) by 2008. But the changes are not as fast as it needs to be especially in pulping and bleaching. Most of the mills are still using conventional batch digester for cooking of raw material, and hence production of a low unbleached pulp kappa number (>15) is not viable. This affects negatively on unbleached pulp yield and strength. The bleaching of unbleached pulp of low kappa number

results in better leachability and low effluent load. Post digester treatment of unbleached pulp by oxygen reduces, bleach chemical demand substantially. Some of the large paper mills have adopted oxygen pretreatment technology, but the number is in single figure.(1)

### Cooking Conditions:

Parameter	Raw material			
	Bagasse	Wheat Straw	Eucalyptus	Bamboo
Bath ratio	1:5	1:5	1:4	1:4
Cooking temperature °C	<b>155</b>	<b>155</b>	<b>165</b>	<b>168</b>
Cooking time, min.	120	120	120	120

The adoption of oxygen pretreatment technology is a costly affair and it needs better treatment efficiency in order to reduce the payback period. In comparison to laboratory scale results of kappa number reduction after oxygen treatment which is ~50% the mill scale results achieved in between

### Conditions for Acid treatment

Pulp consistency	:	10%
pH maintained	:	3-4
Treatment temp.	:	65 °C
Treatment time	:	30 minutes

### Oxygen treatment conditions:

Pulp consistency	:	10%
NaOH charged	:	2.0 %
Hydrogen peroxide	:	0.5 %
Oxygen pressure	:	0.6 Mpa
Treatment temp.	:	90 °C
Treatment time	:	60 minutes

35-40% drop in unbleached pulp kappa number after oxygen pretreatment.

The acid pretreatment of unbleached pulp is discussed in literature for the minimization of soda carryover and better bleaching point of view, but in some recent studies, the elimination of hexenuronic acid (HexA) by acid pretreatment and reduction of bleach chemical demand is discussed. (2). The unsaturated sugars derived from hemicelluloses undergoes alkaline degradation during pulping and form glucuronic acids, also called hexenuronic acid, HexA. These compounds readily consume bleaching reagents such as chlorine, chlorine dioxide, ozone, and hydrogen peroxide (3).

Analysis of hardwood data indicates that HexA contribute approximately 20-60% of total kappa number for the commercial hardwood kraft pulp (4).

It can be eliminated by acid pretreatment in certain conditions. And this can follow in bleach chemical requirement of unbleached pulp. ECF bleaching studies of birch kraft pulp suggested that an acid hydrolysis stage prior to Do stage could lead to a 50% reduction in bleaching cost (5). Acid pretreatment prior to oxygen pretreatment along with peroxide fortified treatment can lead to enhanced efficiency of oxygen pretreatment technology.

In the present studies we have combined the two-treatment stage, acid pretreatment, followed by Op (oxygen fortified with hydrogen peroxide) pretreatment of pulp. This combination of two treatment followed by DEpD

bleaching of indigenous non-wood raw materials viz bagasse, wheat straw, eucalyptus and bamboo is studied. A comparison with oxygen pretreatment followed by DEpD bleaching of these raw materials is also given here.

## EXPERIMENTAL

### Collection of raw material

The raw material samples viz. bagasse, wheat straw, eucalyptus and bamboo were collected from different sources and kept in a polythene bag to attain an uniform moisture level, before pulping experiment.

### Optimization pulping chemical requirement

Optimization of soda/ Kraft pulping chemical requirement to obtain desired kappa numbers was carried out with different chemical dosage to attain a desired kappa number.

Experiments were performed in a series digester consisting of six bombs each of 2.5-liter capacity, rotating in an electrically heated polyethylene glycol bath. At the end of the cooking time, the bombs were removed and quenched in the water tank to cool down and the cooked mass from each bomb was taken for washing. Washing was carried out with hot water till the cooked mass was free from spent liquor. After through washing, the unscreened pulp yield was determined and the pulp was screened in laboratory 'Somerville' screens by using mesh of 0.25 mm slot width. Kappa number of the screened pulp was determined as per the Tappi

standard procedure T-236-OS-76. The cooking conditions are given table on previous page.

## ACID TREATMENT OF UNBLEACHED PULP

Acid-alkaline peroxide treatment (AALP) of the pulp was given in polythene bags in a water bath maintaining the conditions for consistency and pH. Acid treatment followed by alkaline peroxide treatment was given in the similar conditions of time temperature and consistency.

### Oxygen pre-treatment of pulp

Oxygen pre treatment of unbleached pulp samples were carried out in Quantum mixer. Pulp weighing 250 gm was taken for each oxygen treatment in reactor vessel. After mixing the sodium hydroxide to the pulp, the pulp was pre-heated in the microwave oven to 90°C and pH of the pulp was determined. Volume of the reactor vessel is 3.5 liters and it is electrically heated, the temperature of the reactor vessel was maintained 95°C prior starting the experiment. The preheated pulp was placed in reactor vessel. The oxygen gas was injected in to the reactor vessel through the cylinder. Mix time/heat transfer time was given after every 15 minutes for 12 seconds. The oxygen treatment was given using following conditions.

### Oxygen treatment conditions

pH of pulp was determined after oxygen treatment. Kappa number, brightness, viscosity and yield of the oxygen treated pulps were determined after thorough washing of the pulp.

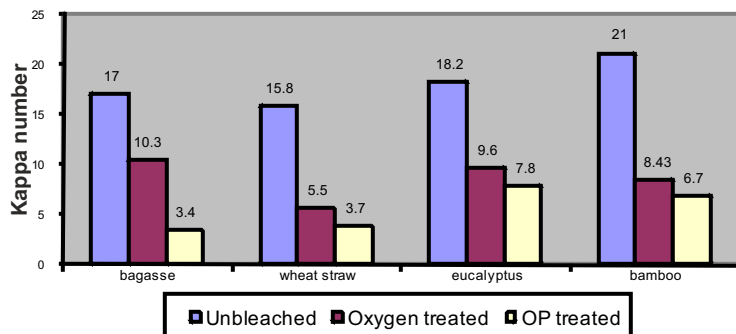
## BLEACHING EXPERIMENTS

Bleaching experiments were carried out on unbleached pulps of different raw materials by DEpD sequence. The standard optimized conditions were maintained during the bleaching experiment. Bleaching conditions used for different stages of bleaching are recorded in table below.

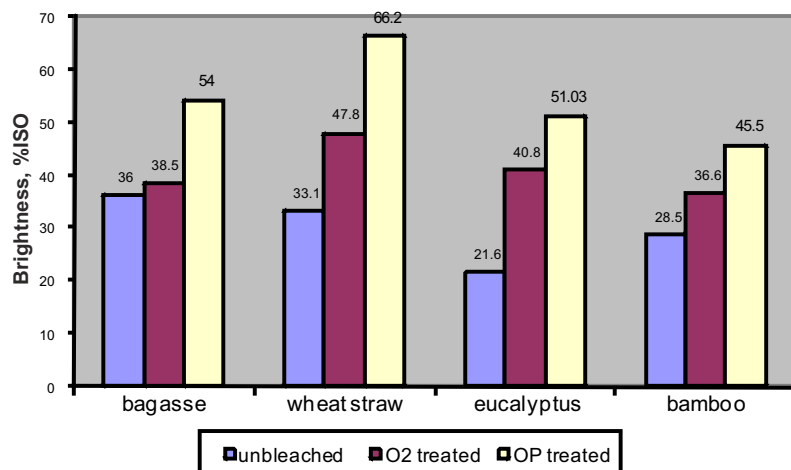
	Unit	D1	Ep	D2
Consistency	%	5	10	8
Reaction time	Min	60	60	180
Temperature	°C	50	70	75

**Table 1**  
**Unbleached pulp characteristics of different raw material**

Parameters	Bagasse	Wheat straw	Eucalyptus	Bamboo
Cooking process	Soda AQ	Soda AQ	Kraft	Kraft
Cooking chemical NaOH/Na <sub>2</sub> O%	15	15	16	18
Unbleached pulp kappa	17	15.8	18.2	21
Unbleached pulp brightness, %	36	33	21.6	28.5
Unbleached pulp viscosity cm <sup>3</sup> /g	1020	863	650	953



**Fig. 1 - Kappa number of pulp samples**



**Fig -2 Initial Brightness of Pulp samples, %ISO**

## RESULT AND DISCUSSION

### Pulping of raw material

The results of pulping experiments are given in table 1. The cooking conditions were selected according to produce unbleached pulp of kappa number in the range of 15-21. It is indicated by the table that unbleached pulp brightness of three raw materials

### Effect Of ODL And A-Op Treatment On Pulp Kappa Number

The impact of oxygen pretreatment and A-Op pretreatment is shown below in figure 1

The impact of modified treatment is observed in all four raw materials but it was maximum in case of bagasse, followed by wheat straw bamboo and eucalyptus

### Effect Of ODL And A-Op Treatment On Unbleached pulp brightness

The impact of A-OpDI on unbleached pulp brightness is depicted in fig. 2

It is indicated by fig. 2 that Acid followed by Op treatment has good impact on pulp brightness, before bleaching. The unbleached pulp brightness which was 36, 33.1, 21.6 and 28.5% iso for four raw materials, bagasse, wheat straw, eucalyptus and bamboo has increased to 54, 66.2, 51.03 and 45.5% iso after the treatment. A comparison of brightness gain after ODL treatment is also shown in figure.

### Effect Of ODL And A-Op Treatment On Unbleached pulp Viscosity

The impact of ODL and A-OpDL treatment is given below in fig. 3

The ODL treatment resulted in drop of viscosity, the trend is similar in case of A-OPDL treatment.

### Effect Of ODL And A-Op Treatment On DEp Stage brightness

The effect of ODL and A-OP DL treatment on DEp stage brightness is shown in fig. 4

It is observed that effect of A-Op treatment on brightness after DEp stage is very positive. Since initial brightness of unbleached which has improved by ODL and A-OpDL treatment resulted further gain in DEp stage brightness also. Only after DEp stage the brightness was 80, 81, 77 and 78% iso for bagasse, wheat straw, eucalyptus and bamboo respectively.

### Effect Of ODL And A-Op Treatment On DEp Stage Viscosity

The impact of DEp treatment on intrinsic viscosity of the pulp sample is depicted in fig. 5

There is no negative impact on DEp stage viscosity was observed after A-Op Preachment of pulp

### Effect Of ODL And A-Op Treatment On DEpD Stage Brightness

The impact of ODL And A-OpDL treatment on DEpD brightness is shown in fig 6

As indicated in fig the response of A-OpDL treated pulp on DEpD bleached pulp brightness for all four raw materials is very positive. The brightness of pulp after DEpD bleaching is very low as 83, 83, 82 and 81%ISO for bagasse, wheat straw, eucalyptus and bamboo pulp

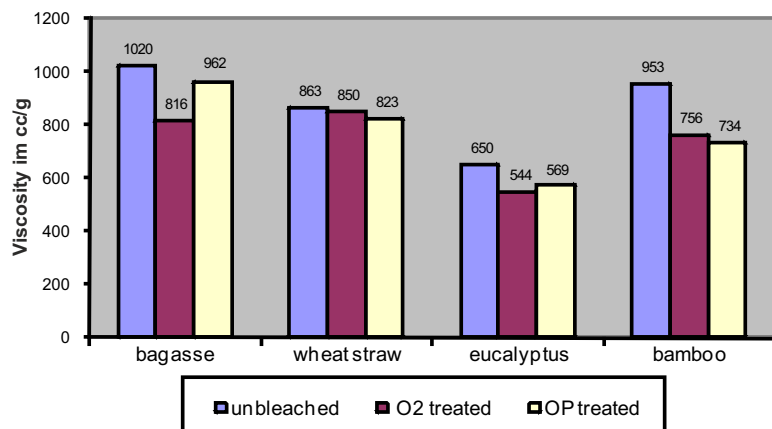


Fig 3-Initial Viscosity of Unbleached pulp(cc.g)

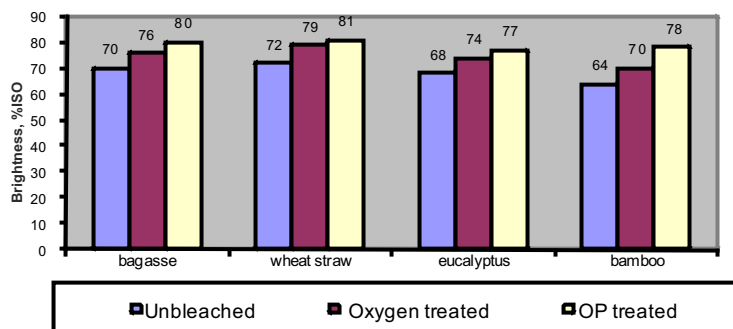


Fig 4- DEp Stage Brightness, %ISO

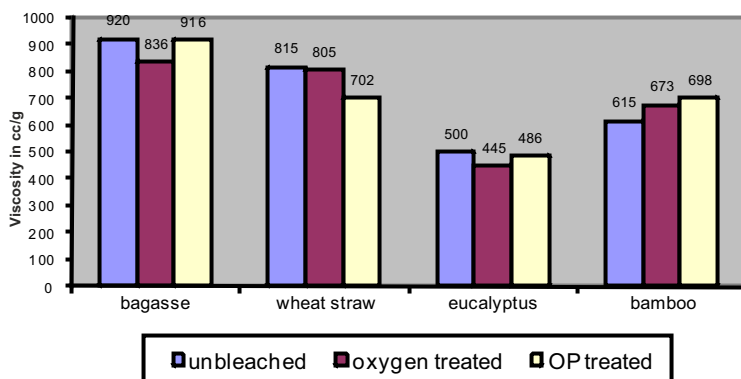


Fig. 5 DEp Stage Viscosity (cc/g)

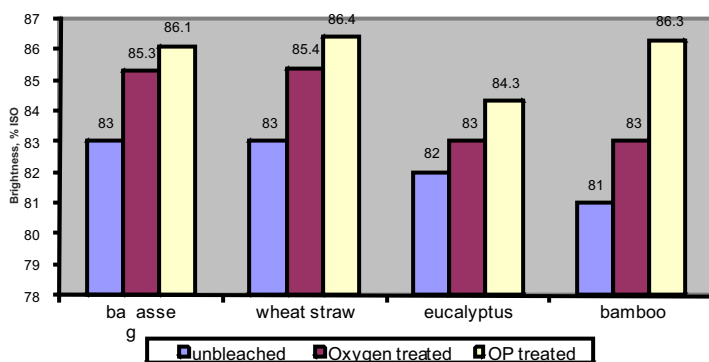


Fig. 6 DEpD Stage Brightness, %ISO

respectively. The brightness of ODL pulp after DEpD bleaching is increased to 85.3, 85.4, 83 and 83%ISO for bagasse, wheat straw, eucalyptus and

bamboo pulp respectively. The brightness of pulp after AOp-DEpD bleaching is enhanced to 86.1, 86.4, 84.3 and 86.3%ISO for bagasse,

wheat straw, eucalyptus and bamboo pulp respectively. The acid pretreatment extract out the hexenuronic acids which are ultimately responsible for poor final brightness as clearly indicated in fig. 6

### Effect Of ODL And A-Op Treatment On DEpD Stage Viscosity

The impact of DEpD bleaching on untreated, ODL treated and A-Op treated pulp is shown in fig. 7

The viscosity of pulp remained unaffected after DEpD bleaching of ODL and AOp treated pulp in comparison of untreated pulp. There was very marginal affect on pulp viscosity in case of bagasse and bamboo.

### The Total Chlorine Demand of Pulp

The consumption of chlorine as dioxide is depicted in fig. 8

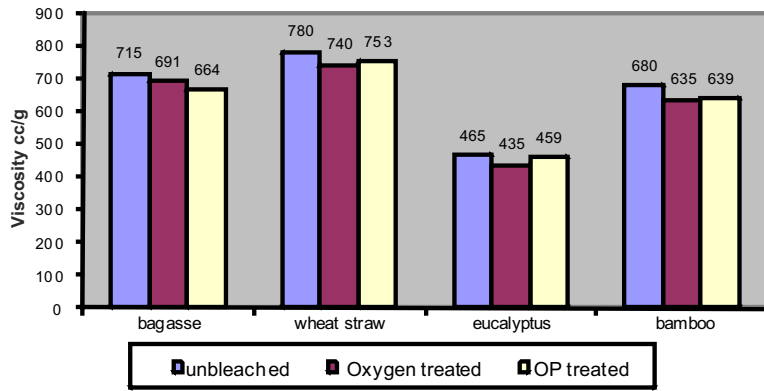
The total chlorine demand is directly related to pulp kappa number entering to bleach plant. The total chlorine demand for A-Op treated pulp is lowest for all four raw materials, as indicated in figure

### CONCLUSIONS

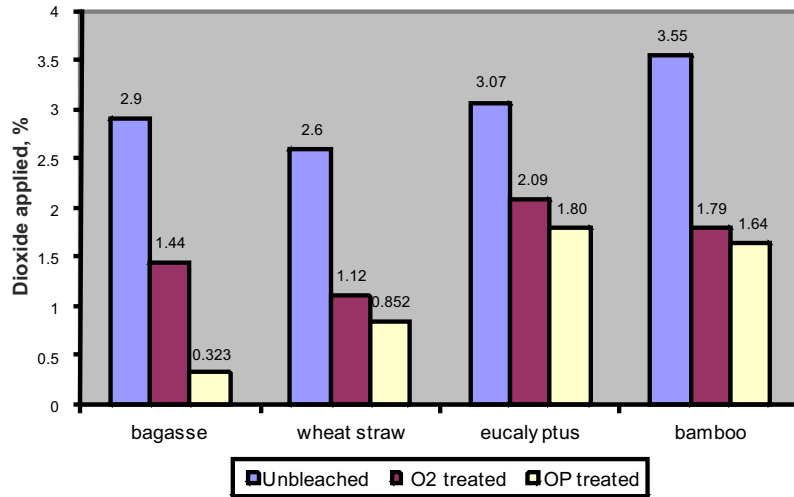
- In terms of compatibility of A-Op with ODL treatment, Acid treatment followed by oxygen fortified peroxide treatment enhance the performance of oxygen treatment.
- A sharp drop in unbleached pulp kappa number after AOp treatment has resulted in lower bleach chemical demand, better brightness gain low bleach plant effluent load.
- A-Op treatment is resulted in better final brightness in comparison to oxygen pretreatment (ODL) and untreated pulp.
- It does not has any negative impact on pulp intrinsic viscosity after DEpD stage brightness.

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**Fig. 7 DEpD Stage viscosity, cc/g**



**Fig. 8 Total Chlorine demand in DEpD bleaching, %**

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