# A Predictive Model of ODE<sub>P</sub>D Elemental Chlorine Free Bleaching Sequence for Wheat Straw Soda Pulp

# **U.K.Ghosh and A.M.Singh**

The response of wheat straw soda pulp in various bleaching stages depends on the condition of the pulp entering that stage. To achieve target brightness with minimum amount of  $\mathrm{ClO}_2$  it is necessary to optimize the chemical dose in different stages. In this investigation wheat straw pulps were produced by soda pulping process at different alkali charges. The resulting pulps after oxygen delignification were bleached through  $\mathrm{DE}_p\mathrm{D}$  elemental chlorine free (ECF) bleaching sequence with various combinations of chemical charge in the two different D stages. Oxidative alkali extraction (E<sub>p</sub>) was done at constant conditions. The bleaching process was simulated by a model consisting of simple equations that describe the relationship between brightness development and variation in the chemical doses in different D stages, together with additional equation that relates the  $\mathrm{D}_2$  stage response parameter to the outcome of the  $\mathrm{E}_p$  stage.

Keywords: Wheat straw, Soda pulping, ECF bleaching, Mathematical model, Optimization

#### INTRODUCTION

For pulp mills, the major concern of conventional and non-conventional pollutants is from the bleach plant. Ever increasing cost of bleach chemicals and strict legislation of the pollution control authorities has forced the paper industry to optimize various bleaching processes to be effective in a most economical way. To get a complete description of the bleaching process, many variables including bleach sequence, characteristics of the entering pulp, retention time, operating temperature, conditions of the inter-stage bleach washing, mixing efficiency in the mixer, etc. are to be taken into account. However, development of such highly complex model is virtually

Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur 247001. impossible and may be necessary to simulate process dynamics only. Sklarewitz and Parker [1] developed a dynamic bleach plant models for CEDED bleaching sequence. The models were concerned only with chemical species and no attempt has been made to predict the pulp quality as brightness or viscosity. Axegard and coworkers [2] used kinetic data to develop a model of the DED sequence for an industrial softwood kraft pulp prebleached in an O(C+D)E sequence. Wang and coworkers [3] used mass transfer and kinetic data for modeling of bleach plant operation where consistencies were low and bleach chemical concentrations and pH were kept constant. Gupta and coworkers [4] have developed a detailed optimization scheme for multi-stage bleach plant and simulated a typical bleaching sequence, CEDED, as an example. The control set points were

optimized using annual operating cost as decision variable. The total annual cost as objective function has been formulated and the models were tested with various values of operating conditions such as, consistency, temperature, time of reaction, chemicals consumed and final pH within their respective ranges normally adopted by the industries. A simple steady state model applicable to DED elemental chlorine free bleaching of craft pulp from hardwood prebleached in a D(EO) sequence has been suggested recently by Thomas and coworkers [5]. The process variables selected for study were the amounts of ClO, charged in the second and third D stages. This model finds application in optimizing the load sharing among the different stages of the process for any given target brightness. Also, it can be used to compare the bleachability of different pulps in terms of their minimum bleach chemical requirement to attain a given brightness.

Due to increasing demand of paper products and limited availability of conventional forest based raw materials like wood and absence of organized waste paper collection system in India, the use of alternative raw materials, mainly agro residues, is increasing day by day. Wheat is the second largest crop being produced in India and wheat straw is used as a potential raw material for the manufacture of paper. But it has a major limitation of poor strength properties, which are reduced further in conventional bleaching processes using elemental chlorine hypochlorite. Ghosh [6] showed that wheat straw pulp, obtained through soda process, may be subjected to DEpD elemental chlorine free bleaching sequence after oxygen delignification to produce pulp with high brightness and excellent mechanical strength properties suitable for the manufacture of writing and printing grades of paper. In the present study we developed a steady state model [5] for ODEpD elemental chlorine free short bleaching sequence which is directly applicable to non-wood raw material, like wheat straw soda pulp.

#### Materials and Method

Locally available wheat straw was collected, washed with water, air dried. Proximate analysis of the wheat straw has been reported elsewhere (6). Three sets of pulping experiments were carried out in the laboratory digester at three different alkali charges, keeping other conditions constant. After pulping the pulps were refined, washed and screened. The cooking conditions and the characteristics of the resulting pulps are given in Table 1. Pulps with Kappa number 21 (LK) and 23 (HK) were selected for further bleaching experiments. All the calculations have been done on O.D. basis.

Table 1: Cooking conditions and results of pulping

Active alkali charge as NaOH, %	12	16	20
Bath ratio	1:5	1:5	1:5
Maximum cooking temperature, °C	160	160	160
Time to temperature, min	60	60	60
Time at temperature, min	60	60	60
Kappa number	28	23	21
Screened pulp yield, %	48	45.5	42

Table 2: Experiment results of the D, and E, stage

Pulp	ClO <sub>2</sub> applied	End	Brightnes	Brightness (ISO)	
	in D <sub>1</sub> as %	pН	$D_1$	$\mathrm{E}_{_{\mathrm{p}}}$	
	of O.D. pulp			•	
LK	0.4	4.2	50.6	54.2	
	0.8	4.7	5 <b>7.7</b>	61.9	
	1.2	4.1	62.8	65.1	
	1.8	4.0	66.2	71.0	
HK	0.4	4.6	47.2	51.1	
	0.8	4.5	55.5	59.8	
	1.2	4.1	61.2	64.7	
	1.8	4.7	64.1	67.2	

Table 3: Experiment results of the D, bleaching stage

Pulp	ClO <sub>2</sub> applied	ClO <sub>2</sub> applied	End	Brightness
	in D <sub>1</sub> as %	in D <sub>2</sub> as %	pН	after D <sub>2</sub>
	of O.D. pulp	of O.D. pulp		(ISO)
LK	0.4	0.2	4.5	69.04
		0.4	4.7	77.9
		1.0	4.4	82.32
		1.8	4.2	84.25
LK	0.8	0.2	4.3	75.27
		0.4	4.6	83.79
		1.0	4.2	88.12
		1.8	4.8	88.16
LK	1.8	0.2	4.7	83.27
		0.4	4.8	87.91
		1.0	4.4	89.04
		1.8	4.7	89.2
ΗK	0.4	0.2	4.2	66.6
		0.4	4.7	<b>74.</b> 5
		1.0	4.6	79.8
		1.8	4.1	82.6
HK	0.8	0.2	4.1	73.22
		0.4	4.7	76.1
		1.0	4.6	85.3
		1.8	4.3	87.1
HK	1.8	0.2	4.5	80.8
		0.4	4.7	83.1
		1.0	4.4	87.0
	##	1.8	4.7	88.1

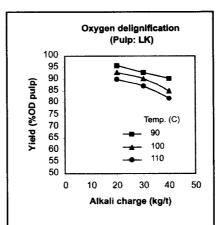
Oxygen delignification of the wheat straw pulps was carried out in the same laboratory digester with three different alkali doses (2, 3 and 4% NaOH) at three different temperatures (90, 100 and 110°C). Oxygen pressure of 6 kg/cm², pulp consistency of 10%, magnesium sulphate charge of 1 kg/t and retention time of 75 minutes, were kept constant in all the experiments.

After oxygen delignification each pulp was divided into four parts which were then treated with different doses of chlorine dioxide in the first D stage (D<sub>1</sub>). Experiments were carried out in polyethylene bags. Sodium chlorite solution was used in this stage. The constant operating conditions for this stage were as follows: temperature, 70°C; pH, 4-5 and time, 2 hours. As oxidative extraction has proved to be a very effective approach to achieve higher brightness pulp [7], all the resulting D, pulps were extracted with caustic with 0.5% hydrogen peroxide (H,O,) added to it, in the extraction stage (Ep). The conditions maintained in the Ep stage were, temperature, 70°C; time, 70 minutes and end pH, 10.5-11. Table 2 shows the experimental results of D<sub>1</sub> and Ep stage. Pulp obtained after extraction was further subdivided into four parts for bleaching with different doses of  $ClO_2$  in the second D stage  $(D_2)$ . Operating conditions for this stage was same as D, stage. Kappa number and brightness were determined according to TAPPI test methods. Results of the D, stage bleaching are recorded in Table 3.

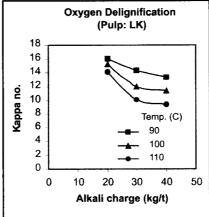
# **RESULTS AND DISCUSSION**

#### Oxygen delignification

Oxygen delignification at various temperatures with different doses of alkali was performed to achieve maximum delignification and minimum carbohydrate degradation. Thus, the target was above 40% reduction in Kappa number with minimum drop in pulp yield. From Fig.1 it can be seen that



**Fig.1**: Effect of alkali charge on pulp yield at different temperatures



**Fig.2**: Effect of alkali charge on Kappa no. at different temperatures

for the pulp with initial Kappa number of 21, yield decreases significantly with increase in temperature and this decrease in pulp yield is more severe in case of higher alkali charge in oxygen delignification stage. Fig.2 shows the effect of alkali charge on Kappa number at different temperatures. It can be observed that increasing the alkali charge from 3% to 4%, Kappa number of the pulp delignified at 100°C, reduced by only 0.2, whereas, the pulp vield was drastically reduced by 5.8% (Fig.1). Similar trend was exhibited by the other pulp with initial Kappa number of 23. Therefore, considering over 90% pulp yield and more than 42% reduction in pulp Kappa number for

both the pulps, it can be concluded that within the domain of the present experimental investigation, oxygen delignification at 100°C with 3% alkali charge gives the optimum result. Optimum conditions for oxygen delignification and pulp characteristics have been recorded in Table 4.

Table 4: Optimum conditions for oxygen delignification and resulting pulp characteristics.

O <sub>2</sub> pressure, kg/cm <sup>2</sup>	6
Consistency, %	10
Time, min	75
Temperature, °C	100
Alkali charge, kg/t	30
MgSO <sub>4</sub> kg/t	1.0
Pulp yield, % (Pulp-LK)	90.4
Pulp yield, % (Pulp-HK)	91.1
Kappa no. (Pulp-LK)	12.0
Kappa no. (Pulp-HK)	13.6

## D<sub>1</sub> stage

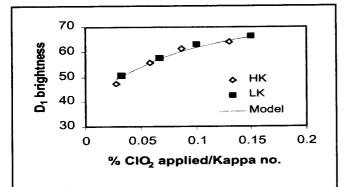
The results of  $D_1$  stage bleaching of both the pulps are shown in Fig.3. Analysis of the data showed that equation of the following form can successfully describe the experimental data obtained for  $D_1$  stage bleaching:

$$B_{D1} = a_{01} + a_{11} [1 - \exp(-a_{12} m)]$$
 (1)

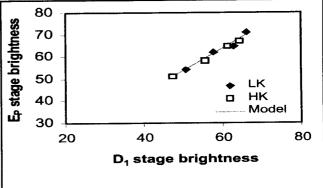
where BD<sub>1</sub> is the brightness developed after D, stage and m is the amount of ClO, charged (as % of OD pulp) per unit Kappa number of the pulp leaving O-stage. The constants  $a_{01}$ ,  $a_{11}$  and  $a_{12}$  are, the brightness of the pulp leaving Ostage, maximum brightness gain achievable and a response factor that is characteristic of the rate of approach to the maximum achievable brightness as the chemical charge is increasing, respectively. For the curve shown in Fig.3 the values of  $a_{01}$ ,  $a_{11}$  and  $a_{12}$ were found to be 39.8, 31.2 and 12.12, respectively.

#### Ep stage

The Ep stage brightness depends on



**Fig.3**: Brightness after  $D_1$  stage as a function of  $\%ClO_2$  charged per unit Kappa no. of pulp leaving O-stage



 $\textbf{Fig.4}: \mathbf{E_{P}} \text{ stage brightness as function of } \mathbf{D_{1}} \text{ stage brightness}$ 

the brightness of the pulp leaving  $D_1$  stage. A graph has been plotted between Ep brightness and  $D_1$  brightness as shown in Fig.4. The relationship may be described by the following equation:

$$B_{EP} = 1.025 B_{D1} + 2.73$$
 (2)

where  $B_{EP}$  is the  $E_P$  stage brightness.

## D, stage

Fig.5 and 6 show the brightness

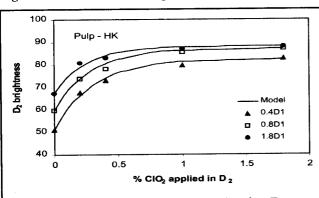
increases. The effects of variation in incoming pulp brightness and ClO<sub>2</sub> charge on final brightness development can be described by a model equation similar to D<sub>1</sub> stage as follows:

$$B_{pp} = B_{pp} + a_{21} [1 - \exp(-a_{22} .x)]$$
 (3)

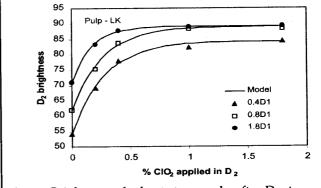
where,  $B_{D2}$  is the  $D_2$  stage brightness and the constants  $a_{21}$  and  $a_{22}$  are, respectively, the maximum stage. Relationship between maximum brightness gain in  $D_2$  stage and the brightness of the pulp leaving Ep stage has been shown in Fig.7. The linear relationship may be given by the equation:

$$a_{21} = -0.674 B_{EP} + 66.766$$
 (4)

Fig.8 shows dependence of the  $D_2$  stage response factor  $a_{22}$  on brightness of the pulp leaving Ep



**Fig. 5 :** Brightness of wheat straw pulp after  $D_2$  stage as a function of  $D_2$  stage  $ClO_2$  charge (Pulp – HK)



**Fig. 6 :** Brightness of wheat straw pulp after  $D_2$  stage as a function of  $D_2$  stage  $ClO_2$  charge (Pulp – LK)

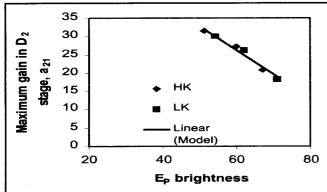
achievement of wheat straw pulps after addition of various doses of  $\text{ClO}_2$  in  $\text{D}_2$  bleaching stage. Unlike  $\text{D}_1$  stage, in  $\text{D}_2$  stage only  $\text{ClO}_2$  charge was taken as variable as we are interested in finding the optimum load sharing between the  $\text{D}_1$  and  $\text{D}_2$  stages. It can be seen that, for both the pulps, as the brightness of the entering pulp increased the brightness gain decreases although maximum achievable brightness

brightness gain in  $D_2$  stage and a response factor that is characteristic of the rate of approach to the maximum achievable brightness as the chemical charge is increased. Both the constants depend on the brightness of the entering pulp. Therefore, it would be appropriate to find their individual mathematical relationships with the brightness of the entering pulp to the  $D_2$  stage which is nothing but the brightness of the pulp leaving Ep

stage. The following equation describes the curve shown in Fig.8:

$$a_{22}=0.0115X^2-1.281X+38.911$$
 (5)

where, X is equal to  $B_{\rm EP}$ , the brightness of the pulp leaving  $E_{\rm P}$  stage. Thus the bleaching sequence may be described by the model consisting of Equation 1 to 5 when Kappa number of the O stage pulp is close to 12. To illustrate the application of the model total  ${\rm ClO_2}$ 



**Fig.7**: Maximum gain in  $D_2$  stage as a function of  $E_p$  brightness

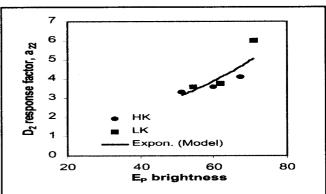
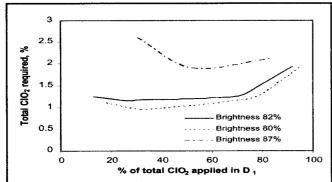
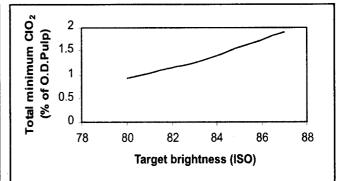


Fig. 8 : Relationship between the  $D_{\scriptscriptstyle 2}$  stage response factor and brightness of the pulp leaving  $E_{\scriptscriptstyle P}$  stage



**Fig.9**: Minimum total  $ClO_2$  requirement as a function of final brightness and distribution of  $ClO_2$  between  $D_1$  and  $D_2$  stage.



**Fig.10 :** Minimum total  ${\rm ClO_2}$  requirement as a function of target brightness

requirement is plotted in Fig.9 as function of ClO, charge in the D<sub>1</sub> stage (expressed as % of total ClO, charge in D<sub>1</sub> and D<sub>2</sub> stages) for different target brightness. Optimum distribution of ClO, in D<sub>1</sub> and D, stages may be predicted from this plot. Using the above model, minimum total CIO, required as a function of desired brightness, has been plotted in Fig.10. By plotting similar graphs one can compare the bleaching response of different pulps in the specified bleaching sequence.

#### **CONCLUSIONS**

The ODE<sub>p</sub>D bleaching sequence for wheat straw pulp can be effectively modeled by simple empirical correlations. With the help of the developed model minimum ClO<sub>2</sub>

requirement and the optimum distribution of ClO<sub>2</sub> in D<sub>1</sub> and D<sub>2</sub> stages to achieve a desired brightness level may be determined. This model can also be used to compare the bleachability of different pulps when subjected to this specified bleaching sequence.

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