# Optimization of D<sub>o</sub>E<sub>D</sub>D<sub>1</sub> bleaching of Trema orientalis (Nalita) Soda-AQ Pulp

# Jahan M. Sarwar, Rowshan Sabina, Islam Shamirul, Sultana Tamanna

# **ABSTRACT**

This paper deals with  $D_o E_p D_1$  bleaching of *Trema orientalis* (Nalita) soda-AQ pulp with kappa number 17.8. The effects of kappa factor, bleaching temperature and consistency in the  $D_o$  stage on final pulp properties were studied. This allows a thorough understanding of the performance of these parameters so that the stage can be effectively designed and implemented in normal mill conditions. Responses of bleached pulp properties to the process were analyzed using statistical software (SPSS 15). The results show that high temperature resulted in the best brightness gain, with a small decreased in viscosity. To achieve better brightness, kappa factor should be within the normalized value 0-1 (0.22-0.24). It is also observed that the brightness will be improved if  $D_o$  kappa number is lower under constant kappa factor.

Keywords: Chlorine dioxide bleaching, Central Composite design, Brightness, Viscosity, Do Kappa number

# Introduction

An ever-increasing demand for paper combined with a declining fiber supply from the forests of the world is forcing the pulp and paper industry to find technically and economically viable fiber sources to supplement the forestbased resource. Although a rather large amount of the paper produced today in developing countries from various annual nonwood fibers plant, but need wood pulp for technically and economically feasible pulp processing. Forestland in Bangladesh is only 10.2 %. Population density of our country is very high. Therefore, forestland for industry is decreasing in competing with other land uses. So, it is hard to supply pulpwood from our forest to keep the growth of paper industry. To achieve this, plantation of fast growing species must be established to compensate for the dwindling supply from natural forest. Fast wood plantation can produce one and a half to two times more wood per hectare per year, and reach maturity two to three times faster than longer-rotation softwood plantations (1). Higher the yield lowers the cost of raw materials, less land is needed to produce the same amount of wood. So we can say that restricted access to the natural forest attracts short rotation wood as sources

Recent literature (2) showed that *Trema* orientalis is one of the fastest growing trees. Local name of *T. orientalis* in Bangladesh is Nalita. Nalita is one of the fastest-growing trees, which may be

a suitable source of fiber for papermaking in near future (2-5). Chemical compositions of Nalita wood were 20-24% lignin, 22-23% pentosan, 48-50% α-cellulose along with extractive, ash etc (Jahan and Mun 2004).

The increasing numbers of environmental and marketing constraints are leading the pulp mills to change their bleaching sequences in order to reduce the impact over environment, specially the amount of chlorinated organics produced in the bleach plant. 100% substitution with chlorine dioxide to replace chlorine is now a well-known technique very efficient to produce high quality and full brightness chemical pulps while decreasing the impact on the environment. With more stringent regulations concerning AOX, ECF bleaching sequences with chlorine dioxide have to be optimized in order to respect these new regulations.

Now most of the global bleached pulp is produced by conventional and ECF bleaching technologies, and only a minor share was produced by the TCF bleaching technology. The trends of bleached chemical pulps (BCP) production indicates that in the future most of them will be produced by ECF technology. It is therefore both reasonable and relevant to optimize and develop further the existing ECF bleaching processes. Final pulp quality and reagent consumption in ECF bleaching are directly or indirectly affected by numerous factors: consistency, temperature, retention time, carryovers, quality of the process waters, amounts of chemicals used, and pH of the bleaching stages (6-9). Even though the optimum operating conditions for each stage of ECF bleaching are rather well known, actual optimization of the complete bleaching sequence is still inadequate particularly the question of optimum chlorine dioxide dosages in each D-stage is much discussed. Traditionally, in ECF bleaching the major part of the total chlorine dioxide dosage is added to the first chlorine dioxide stage ( $D_{\circ}$ ) while the dosage is considerably lower in the subsequent stages.

In this paper, we try to optimize D<sub>o</sub> stage by varying kappa factor, temperature and consistency in order to get maximum brightness, viscosity and less chemical consumption at the end.

# Experimental Pulping

Trema orientalis (Nalita) pulp was prepared in the laboratory by sodaanthroquinone (AQ) process. Pulping was done in a 20 l capacity thermostatically controlled electrically heated rotary digester under constant cooking conditions. The active alkali was constant 17 % as Na<sub>2</sub>O on oven dried (o.d.) sample in the liquor ratio of 1:4. The cooking was continued for 120 min at the maximum temperature (170 °C). At the end of pulping, pressure was relieved to atmospheric pressure, pulp was taken out from the digester, disintegrated and washed by continuous flow of water. Pulp was screened in a Yasuda flat vibratory screened yield and reject determined gravimetrically. Pulp yield was determined as dry matter obtained on the basis of o. d. raw material. Kappa number was determined in accordance with T 236 cm-85. Kappa number and brightness of the unbleached pulp was 17.8 and 23.98 %, respectively. The

Pulp and Paper Research Division, BCSIR Laboratories, Dhaka, Dr. Qudrat-I-Khuda Road, Dhaka-1205, Bangladesh residual ClO, was determined by iodometric titration

# **Bleaching**

Pulps were bleached by DoEpD1 bleaching sequences (where D represents chlorine dioxide and Ep represents peroxide reinforced alkaline extraction). The kappa factor was varied from 0.20-0.24 in the first stage of DoEpD<sub>1</sub> bleaching sequences. The temperature was 60, 70 and 80 °C in D. stage for 60 min. Pulp consistency was varied from 2.5 to 10 %. The pH was adjusted to 2.5 by adding dilute H<sub>2</sub>SO<sub>4</sub>. In alkaline extraction stage, temperature was 70°C for 60 min in a water solution of 2 % NaOH and 0.2% H<sub>2</sub>O<sub>2</sub> (on od pulp). Pulp consistency was 10 %. In the final D<sub>1</sub> stage, end pH was adjusted to 3.5-4 by adding NaOH. The ClO<sub>2</sub> charge, temperature, time and consistency were held constant in D<sub>1</sub> stage at 1.3 %, 70 °C, 120 min and 5 %, respectively.

#### Experimental design

A central composite design was used to relate the dependent and independent variables. The model used a series of points (experiments) around central one and several additional points to estimate the first- and second-order interaction term of a polynomial (shown in Eq 1).

$$\dot{\mathbf{Y}} = \mathbf{ao} + \frac{1}{12} a_0 X n i \frac{1}{12} a_2 X_m^2 \cdot (1)_{i=1,j=1}^3 a_3 X_{ni} X_{nj}$$

This design meets the general requirement that each parameter in the mathematical model can be estimated from a fairly small number of experiments (10).

The total number of experiment 'N' required for the three dependent variables k (viz temperature, T; consistency, C; and Kappa factor, KF) was calculated from the following formula (11):

$$N = 2k + 2*k + 1....(2)$$
  
And was found to be 15

Independent variables were normalized by using the following equation:

$$Xn = \underbrace{X \overline{X}}_{(X \cdots (X \cdots X))/2} \cdots (3)$$

 $\cdots \overline{(X\cdots X)}/2$ ....(3) Where X is the absolute value of the independent variable concerned,  $\nabla$  is the average value, and Xmax and Xmin are its maximum and minimum value, respectively.

# **Results and Discussion**

The characteristics of the Do and D1 bleached pulp of Nalita pulp obtained in the 15 bleaching runs (each run having

Table 1. Values of the independent variables and the bleached pulp properties of the soda-AQ pulp bleached by D<sub>0</sub>E<sub>0</sub>D<sub>1</sub> bleaching.

$X_{KF}$	$X_{C}$	$X_T$	KF	Cons.	Temp	After Do stage		В	Consumption	V
						KN	В		Kg/ton	
0	0	0	0.22	5.0	70	2.2	54.9	74.6	64.6	15.5
0	-1	0	0.22	2.5	70	2.2	53.3	72.9	64.1	16.5
0	1	0	0.22	7.5	70	1.3	60.6	75.8	65.0	15.7
0	0	1	0.22	5.0	80	1.7	60.9	76.9	65.4	15.2
0	0	-1	0.22	5.0	60	3.9	51.9	68.7	62.0	18.8
-1	-1	-1	0.20	2.5	60	3.9	51.3	68.6	59.8	18.5
-1	-1	1	0.20	2.5	80	4.0	52.6	72.5	60.1	16.5
1	1	-1	0.24	7.5	60	1.7	52.0	71.4	65.1	16.8
1	1	1	0.24	7.5	80	1.5	63.0	78.1	66.3	15.0
-1	1	1	0.20	7.5	80	2.5	56.8	76.9	60.5	15.3
-1	1	-1	0.20	7.5	60	1.5	50.9	70.4	59.9	16.9
1	-1	-1	0.24	2.5	60	3.0	50.8	70.7	62.3	17.0
1	-1	1	0.24	2.5	80	1.8	55.0	75.5	65.2	15.5
1	0	0	0.24	5.0	70	2.0	55.8	75.2	65.0	15.8
-1	0	0	0.20	5.0	70	2.5	54.6	73.3	63.6	16.2

KF- Kappa factor. C- Consistency, T- Temperature, B- Brightness, V-viscosity, KN- Kappa number

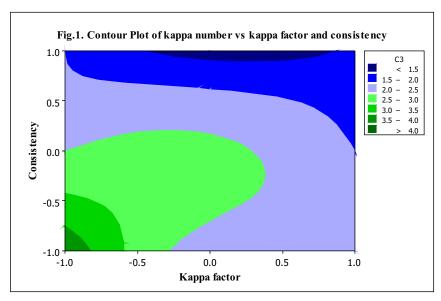
three repetitions) are summarized in Tables 1. Data processing enabled estimation of the main effects and the interactions of the factors for the responses considered. The effect of a factor is the change in the response when it is changed from the low (-1) to the high level (+1). The main effect of each factor estimates its average effect over all possible conditions of the other variables. Each of the responses analyzed can be affected only by the main effects or by interactions among them. The main effect of a variable should be individually interpreted only if there is no evidence that the variable interacts with other variables. When

there is evidence of one or more such interactions, the interacting variables should be considered jointly. Equations allow the estimation of the variation of the properties of the pulp with changes in each independent variable, over the range considered, while holding the other two variables constant.

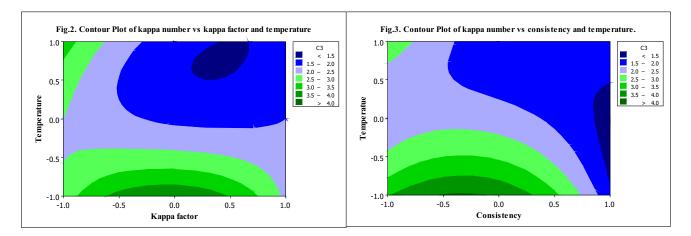
Kappa Number = 2.169 - 0.44 XKF 0.64 XC 0.25 XT + 0.089 XKF2 0.411 XC2 + 0.639 XT2 + 0.288 XKF XC -0.312 XKF XT + 0.237 XT XC

Equation 4 shows that kappa number

was decreased by increasing kappa



In figs C3 represent dependent variable



factor, temperature or consistency. There are some of the statistical parameters such as: S, R-Sq, and R-Sq (adj) in front of each equation which indicates the fitting the data in the model. The kappa number is almost

The temperature had a great influence on the pulp brightness as shown by equation 5 and 6. Both Do and D1 brightness was dependent mostly on temperature followed by consistency. The kappa factor was least effect (1.04)

for Do and 0.92 for D1). The interaction effect of temperature- consistency had a greatest effect on the Do brightness development, but kappa factor-consistency and kappa factor-temperature had no effect on

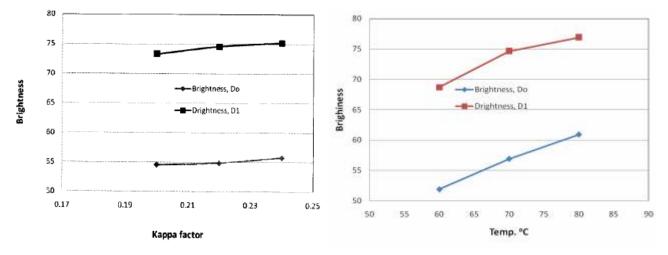


Fig. 4. Effect of kappa factor on D<sub>0</sub> and D<sub>1</sub> brightness.

Fig. 5. Effect of temperature on D<sub>0</sub> and D<sub>1</sub> brightness.

similar sensitive to kappa factor (-0.44), temperature (-0.25) and consistency (-0.64). The interaction effect of temperature and consistency was negative (-0.175) but kappa factor-consistency (0.425) and kappa factor-temperature (0.40) effect was positive. At the central point, the experimental value was 2.2 while the predicted value was 2.17.

Figs. 1, 2 and 3 show the effect of kappa number, temperature and consistency. Lower kappa number was obtained within the normalized range 0 to 1. Brightness (Do) = 56.32 + 1.04 XKF + 2.03 XC + 3.14 XT 2.04 XKF2 + 1.425

XT XC-----(5) S: 1.79, R2= 86.2, R2 (Adj):78.6 Brightness (D1) = 74.36 + 0.92 XKF + 1.24 XC + 3.01 XT 1.39 XT2------(6)

S: 0.84, R2=94.5, R2 (Adj): 92.3

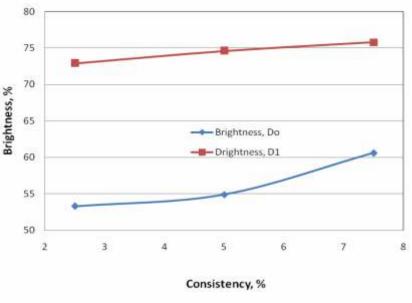
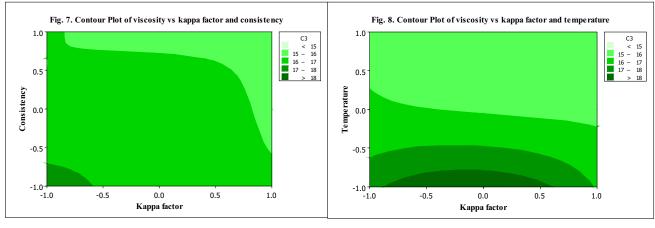
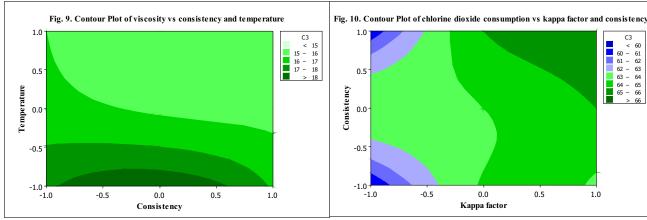
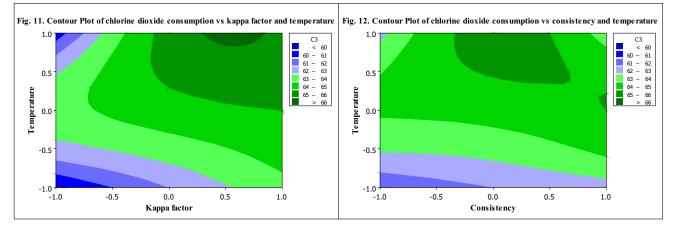


Fig. 6. Effect of consistency on D<sub>o</sub> and D<sub>1</sub> brightness.







brightness. The predicted value of Do brightness was 56.3 % at the central point while the experimental value was 54.9 %. Although the conditions in D1 stage were constant, D1 brightness was varied with Do conditions. The predicted value of D1 brightness was 74.4 % at the central point while the experimental value was 74.6 %. Figures 4-6 show the individual effects of kappa factor, temperature and consistency on Do and D1 brightness. It is clearly seen that temperature had a great effect on both Do and final brightness (Fig. 5). The effect of consistency was pronounced in the final stage (Fig. 6).

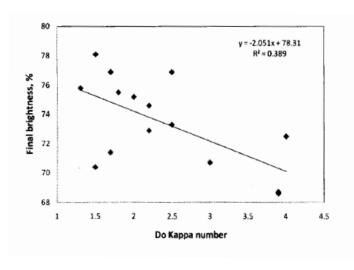
Viscosity = 16.051 - 0.33 XKF 0.43 XC 1.05 XT - 0.279 XKF2 + 0.721 XT2 ----(7) S: 0.63, R2= 85.5, R2 (Adj):77.4

Equation 7 shows the effect of kappa factor, temperature and consistency on final pulp viscosity. The temperature had a detrimental effect on pulp viscosity (-1.05). Kappa factor had the least effect on viscosity (-0.33). From contour plot (Figs. 7-9), it is clearly seen that the higher viscosity was obtained when consistency and kappa factor were lower or lower temperature and medium kappa factor or lower

temperature and medium consistency were applied. The predicted and experimental values of viscosity at the central pint of conditions were 16.05 and 15.5, respectively.

Consumption kg/ton = 64.938 + 2.00 XKF + 0.53 XC + 0.48 XT - 0.722 XKF2 0.472 XC2 1.322 XT2 + 0.425 XKF XC + 0.40 XKF XT - 0.175 XT XC-----(8) S: 1.16, R2=90.8, R2 (Adj):74.

Optimizing bleaching chemical consumption in an ECF sequence should consider the following key factors: - what species of wood is being



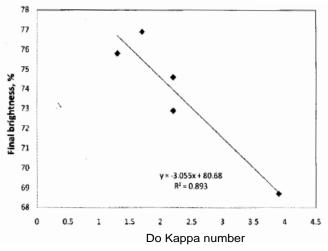


Fig. 13. Relationship between Do kappa number and final brightness regardless of bleaching conditions

Fig. 14. Relationship between Do kappa number and final brightness under constant kappa factor.

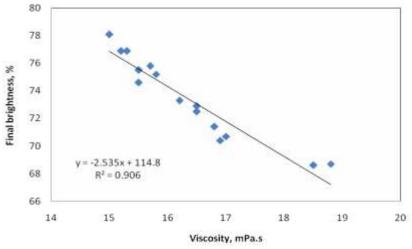


Fig. 15. Relationship between viscosity and final brightness.

bleached (hardwood or softwood); has the pulp been delignified with oxygen prior to ECF bleaching; the amount of black liquor carryover to the first stage; the number of bleaching stages and applications of oxidizing chemicals; the final brightness required.

It is seen from equation 8 and figures 9-12 that the ClO<sub>2</sub> consumption (kg/ton) was increased with the increase of kappa factor, consistency and temperature. Kappa factor had a marked influence on ClO<sub>2</sub> consumption. The effect temperature on ClO<sub>2</sub> consumption was lower (0.48) than kappa factor (2.00) and consistency (0.53). At the central point of normalized value of bleaching conditions, the experimental and predicted values were 64.6 and 64.94 respectively.

Bleaching at the optimal pH (3.5-4) in D1 stage leads to a small measured residual ClO<sub>2</sub> plus ClO<sub>2</sub>-. The residual ClO<sub>2</sub> plus ClO<sub>2</sub>- after D1 measured 0.007-0.01 g/L in these bleaching (data not shown in Table). Hart and Connell

(12) shown that the optimum pH occurred in the presence of some amount of measured ClO<sub>2</sub> residual, which increased with the further increase of residual ClO<sub>2</sub>. In our experiment, we tried to maintain optimum pH.

Figure 13 presents the relationship between Do kappa number obtained under different conditions and final brightness (DoEpD1). It is seen from the figure that the relationship is not fitted well. This may be the reason of different condition of Do stage, which was resulted different residual lignin structure. So we tried to fit the relationship by the Do kappa number obtained under constant kappa factor. The relationship is well fitted as shown in figure 14.

Fig. 15 shows the relationship between viscosity and final brightness of pulp. It is clearly seen that the pulp brightness was increased with the sacrifice of viscosity. For every point of brightness increase, 0.39 mPa.s of viscosity decreased.

#### **Conclusions**

Bleaching temperature at Do stage had a pronounced effect followed by kappa factor on final pulp brightness. The Do kappa number was also largely dependent on temperature and kappa factor. The chlorine dioxide consumption was increased with the increase of kappa factor and temperature. Do kappa number obtained under constant kappa factor correlated well with the final pulp brightness. Higher consistency also slightly affects the final pulp brightness.

# **Literature Cited**

- Cossalter, C. and P.C. Smith. 2003. Fast-Wood Forestry Myths and Realities. CIFOR, Jakarta, Indonesia. p 50.
- Jahan, M. Sarwar; Mun, Sung Phil. Characterization of Nalita wood (Trema orientalis) as a source of fiber for papermaking: (part I): Anatomical, morphological and chemical properties. Polpu, Chongi Gisul (2003), 35(5), 72-76.
- Jahan, M. Sarwar; Mun, Sung-Phil. Effect of tree age on the sodaanthraquinone pulping of Nalita wood (Trema orientalis). Journal of Industrial and Engineering Chemistry (2004), 10(5), 766-771.
- 4. Jahan, M. Sarwar; Rubaiyat, A.; Sabina, R. Evaluation of cooking processes for Trema orientalis pulping. Journal of Scientific & Industrial Research (2007), 66(10), 853-859.
- Jahan, M. S., Ahsan, L., Noori, A., and Quaiyyum, M. A. (2008). "Process for the production of dissolving pulp from Trema orientalis (nalita) by prehydrolysis

- kraft and soda-ethylenediamine (EDA) process, "BioRes. 3(3), 816-828.
- 6. Dence, C., W and Reeve, D. W., "Pulp Bleaching - Principles and Practice", Tappi Press, 1996, Atlanta, 868 p.
- 7. Dahl, O., Niinimäki, J., Tirri, T., and Kuopanportti, H., "Bleaching softwood kraft pulp: the role of chlorine dioxide dosage and final pH in the D stages", Paper and Timber 79(8), pp. 560-565(1997).
- 8. Singh, R. P., "The Bleaching of Pulp", Standard Press, 1979, Atlanta, 694 p.
- 9. Smook, G. A., "Handbook for Pulp and Paper Technologists", Angus Wilde Publications, 1992 Vancouver, 419p.
- Montgomery, D.C., 1991. Diseno Y. analisis de experimentos. Grupo Editorial Iberoamericano
- 11. Aknazarova S. and Kafarov V. 1982. Experiment optimization in

- Chemistry and Chemical Engineering, Mir Publisher, Moscow.
- 12. Hart P. and Connell D. Improving chlorine dioxide bleaching efficiency by selecting the optimum pH targets, TAPPI JOURNAI, July 2008, 3-11.