Generalized steady-state model for chlorine dioxide brightening of hardwood kraft pulps

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ABSTRACT: A generalized, steady-state model for the first chlorine dioxide brightening (D_1) stage is proposed for North American hardwood kraft pulps. The model predicts the post-D_1 brightness obtained for a given chlorine dioxide (ClO_2) charge based on three equation parameters. Data from laboratory D_1 studies were examined with the model to determine the relationships of the parameters to extracted pulp properties. The asymptotic D_1 brightness limit at extremely high bleach charges was ~93% ISO for most hardwood pulps. This parameter can be calculated from the limiting light absorption coefficient of D_1 kinetic studies (≈ 0.10 m^2/kg) and the unbeaten light scattering coefficient of the pulp. A second parameter was linearly correlated to the extracted kappa number of the hardwood pulp. This relationship seems to be affected by the chosen kraft pulping process (e.g., liquor or dissolved solids profiling). The final parameter is the extracted pulp brightness. The hardwood D_1 model forecasted the brightness values of laboratory pulps that differ from measured values of ±0.5 to ±0.6 points. Daily averages of bleach plant data for a southeastern U.S. hardwood fiber line were examined with the model. Predictions were generally 0.5 points higher than the measured mill brightness values. This observation implied that the D_0(EOP) pulp contained a small amount of extraction washer carryover (~0.4 kappa units on pulp) that was consuming ~1.2 kg ClO_2/ton pulp, which was not accounted for in the hardwood D_1 model.

Application: These models are simple and can be easily programmed into computer spreadsheets, which can be used to calculate optimum bleach set points and to minimize manufacturing costs.

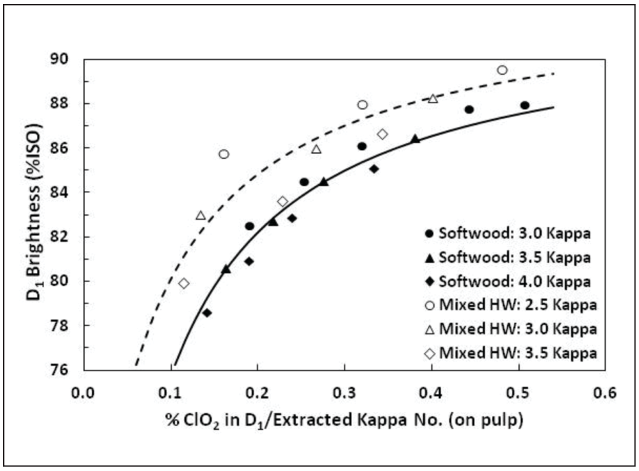
In North America, elemental chlorine-free (ECF) bleaching is the dominant process used to delignify and brighten brownstocks and oxygen-delignified pulps. Chlorine dioxide delignification (D_0) and brightening (D_1 and D_2) stages are major components in these bleach sequences [1]. It is important to balance the amount of chlorine dioxide used in these stages with the kappa number of the softwood or hardwood pulp entering the bleach plant [2-10]. Unbalanced proportioning of chlorine dioxide for delignification and brightening can lead to higher bleach usage and cost.

Multistage ECF sequence models [3-16] can be used to help estimate the optimum proportioning of chlorine dioxide among the various stages based on the kappa number and washer carryover entering the bleach plant, as well as other constraints. Previous works [11-15] have proposed generalized expressions for bleaching stages of softwood kraft pulps. These steady-state models can predict bleach consumption, extracted kappa numbers, and final brightness values based on inputs and constraints, such as brownstock kappa number, washer stage carryover, extraction stage conditions, and entering and exiting pulp brightness. Similar expressions for chlorine dioxide delignification have been proposed for hardwood pulps [16]. Nonetheless, generalized models for chlorine dioxide brightening stages for hardwoods are lacking. Thus, one objective of this study was to extend a softwood model for a chlorine dioxide brightening (D_1) stage [13,15] to apply to hardwood pulps. A second objective was to test the veracity of the hardwood model by examining actual bleach plant data.

BACKGROUND

Most laboratory studies have focused on bleaching softwood kraft pulps. It was assumed that the findings and conclusions obtained from these investigations would be equally applicable to hardwoods. In some cases, however, the extrapolation of these results can yield incorrect conclusions. Hardwoods have noteworthy differences. Among the softwood species as a group, the tracheids tend to be somewhat similar in their morphological characteristics [17,18], such as fiber length, width, and wall thickness. In contrast, the various hardwood species have greater heterogeneity regarding these characteristics and fiber types (e.g., fibers, parenchyma cells, and vessel elements) [17,18]. Hardwood brownstocks entering the bleach plant typically contain lower lignin and higher hexenuronic acid (HexA) levels than do their softwood counterparts.

These factors result in different delignification and brightening responses for the two types of pulps. For example, using aggressive (EO) or (EOP) stages increases the delignification of D_0 softwoods, whereas applying the same approach to D_0



1. D_1 brightness versus D_1 multiple (% ClO_2/extracted kappa number) plot for softwood (solid symbols) and mixed hardwood (open symbols) pulps. Solid and dotted lines denote the normalized brightening responses of softwood and hardwood pulps, respectively, for the range of extracted kappa numbers. D_1 data are from the $D_0(EO)D_1$ bleaching of softwood pulp [21] and $D_0(EOP)D_1$ bleaching of mixed hardwood pulp [22,23].

hardwoods affords marginal to negligible benefits [7,9,19,20]. Generally, for softwoods, plotting D_1 brightening versus D_1 multiple yields a normalized brightening response for a range of extracted kappa numbers (**Fig. 1**). Similar plots for mixed hardwood pulps, on the other hand, often do not exhibit a well-defined brightening response. This phenomenon might be related to the post-extracted brightness values of hardwood pulps, which are typically higher than softwoods [3-5,7,9,12,19-25]. This phenomenon also might be related to the higher levels of hexenuronic acids in post-extracted hardwood pulps [9,10,19,20].

Most laboratory D_1 studies of hardwoods [3-5,24-31] have examined single species pulps, such as sugar maple (*Acer saccharum*), red oak (*Quercus falcate/Q. rubra*), sweetgum (*Liquidambar styraciflua*), birch (*Betula papyrifera*), and eucalypt (*Eucalyptus globulus*). Reeve and Weishar [26] reported that brownstock and oxygen-delignified pulps made from either sugar maple or sweetgum required less bleach in the D_1 stage to bleach to 86% ISO than did red oak pulps. McDonough and co-workers [3-5,30,31] performed several D_1 bleach studies with oak kraft pulps. These authors examined pulps produced using different pulping conditions and quantified their D_1 bleachability by using steady-state models. Rawat and McDonough [24,25] used similar techniques to characterize the D_1 bleachability of birch and maple kraft pulps produced by various pulping conditions. Germgård and co-workers [27,28] reported that hardwood kraft pulps (e.g., birch and eucalypt) at a given E_1 kappa number required more bleach in the $D_1E_2D_2$ sequence than did softwoods to reach 90% ISO [26]. Ragnar [20] observed similar results for the D_1 bleaching of mixed hardwood and softwood pulps. Barroca and Castro [29] developed a dynamic model to describe the D_1 stage bleaching of eucalypt kraft pulps.

Several D_1 investigations have been conducted using mixed hardwood pulps. Parthasarathy et al. [22,23] examined the D_1 bleaching of a mixed hardwood pulp produced at a kraft mill. The pulp was predominantly composed of North American oaks and hickories. These investigators developed a statistical response surface model that related how D_1 brightness was influenced by D_0 kappa factor charge, D_0 consistency, (EOP) temperature, and D_1 bleach charge. Hart and Connell [32] examined how D_1 stage brightening was affected by stage pH for mixed hardwood kraft pulps produced at various North American mills. Brogdon used statistical response surface models [9], which were developed from various ECF bleaching datasets [4,5,22,23,26], to study how various process variables influenced bleach sequence optimization for hardwood kraft pulps.

Previous D_1 models are able to predict the amount of chlorine dioxide needed to reach a targeted D_1 brightness for hardwood kraft pulps [3-5,9,22-25,30,31]. Nevertheless, these steady-state expressions have limitations. The statistical response-surface models do not explicitly express how kappa numbers and brightness values of extracted pulps affect D_1 brightness for applied bleach charges. The steady-state D_1 models of McDonough et al. [3-5] are based on kraft pulps made from a single hardwood species. The mathematical expressions could be used to model other hardwood pulps made from other species or species mixes. However, additional bleaching experiments are required to determine and tune the model parameters for each hardwood kraft pulp. An alternative approach would be to develop a more generalized steady-state model for the D_1 stage where the tunable parameters can be determined by measured properties of the post-extracted hardwood pulp. Such an approach was undertaken in this study.

DATA ANALYSIS

Brightness versus bleach consumption data were obtained from various D_1 laboratory studies for single and mixed hardwood species [3,4,22,23-26,30,31,33-35]. In these investigations, the kraft or oxygen delignified pulps were treated with a D_0 stage, which was followed by an (EO), (EOP), or (EP) alkaline extraction stage. Individual data sets were fitted to D_1 model and regressions were analyzed using the curve-fitting program CurveExpert Professional (Daniel G. Hyams, version 2.5.1; Madison, AL, USA). The software calculated the values of the equation parameters of the models and the corresponding 95% confidence intervals (CIs). Regressions made to models containing three and two tunable parameters were statistically compared with one another using the *F*-test, where the F_0 ratios and critical *F*-values were calculated by the software program.

After a generalized D_1 model was finalized, a second curve-fitting analysis was conducted on the data sets collectively. These computations were performed in a spreadsheet program (Microsoft Office Excel 2007; Microsoft, Redmond, WA, USA), which used the software's Solver routine. Simultaneous regressions minimized the sum of squares errors (SSE) of the model when fitted to the data sets, while simultaneously regressing one of the model's parameters to the post-extracted kappa number of the pulp. The calculated 95% SSE limits were calculated from the SSE of the pooled datasets and the *F*-test. The elliptical 95% CI bounds for the slope and y-intercept values of the linear regression were determined from 95% SSE limits.

RESULTS

Chlorine dioxide brightening stage model for hardwoods

A generalized D_1 model for softwoods [13,15] has been successful at forecasting the chlorine dioxide needed to reach a desired brightness and vice versa for extracted pulps with a range of extracted kappa and brightness values. The model is a modification of an earlier steady-state expression that McDonough et al. [4,5] used to numerically quantify the bleachability of oak kraft pulps. The revised model is denoted as follows:

$$y_1 = c_{01} - \frac{\beta_{11}}{x_1 + \beta_{21}} \tag{1}$$

where x_1 is the chlorine dioxide consumed in D_1 (as % ClO_2 on pulp), y_1 is the post-D_1 brightness (% ISO), c_{01} is the asymptotic D_1 brightness limit, and β_{11} and β_{21} are fitted equation parameters. The β_{21} parameter is a function of post-extracted brightness (B_E), c_{01}, and β_{11}:

$$\beta_{21} = \frac{\beta_{11}}{c_{01} - B_E} \tag{2}$$

For softwood kraft pulps, the β_{11} parameter is a linear function of the extracted kappa number ($Kappa_E$) of the pulp entering the D_1 stage [13]. Eq. (1) and Eq. (2) can be combined into a single expression:

$$y_1 = c_{01} - \frac{\beta_{11}}{x_1 + \frac{\beta_{11}}{c_{01} - B_E}} \tag{3}$$

whereby D_1 data sets can be fitted by nonlinear regression to determine B_E, c_{01}, and β_{11} simultaneously. An important distinction of the modified model to the earlier model of McDonough et al. [4,5] is that Eq. (1) uses the chlorine dioxide consumed in D_1 (x_1) rather than the chlorine dioxide multiple (i.e., % ClO_2 applied in D_1/extracted kappa no.). As shown in Fig. 1 for a mixed species hardwood pulps, plots of D_1 brightening versus

Pulp	Pulp Kappa No.	Bleaching Delignification*	Extracted		Model D_1 Asymptotic Brightness, c_{01}	SE of c_{01}	95% CI of c_{01}
			Kappa No.	Brightness			
Oak [30] – modified kraft cook w/ black liquor	15.5	D_0(EO); 0.20 KF	2.7	56.9% ISO	91.1% ISO	±1.2% ISO	±14% ISO
Oak [30] – modified kraft cook (low solids/alkali profiled)	15.0	D_0(EO); 0.20 KF	2.4	64.9% ISO	92.6% ISO	±0.9% ISO	±11% ISO
Red oak [4] – high effective alkali batch kraft cook	14.0	D_0(EO); 0.20 KF	4.4	71.2% ISO	90.5% ISO	±1.4% ISO	±18% ISO
Red oak [4] – low effective alkali batch kraft cook	14.0	D_0(EO); 0.20 KF	3.6	68.8% ISO	90.7% ISO	±1.9% ISO	±24% ISO
Sweetgum [26] – batch kraft cook	12.1	OD_0(EO); 0.16 KF	4.7	71.2% ISO	90.7% ISO	±0.3% ISO	±3.8% ISO
Maple – high effective alkali batch kraft cook [24]	20.3	D_0(EO); 0.20 KF	2.8	74.9% ISO	94.6% ISO	±0.3% ISO	±3.4% ISO
Maple – intermediate effective alkali batch kraft cook [25]	15.0	D_0(EO); 0.20 KF	4.0	74.3% ISO	92.6% ISO	±1.2% ISO	±16% ISO
Southeastern U.S. mixed hardwood kraft pulp [35]	12.4	D_0(EP); 0.22 KF	4.4	64.0% ISO	93.6% ISO	±0.8% ISO	±9.6% ISO
Northeastern U.S. mixed hardwood kraft pulp [34]	12.0	OD_0(EOP); 0.21 KF	3.3	71.2% ISO	92.2 % ISO	±0.4% ISO	±1.1% ISO
Midwestern U.S. mixed hardwood kraft pulp [22,23]	15.0	D_0(EOP); 0.26 KF	2.8	65.9% ISO	91.8% ISO	±1.3% ISO	±17% ISO

* Sequence and kappa factor (KF).

I. Calculated D_1 asymptotic brightness values, c_{01}, of Eq. (3) from the nonlinear regression of various laboratory bleaching data sets [4,22-25,34,35] with Eq. (3) with the standard errors (SE) and 95% confidence intervals (CIs) of c_{01}. In all cases, the coefficient of determination (r^2) values for the regressions were greater than 0.994.

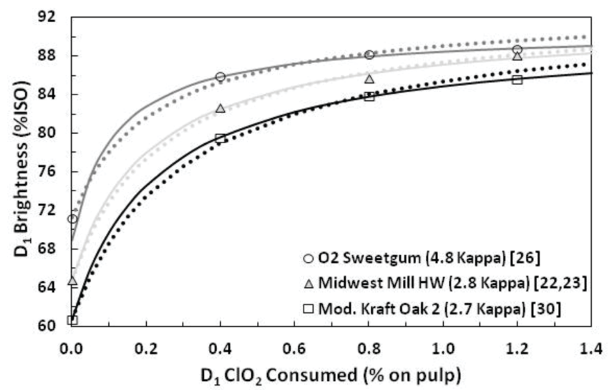
Pulp	Unbeaten Light-Scattering Coefficient, *s*	Estimated Asymptotic Brightness, c_{01}
Southern U.S. oaks	29 to 33 m^2/kg	92.0% to 92.5% ISO
Sweetgum	32 to 37 m^2/kg	92.4% to 92.9% ISO
Maple	45 to 53 m^2/kg	93.6% to 94.0% ISO
Aspen	~41 m^2/kg	~93.3% ISO
Birch	36 to 38 m^2/kg	92.8% to 93.0% ISO
Southeastern U.S. mixed hardwood	38 to 42 m^2/kg	93.0% to 93.3% ISO
Northeastern U.S. mixed hardwood	38 to 45 m^2/kg	93.0% to 93.6% ISO
Midwestern U.S. mixed hardwood	36 to 39 m^2/kg	92.8% to 93.1% ISO

II. Calculated D_1 asymptotic brightness values, c_{01}, for various single and mixed species hardwoods using Kubelka-Munk remission function with the limiting light absorption coefficient (k_∞) value of 0.10 m^2/kg [29,36] and the appropriate unbeaten light scattering coefficient (s) value [38-42].

the chlorine dioxide multiple do not always afford a normalized response curve that is well defined.

Hardwood data from various investigations were analyzed [3,4,22-26,30,31,33-35]. These studies explored a range of bleach charges in the D_1 for pulps made from either single hardwood species or mixed hardwoods. These data sets were curve-fitted to Eq. (3) to evaluate the D_1 asymptotic brightness limit (c_{01}). The curve-fitted c_{01} values were scattered, ranging from 91% to 95% ISO. However, the c_{01} values for single species and mixed hardwood pulps in **Table I** are not statistically different from one another, based on their calculated 95% CIs. In most cases, the curve-fitted c_{01} values are indistinguishable from one another when their standard errors are considered. Similar results have been observed in the corresponding D_1 modeling study for softwood pulps [13].

An alternative approach was undertaken to obtain estimates of c_{01} based on the optical properties of the pulps. Kinetic D_1 studies for softwoods [36] and eucalypts [29] have shown an asymptotic light absorption coefficient (k_∞) at 457 nm to be ~0.10 m^2/kg. This k_∞ value likely represents the light absorption coefficient (k) of the cellulose and hemicelluloses in the nearly lignin-free pulps, which has been noted by Middleton and Scallan [37]. A c_{01} value can be estimated from this k_∞ if the light-scattering coefficient (s) of the unbeaten pulp is known. Light-scattering coefficients for most unbeaten softwood pulps range from 26 m^2/kg to 33 m^2/kg, whereas the s values of unbeaten North American hardwood pulps range from 30 m^2/kg to 53 m^2/kg [38-42]. For softwoods, a c_{01} value of ~92% ISO can be calculated using the Kubelka-Munk remission function [13]. The c_{01} values of single and mixed hardwood species pulps have been determined similarly (**Table II**). The c_{01} value for oak, ~92% ISO, was similar to that of softwoods, whereas the values for maple, sweetgum, and various mixed hardwoods were ~94%, ~93%, and ~93% ISO, respectively. In the 1960s, Rapson [43] showed that mixed hardwood kraft pulps, when bleached with multiple chlorine dioxide stages, had an upper brightness limit that was 1 to 2 points higher than softwood kraft pulps. Rapson's observations seem consistent with the c_{01} values calculated from k_∞ and s.

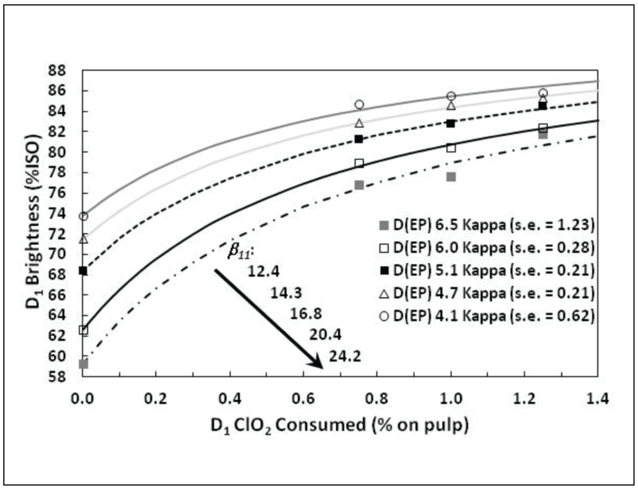


2. Nonlinear regression with selected D_1 data sets [22,23,26,30] of Table I to Eq. (3). Solid lines denote regression analysis to determine the values of c_{01}, B_E, and β_{11} simultaneously (Model 1). Dotted lines denote nonlinear regression analysis to determine the values of B_E and β_{11} only (Model 2); c_{01} set constant to 93% ISO for $OD_0(EO)$ sweetgum and $D_0(EOP)$ mixed hardwood pulps, and to 92% ISO for $D_0(EO)$ oak (Table II).

Figure 2 plots Eq. (3) where the c_{01} was determined by nonlinear regression (Model 1) and by Kubelka-Munk (Model 2). Visually, both models fit the D_1 data well over the dosage range of 0.4% to 1.2% ClO_2, regardless of how c_{01} was determined. The two models were compared with one an-

Pulp	Computed F_0 Ratio	*p*-value	Critical *F* value	Critical *p*-value	Accepted Model
Oak [30] – modified kraft cook w/ black liquor	0.516	0.603	161.448	0.05	Model 2
Red oak [4] – high effective alkali batch kraft cook	0.991	0.501	161.448	0.05	Model 2
Sweetgum [26] – batch kraft cook	48.304	0.0910	161.448	0.05	Model 2
Maple [24] – high effective alkali batch kraft cook	5.447	0.257	161.448	0.05	Model 2
Southeastern U.S. mixed hardwood kraft pulp [35]	0.547	0.594	161.448	0.05	Model 2
Northeastern U.S. mixed hardwood kraft pulp [34]	4.282	0.107	7.709	0.05	Model 2
Midwestern U.S. mixed hardwood kraft pulp [22,23]	16.929	0.152	161.448	0.05	Model 2

III. Statistical comparisons of Model 2, where c_{01} is calculated from the Kubelka-Munk remission function, versus Model 1, where c_{01} is determined from nonlinear regression. Examples are presented for several of the data sets from Table I. Inferences are based on a 95% confidence level (i.e., p-value ≤ 0.05) that Model 2 is an adequate representation of a generalized D_1 brightening model for hardwood kraft pulps.



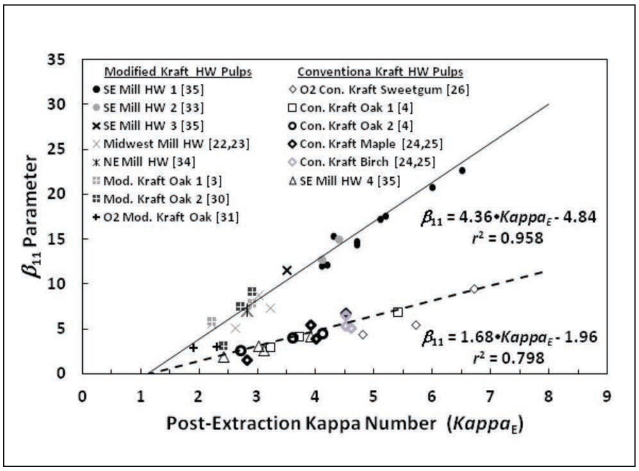
3. Predicted brightness values from Eq. (3) (various lines) compared with experimental D_1 data (symbols) for a southeastern U.S. mixed hardwood pulp [35]. Model's standard error usually ranged from 0.2% to 0.6% ISO units and r^2 ranged from 0.990 to 0.999. Hardwood kraft brownstock (12.4 kappa) was delignified by the D_0(EP) sequence.

other using the analysis of variance from the nonlinear regression provided by the curve-fitting software program. The null hypothesis (H_0) was defined as c_{01} being equal to the Kubelka-Munk calculated value (i.e., Model 2), whereas the alternative hypothesis (H_1) was defined as c_{01} is not equal to the Kubelka-Munk value (i.e., Model 1). **Table III** shows the summarized results. The null hypothesis could not be rejected at the 95% confidence level. Thus, Eq. (3) could be simplified to two tunable equation parameters, namely β_{11} and B_E, whereas the c_{01} value can be determined from the pulp's s and k_∞ values, provided that reasonable estimates are known for these intrinsic pulp properties.

Relationships of D_1 model parameters to extracted kappa number

Figure 3 shows the fitting of the model to the D_1 bleaching data for a mixed hardwood kraft pulp from a southeastern U.S. mill [35]. This 12.4 kappa brownstock was delignified by the D_0(EP) sequence using various D_0 kappa factors (0.15 to 0.30) and peroxide levels in the (EP)-stage (0.2% to 0.8%). Curve fittings to the model were performed with c_{01} set to 93% ISO, which was based on the pulp's unbeaten s value of 38 m²/kg. The model represents the D_1 brightening data well, with an $r^2 \geq 0.990$. The curve fits for this mixed hardwood kraft pulp have standard error values that generally range from 0.2% to 0.6% ISO units. The β_{11} values seem to vary in accordance with the extracted kappa of the D_0(EP) pulp.

Data from the other D_1 studies were curve-fitted to the model where the c_{01} values were calculated and the B_E values were set to the measured values. These studies investigated kraft pulps that were produced either in the laboratory or at the mill and were treated with D_0 and D_1 stages that used multiple bleach charges. The rationale was to determine if there was a correlation between the pulp's β_{11} parameter and its extracted kappa number, which has been observed for softwood kraft pulps [13]. The curve-fitted β_{11} values decreased linearly as the extracted kappa ($Kappa_E$) of the hardwood pulp decreased (**Fig. 4**). Two different linear trends were observed. Pulps produced where the digesters used alkali profiling, dissolved solids profiling, or black liquor impregnation showed a linear correlation with a larger slope value, as well as a high r^2. The other linear relationship, which exhibited a lower slope and r^2, had digesters that used conventional kraft or older modified kraft pulping technology (i.e., pre-1990s). Both trends had a common x-intercept that approached an extracted kappa of 1.1 to 1.2. The slopes and y-intercepts that related the β_{11} values to extracted kappa numbers for the two groups were statistically different from one another (**Fig. 5**).

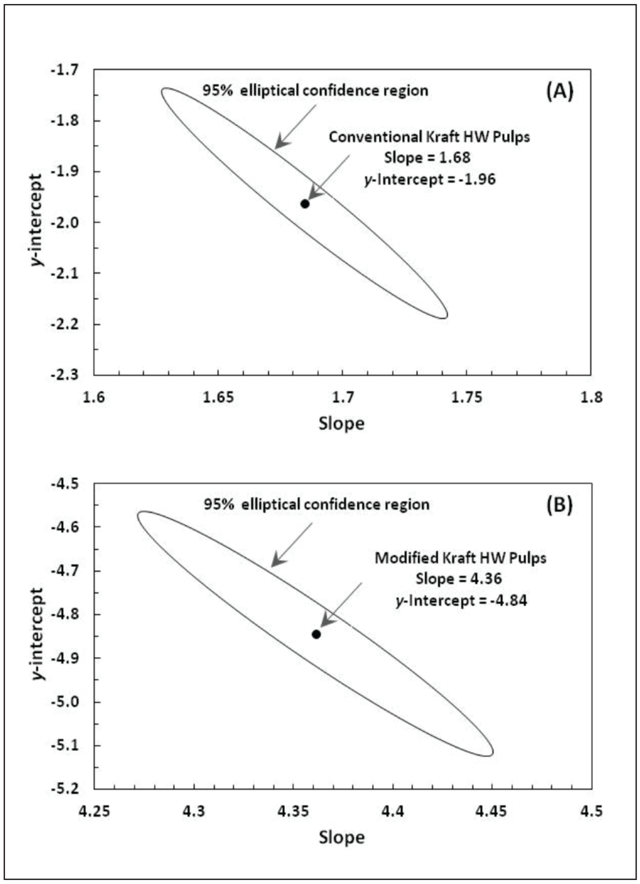


4. Relationship of the β_{11} parameter of Eq. (3) to the post-extraction kappa number (Kappa$_E$) for various hardwood kraft pulps [3,4,22-26,30,31,33-35]. The β_{11} values were determined by nonlinear regression of the model to the D_1 brightening data with c_{01} values calculated by the Kubelka-Munk remission function. β_{11} values typically had standard errors of ±0.8.

The curve-fitted β_{11} parameters for the conventional kraft pulps were also plotted versus the extracted pulp brightness (not shown). As a group, the β_{11} values showed a weak linear correlation to the extracted brightness ($r^2 = 0.696$). When the β_{11} values versus extracted brightness for each individual pulp were examined, the β_{11} value was linearly correlated to the pulp's brightness ($r^2 > 0.93$). However, no generalized relationships were discerned that related the slope, abscissa intercept, or ordinate intercept values among the pulps as a group.

Testing the D_1 model with mill data

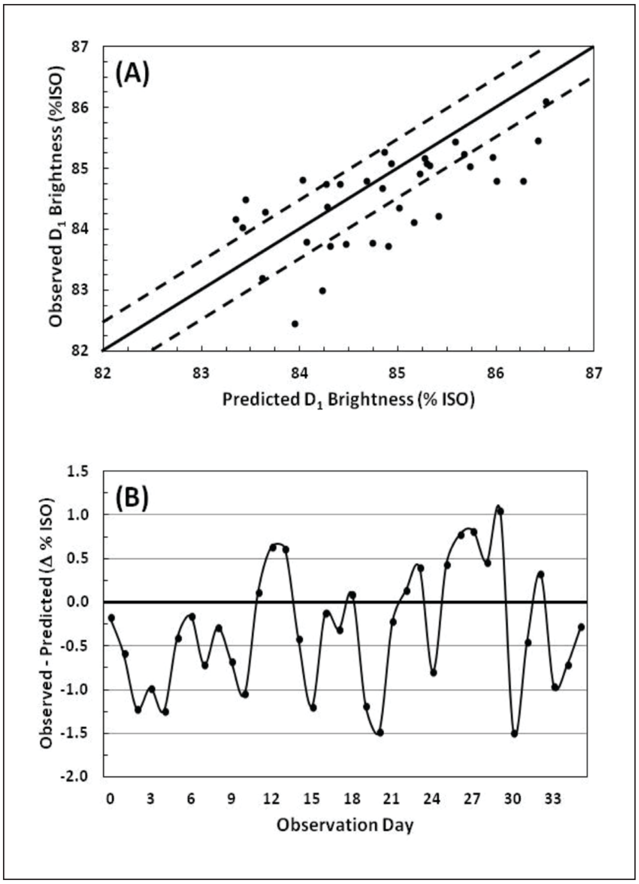
The generalized D_1 model for hardwood kraft pulps was tested against actual bleach plant data to evaluate its veracity. Process data from a southern U.S. hardwood kraft mill were obtained. This mill bleaches a mixed hardwood pulp, which is made primarily from southern U.S. red and white oaks and sweetgum with small amounts of poplar and maple species. The pulp is produced using a Lo-Solids continuous digester (Andritz; Graz, Austria). Daily averages were calculated from the hourly process data over a 1-month period. **Table IV** presents the prevailing conditions at the bleach plant. The mill uses a D_0(EOP)D_1 sequence to brighten the hardwood pulp to an 84% ISO target. The bleachery did not monitor the (EOP) washer carryover into the D_1 stage. However, previous bench-



5. Slope and y-intercepts values from the linear regression of the β_{11} parameter to the extracted kappa number from Fig. 4: (A) conventional and (B) modified hardwood kraft pulps. Ellipses represent the 95% confidence region for paired slope and y-intercept values, whereas the central points represent the regressed values. The two groups of kraft pulps have statistically different linear regression parameters.

Condition	Monthly Range	Monthly Average	Monthly Standard Deviation
Brownstock kappa No.	9.5 to 17.8	14.1	0.7
D_0(EOP) kappa No.	2.85 to 4.21	3.60	0.29
D_0(EOP) brightness, % ISO	68.4 to 77.3	71.3	1.8
D_1 ClO_2, % on o.d. pulp	0.60 to 1.03	0.80	0.10
D_1 vat pH	3.6 to 5.3	4.6	0.4
D_1 brightness, % ISO	82.5 to 86.6	84.6	0.8

IV. Hardwood bleach plant conditions during the data collection over a 1-month period.



6. D_1 brightness values calculated by Eq. (3) based on mill data for x_1, $Kappa_E$, and B_E inputs over a 1-month period: (A) mill measured versus predicted model brightness values and (B) differences between the values for each observation day. Model's β_{11} value is based on modified kraft pulp relationship of Fig. 4 and c_{01} = 93% ISO. Dotted lines represent ±0.5% ISO units difference of the model's values from mill measured values.

marking studies have indicated this fiber line operates with very low bleach chemical consumption when compared with similar ECF fiber lines. The mill runs the D_1 with a low post-stage bleach residual (~0.1 g to 0.2 g ClO_2/L).

Daily bleach charges (x_1), extracted kappa numbers ($Kappa_E$), and extracted brightness values (B_E) were used as the input variables into the model. The c_{01} parameter was set to 93% ISO. This parameter was estimated from the Kubelka-Munk remission function, which used an unbeaten light scattering coefficient (s) of 38 m^2/kg and asymptotic light absorption coefficient (k_∞) of 0.10 m^2/kg. The β_{11} parameter was determined from the correlation shown in Fig. 4 for modified hardwood kraft pulps, which was verified with laboratory D_1 bleaching data on the mill's pulp (not shown).

Figure 6 compares the predicted brightness values to the bleach plant data. Forecasted values were relatively close to the measured values for this hardwood fiber line. However, the generalized D_1 model consistently over-predicted the brightness, usually by ~0.5 points over the mill-measured value. This discrepancy was somewhat anticipated. Similar results have been observed when using the softwood D_1 model to analyze data from a bleach plant that had extraction stage carryover [15].

One item that was not considered with the brightness (D_1) model was the bleach consumed by extraction washer carryover. Most bleach plants do not monitor the entrained dissolved solids entering the D_1 stage. This carryover can be approximated by measuring the well-washed and the unwashed (or "wet") kappa numbers of the pulp mat leaving the extraction washer [44,45]. The difference between these two tests provides an estimate of the entrained dissolved solids expressed as kappa units on pulp (i.e., 1 mL of 0.1 N potassium permanganate/g pulp). The hardwood mill data were re-analyzed with the model by using similar techniques developed for analyzing softwood bleach plant data [15] to estimate the carryover contained in the hardwood pulp mat. The analysis indicated that pulp mat leaving the (EOP) washer contained, on average during this 1-month period, 0.4 kappa units of carryover. This (EOP) carryover was consuming ~0.12% ClO_2 on pulp (1.2 kg ClO_2/o.d. ton pulp).

DISCUSSION

The generalized steady-state model for the D_1 stage accurately predicts the brightening of hardwood kraft pulps produced from single or mixed wood species delignified by chlorine dioxide sequences such as D_0(EOP), OD_0(EO), etc. For well-washed extracted pulps, the predicted brightness values from the hardwood model are generally within ±0.6 points from the laboratory measurements. These observations with the D_1 model are similar to observations noted in an earlier report for a softwood D_1 model [13]. Predicted versus measured differences are close to the 95% CIs observed with well-controlled D_1 laboratory studies (±0.7 points).

The model is defined by three equation parameters. The first parameter is asymptotic or upper brightening limit, c_{01}. It can be calculated with the Kubelka-Munk remission function. This calculation uses the asymptotic k value of 0.10 m^2/kg and the *s* for of the unbeaten hardwood pulp, which can vary considerably depending on species comprising the pulp ($s \approx 32$ m^2/kg to 53 m^2/kg). For many North American pulps made from mixed hardwood species, this c_{01} value is ~93% ISO. The c_{01} values determined by this method are close to the c_{01} values from nonlinear regression, usually within the calculated standard errors of the parameter. Additionally, this simplification eliminates one tunable equation parameter without sacrificing the accuracy of the D_1 model.

The next parameter is β_{21}. It is a function of the extracted pulp brightness (B_E), c_{01}, and β_{11}. Extracted pulp brightness tends to be linearly related to the $Kappa_E$ of the pulp for a fixed set of extraction stage conditions. This relationship is affected by the oxidant-reinforced conditions of the extraction stage, such as peroxide dosage, as well as the pulping process (e.g., modified kraft) and cooking conditions (e.g., effective alkali) used. Generalized expressions of B_E versus $Kappa_E$ considered for softwood kraft pulps [12] were not explored in this hardwood study. Determination of this relationship would be needed if the hardwood D_1 model is to be coupled with other steady-state models to simulate a hardwood ECF bleach sequence. Further work is needed to establish generalized expressions of B_E versus $Kappa_E$ if B_E is not measured.

The final parameter is β_{11}. Its value is linearly related to $Kappa_E$. This correlation appears to be influenced by the kraft pulping process used. Hardwood pulps produced with the modified kraft process have β_{11} values that are affected more by small changes in $Kappa_E$. On the other hand, conventional hardwood pulps exhibit β_{11} values that are less sensitive to changes in $Kappa_E$. These distinctions might be related to the proportions of lignin and HexA structures in the pulp. Modified pulping tends to generate fewer HexA groups versus conventional pulping when compared with the same kappa number [46]. The conventional pulps would have less lignin content than the modified kraft pulps, although the kappa number measurement implies that both pulps have the same lignin content. McDonough et al. [5] noted D_1 bleachability differences for oak brownstocks that had the same kappa number entering the D_0(EO)D_1 sequence but different proportions of lignin and HexA groups. These differences in constituents likely persist after chlorine dioxide delignification and caustic extraction, which would then influence the β_{11} versus extracted kappa relationship. Additional research would be needed to verify this assertion.

The linear regression of β_{11} to the extracted kappa for modified hardwood pulps has a similar slope to that observed for softwoods (~4.4 vs. ~4.5) but differs with their *x*-axis intercepts (~1.2 vs. ~1.6) [13]. The *x*-axis intercepts are within the range of measured kappa numbers of hardwood pulps bleached by the D_1 to 80% to 86% ISO. The relationships shown in Fig. 4 are the trends observed for the laboratory and bleach plant data examined in this investigation. Further work is needed to confirm these trends with other single and mixed species hardwood pulps, such as eucalypt species.

The hardwood D_1 model can predict pulp brightness from bleach plant data when the bleach dosage (x_1), B_E, and $Kappa_E$ are known. Forecasted brightness values are typically higher than the measured mill brightness. This difference likely reflects the bleach consumption caused by washer carryover, which is not considered. This factor could be incorporated into the brightening model analogous to the corrections proposed to softwood D_1 model [15]. If extraction carryover is monitored, then this variable can be taken into account to improve the model's accuracy. Furthermore, if washer carryover is not measured, then this process variable can be approximated from the bleach plant data using the model (after other contributing factors, such as D_1 pH, chemical mixing, etc., have been eliminated). In the mill example, the monthly average carryover was estimated at ~0.4 kappa units (on pulp). The average amount of bleach consumed by this carryover was ~1.2 kg ClO_2/ton pulp. This level of carryover is low, which indicates good pulp washing efficiency after the extraction stage [15,44,45].

CONCLUSIONS

A generalized hardwood model for the first chlorine dioxide brightening (D_1) stage has been developed (Eq. [3]). The model predicts the D_1 bleaching response based on three parameters that are related to the properties of the extracted pulp.

At extremely high bleach charges, the asymptotic D_1 brightness limit (c_{01}) can be determined by the Kubelka-Munk remission function using the floor-level light absorption coefficient (k_∞) of 0.10 m^2/kg and the light scattering coefficient (s) of the unbeaten hardwood pulp. The c_{01} calculated from these hardwood pulp properties are within the values calculated by the curve-fitting of D_1 bleaching data by nonlinear regression. Another equation parameter in the hardwood model is the brightness of the extracted pulp (B_E) entering the D_1 stage. The last parameter, β_{11}, defines the brightening response of the extracted hardwood pulp. This parameter is linearly correlated to extracted kappa number ($Kappa_E$) of the pulp. The relationship of β_{11} to $Kappa_E$ appears to be affected by the process conditions used in the digester to produce the hardwood kraft pulp. The predicted brightness values from the D_1 model are generally within ±0.5 to ±0.6 points of the measured laboratory value.

When the model was tested against bleach plant data for a southeastern U.S. hardwood fiber line, the forecasted brightness values were ~0.5 points higher than the mill's values. In this scenario, the bleach consumption caused by extraction washer carryover was not taken into account. It was estimated that the D_0(EOP) pulp contained a small amount of carryover (~0.4 kappa units on pulp), which was consuming ~1.2 kg ClO_2/ton pulp. **TJ**

ACKNOWLEDGEMENTS

The author thanks Carl Houtman of the USDA Forest Products Laboratory for his insightful comments and suggestions regarding the regression analyses used to analyze the bleaching data. Portions of this work were presented at the 2016 TAPPI Pulping, Engineering, Environmental, Recycling, and Sustainability (PEERS) Conference in Atlanta, GA, USA (September 27, 2016; Session 2-1).

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This work continues the paper series on steady-state models for elemental chlorine-free (ECF) bleach sequences. It is the companion to the study that models D_1 stages for softwood pulps (*TAPPI J.* 13[3]: 17[2014]). It was anticipated that the findings from the softwood study could be extended to cover North American hardwoods. These models are simple and can be easily programmed into computer spreadsheets, which can be used to calculate optimum bleach setpoints and to minimize manufacturing costs.

This work builds on the earlier D_1 model proposed by Tom McDonough and co-workers of the Institute of Paper Science and Technology (IPST) (e.g., *TAPPI J* 7[1]: 4[2008]). One issue encountered when using the IPST model is establishing the tunable parameter values. These parameters are affected by the conditions used to produce the pulp. This restricts the generalization of the D_1 model because the parameters have to be determined experimentally. The goal of this study was to discover a more general D_1 stage model.

A problem encountered with the generalized D_1 model for hardwoods was establishing the asymptotic limit. Unlike softwoods, the brightness limits for hardwood pulps vary widely from 92% to 94% ISO. Nonetheless, it was discovered that this parameter can be estimated by the fundamental properties of the hardwood pulp by using Kubelka-Munk theory. After this was resolved, it was discovered that one of the tunable parameters could be correlated to the extracted kappa number of the pulp entering the D_1 stage, which is in turn influenced by the kraft pulping process used. This observation matches literature reports on D_1 bleachability differences for hardwood pulps produced by different pulping conditions. These differences reflected by the model might be related to the proportions of residual lignin and hexenuronic acid (HexA) groups in the pulp. However, this speculation will need to be verified by additional laboratory work.

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