Relationship between brightness and kappa number of softwood pulps treated with chlorine dioxide delignification sequences

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ABSTRACT: To couple generalized delignification and brightening models to simulate an entire elemental chlorine-free (ECF) bleach sequence, one needs a mathematical relationship that correlates the extracted kappa number from chlorine dioxide delignification to the extracted brightness entering the chlorine dioxide brightening stage (D_1). This was the focus of the current study. A linear relationship was observed for a given softwood pulp when its extracted kappa number (~2-8) was plotted against the ratio of its adsorption (*k*) to scattering (*s*) coefficient (i.e., its extracted *k*/*s* value). The *k*/*s* ratio was related to the pulp's brightness by the Kubelka-Monk remission function. A common y-axis intercept value of 0.0250 was determined for a variety of brownstocks and oxygen-delignified pulps treated by chlorine dioxide delignification (e.g., D_0[EO], D_0[EOP], etc.). The slope of this line for D_0(EO) delignified pulps varied considerably, from 0.010 to 0.070. This variation was influenced by kraft pulping conditions, such as effective alkali and H-factor, although no specific mathematical function was found. Oxygen delignification decreased the pulp's slope value by approximately one-third when compared to its corresponding brownstock. The slopes of the *k*/*s*-kappa expressions for D_0(EOP) pulps decreased proportionally to the amount of peroxide used in the extraction stage relative to D_0(EO) pulps. On the other hand, the slopes from D_0E_1 delignified pulps was typically 15%-20% higher than for D_0(EO) delignified pulps. Applications of the proposed *k*/*s*-kappa relationship of this study to link chlorine dioxide delignification and brightening models are illustrated.

Application: The proposed *k*/*s*-kappa relationship can be used to link the output data from chlorine dioxide delignification models to the input data of chlorine dioxide brightening models. Combined models can then be used for bleach plant optimizations, computer simulations, and/or process control strategies.

Generally, kinetic and steady state models for elemental chlorine-free (ECF) delignification express how efficient bleach consumption is in terms of the extracted kappa number [1-15]. On the other hand, models for the first chlorine dioxide brightening stage (D_1) denote how efficient bleach uptake is in terms of brightness improvement vs. the extracted pulp brightness [1-8,10-12,16].

Reports on chlorine dioxide delignification of softwoods mainly focus on the extracted kappa number to gauge lignin removal efficiency for a given bleach charge and a given set of extraction conditions (e.g., oxidant reinforcement, temperature, etc.) [9,11-15,17-23]. Historically, the extracted kappa number is a very good prognosticator of chlorine dioxide demand in subsequent brightening stages (D_1 or D_1 and D_2 stages) [1,10-14,16,23-28]; and it is for that reason it is used for bleach plant control. In some instances, the post-extraction brightness can be equally useful for gauging bleach demand and for optimizing a bleach sequence [1,11,16,22,23,25,29]. Extracted brightness can be a more sensitive parameter to bleach demand than extracted kappa, particularly if the extracted kappa value is very low (i.e., <2.5) [22,25].

Previous efforts have led to the development of generalized expressions for chlorine dioxide delignification coupled with oxidant-reinforced extraction [15], and for chlorine dioxide brightening stages [16]. These expressions are refinements of other steady-state models found in the scientific literature [2,10-14], most notably the ones of McDonough et al. However, to simulate an ECF bleach sequence with these models (or with alternative models [1-12]), an expression is needed to relate extracted brightness to extracted kappa number. This allows the output data calculated from chlorine dioxide delignification models to be used as the input data into the brightening models [1,3,6,7,8,10-12,15,16]. Relatively few literature studies [4,6-8,11,12] have commented on how to predict extracted brightness from the kappa number and vice versa. Furthermore, some of these investigations [6,8] assumed that a derived kappa-to-brightness expression is constant for a variety of softwood brownstocks and/or oxygen-delignified pulps; this assertion may or may not be valid [7]. Thus, the goal of this paper was to investigate the

Bleaching Study	Kraft Pulp Type	Kappa No.	D_0-Stage Conditions	Extraction Stage	
				Common Conditions	Oxidant-Reinforcement
Rapson & Anderson [21]	Unbleached spruce	18.6	3.6%-6.0% ClO_2, 6% consistency, 70°C, pH 2.4	3% NaOH, 12% consistency, 60°C	E_1 No
Reeve & Weishar [30]	Unbleached pine, spruce, and fir mix (conventional kraft)	34	1.29%-3.88% ClO_2, 8% consistency, 50°C, pH ~2	2.4%-3.2% NaOH, 8% consistency, 70°C	(EO) 0.14 MPa O_2
Reeve & Weishar [30]	Unbleached pine mix (modified kraft)	15	0.57%-1.71% ClO_2, 8% consistency, 50°C, pH ~2	1.7%-2.5% NaOH, 8% consistency, 70°C	(EO) 0.14 MPa O_2
Reeve & Weishar [30]	O_2 delignified pine, spruce, and fir mix (conventional kraft)	16	0.61%-1.83% ClO_2, 8% consistency, 50°C, pH ~2	1.7%-2.5% NaOH, 8% consistency, 70°C	(EO) 0.14 MPa O_2
Reeve & Weishar [30]	O_2 delignified southern U.S. pines (modified kraft)	18	0.68%-2.05% ClO_2, 8% consistency, 50°C, pH ~2	1.7%-2.5% NaOH, 8% consistency, 70°C	(EO) 0.14 MPa O_2
van Lierop et al. [17]	Unbleached softwood	24.1	0.92%-2.02% ClO_2, 3.5% consistency, 50°C, pH 2.2-3.3	1.6% NaOH, 10% consistency, 70°C-110°C	(EO) 0.15 MPa O_2
van Lierop et al. [13]	Unbleached spruce, pine, and fir mix	31.4	1.79%-3.22% ClO_2, 3.5% consistency, 50°C, pH 2-3	2.25% NaOH, 10% consistency, 70°C-90°C	(EO) 0.15 MPa O_2 (EOP) 0-1% H_2O_2
van Lierop et al. [17]	Unbleached black spruce	29.3	2.45% ClO_2, 3.5% consistency, 50°C, pH 2.2-3.3	1.6% NaOH, 10% consistency, 70°C-110°C	(EO) 0.14 – 0.48 MPa O_2
van Lierop et al. [17]	Unbleached softwood	27.9	2.33% ClO_2, 3.5% consistency, 50°C, pH 2.2-3.3	1.6% NaOH, 10% consistency, 70°C-110°C	(EO) 0.14 – 0.48 MPa O_2
Tessier & Savoie [9]	Unbleached softwood	29-32	1.88%-2.70% ClO_2, 3.1% consistency, 40°C, pH 3	1.5%-2.5% NaOH, 10% consistency, 77°C	(EO) 0.60 MPa O_2 (EOP) 0 - 0.5% H_2O_2
Suess & Davies [22]	Unbleached softwood	29.0	2.76% ClO_2, 70°C, pH <3	2.0% NaOH, 75°C-90°C	E_1 No (EP) 0%-0.5% H_2O_2 (EO) 0.3 MPa O_2 (EOP) 0%-0.5% H_2O_2
Suess & Davies [22]	O_2 delignified softwood	10.0	0.95% ClO_2, 70°C, pH <3	1.0% NaOH, 75°C-90°C	E_1 No (EP) 0%-0.5% H_2O_2 (EO) 0.3 MPa O_2 (EOP) 0%-0.5% H_2O_2
Ragnar [25]	O_2 delignified pine/spruce mix	13.1	1.0% ClO_2, 55°C	1.4% NaOH, 60°C-90°C	E_1 No (EO) 0-0.5 MPa O_2 (EOP) 0%-0.3% H_2O_2
Connell et al. [31]	Unbleached loblolly pine	23-30	2.19%-3.80% ClO_2, 10% consistency, 40°C -50°C	90°C, 10% consistency	(EO) 0-0.22 MPa O_2 (EOP) 0%-0.5% H_2O_2
Ragauskas [32]	Unbleached softwood	22.3	1.70% ClO_2, 3.5% consistency, 50°C	2.2% NaOH, 10% consistency, 70°C-90°C	E_1 No (EO) 0.55 MPa O_2
Vegega et al. [33]	O_2 delignified southern U.S. softwood	16.9	0.96%–1.61% ClO_2, 3.5% consistency, 55°C, pH 2-2.5	10% consistency, 80°C, pH 10.5-11.0 pH	(EO) 0.41 MPa O_2 (EOP) 0%-0.6% H_2O_2
Strunk et al. [34]	Unbleached softwood	28.5	3.03% ClO_2, 3.5% consistency, 50°C, pH 2-2.5	10% consistency, 90°C, pH 10.5-11.0 pH	(EO) 0.41 MPa O_2
Strunk et al. [34]	O_2 delignified softwood	16.0	1.7% ClO_2, 3.5% consistency, 50°C, pH 2-2.5	10% consistency, 90°C, pH 10.5-11.0 pH	(EO) 0.41 MPa O_2
McDonough et al. [35]	Unbleached loblolly pine (low/high effective alkali kraft cooks)	15-27	1.19%-2.05% ClO_2, 10% consistency, 45°C	1.6%–2.8% NaOH, 10% consistency, 70°C	(EO) 0.41 MPa O_2
McDonough et al. [36]	Unbleached southern U.S. softwood kraft	25.1	1.91% ClO_2, 10% consistency, 45°C	10% consistency, 70°C, pH >11	(EO) 0.41 MPa O_2
McDonough et al. [36]	O_2 delignified southern U.S. softwood	8.8	0.67% ClO_2, 10% consistency, 45°C	10% consistency, 70°C, pH >11	(EO) 0.41 MPa O_2

I. Conditions reported for chlorine dioxide delignification sequences (e.g., D_0[EO], D_0[EOP], etc.) for various literature studies from which data were analyzed in this investigation.

extracted kappa-to-brightness relationship for chlorine dioxide delignified pulps and to propose a generalized model, which covers a wider range of brownstocks and oxygen-delignified pulps.

LITERATURE DATA ANALYSIS

Data from various chlorine dioxide delignification studies, which used D_0E_1, D_0(EO), D_0(EP), or D_0(EOP), and disclosed extracted kappa numbers and brightness values, were analyzed. **Table I** lists the conditions reported in these studies. The delignification data were regressed to a mathematical model using a statistical program (WinCurveFit, version 1.1.6) and a quasi-Newton method (Davidon-Fletcher-Powell algorithm) was used to minimize the lack-of-fit. The program's computed standard errors of regression for the equation parameters were multiplied by the appropriate *t*-statistic (Student's t distribution, two-tail) to determine 95% confidence intervals (CIs).

MODELING EXTRACTED BRIGHTNESS VS. KAPPA NUMBER AFTER CHLORINE DIOXIDE DELIGNIFICATION

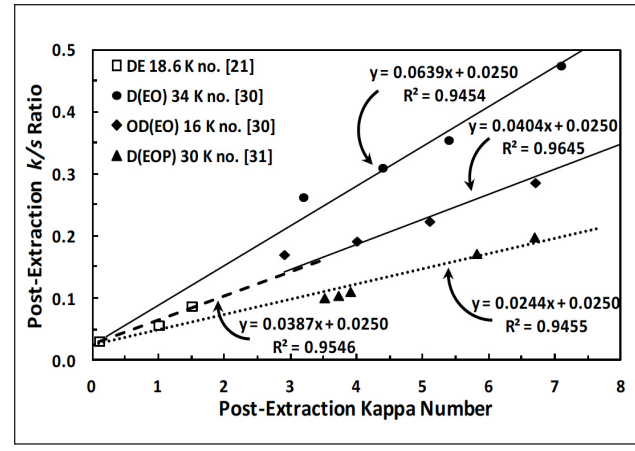
Proposed model

Various mathematical expressions have been proposed [1,4,6-8,11,12] to describe the relationship of the extracted pulp brightness (or its chromophore content) vs. the extracted kappa number for softwood pulps delignified by chlorine dioxide sequences. Typically, as the pulp's extracted kappa number decreases, as a result of the chlorine dioxide charge in the D_0 stage and/or the conditions of alkaline extraction (temperature, oxidant reinforcement charges, etc.), the brightness increases in a nearly linear fashion. Likewise, the pulp's chromophore content decreases in a linear fashion when the extracted kappa number decreases. These linear relationships to extracted kappa number usually hold when the value is below 8. Jain and co-workers [8] noted that the extracted kappa number from chlorine dioxide delignification was not a linear function of the pulp's chromophore concentration when considering a wider extracted kappa number range (i.e., 4-21).

Most investigators relate extracted brightness to its kappa number by converting the ISO brightness (%) to the light absorption coefficient (*k*), or the ratio of the light absorption coefficient to the light scattering coefficient (*s*), *k/s*, by the Kubelka-Munk remission function [1,4,6-8,37]:

$$\frac{k}{s} = \frac{(1 - \frac{\text{Brightness}}{100})^2}{2(\frac{\text{Brightness}}{100})} \quad (1)$$

The *k* value, unlike brightness, is directly proportional to the quantity of light absorbing chromophores contained in the extracted pulp [1,6,37-39]. Likewise, the *k/s* quotient is proportional to the pulp's chromophore concentration because the light scattering coefficient is nearly invariant during bleaching [1,7,8,37]. The *s* values range from 28 m²/kg to 33 m²/kg for unrefined softwoods when formed into handsheets for brightness measurements [40].



1. Plot of extracted k/s ratio vs. kappa number for various chlorine dioxide delignified softwood pulps. See text for conditions of dioxide delignification sequences that were reported for the pulps [21,30,31].

Figure 1 shows plots of extracted *k/s* vs. extracted kappa number values for some unbleached and oxygen-delignified pulps treated with chlorine dioxide delignification sequences. The figure illustrates that *k/s* linearly varies with the kappa number, as is demonstrated by the high coefficient of determination (r^2 >0.94). However, this linear relationship is not the same for the various softwoods and their chlorine dioxide delignification treatments. This finding is consistent with the observations made by Mothra et al. [7] for different softwood kraft pulps treated by various delignification sequences (e.g., CE_1, D_0E_1, etc.). One factor that is similar for the D_0(EO), OD_0(EO), and D_0(EOP) pulps shown in Fig. 1 is the y-axis intercept value. As the extracted kappa number approaches zero, the extracted *k/s* ratio approaches ~0.0250 (~80% ISO brightness). This value for the y-intercept matches the value seen from the D_0E_1 data of Rapson and Anderson [21] (Fig. 1), where they used extremely high D_0 kappa factors (i.e., 0.51-0.86 KF) to examine the limits of using a single oxidant for an entire bleach sequence.

The limiting *k/s* value denotes that the pulp still contains trace levels of chromophores as the extracted pulp approaches zero kappa number (i.e., zero lignin content). This is consistent with the Kubelka-Munk remission function (Eq. [1]), because the pulp's *k/s* value cannot be less than zero [37]. The asymptotic *k/s* ratio at "zero" kappa number indicates that the residual chromophores in the "lignin-free" pulp either consume little to no permanganate, or their concentrations are too low to be detected by the kappa number oxidation test. If the former is true, then the remaining chromophores after extreme chlorine dioxide delignification, as seen from the Rapson and Anderson [21] data, contain relatively few conjugated carbon-carbon double bond structures [41-44], like

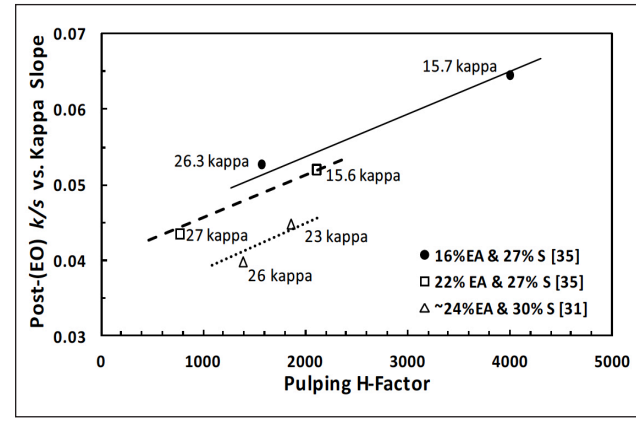
Data Source	Kappa No. before D_0(EO)	Comments	Slope Value	Standard Error of Slope	95% CI of Slope
Reeve & Weishar [30]	34	Conventional kraft	0.0639	±0.0020	±0.0065
Reeve & Weishar [30]]	15	Modified kraft	0.0687	±0.0027	±0.0074
Reeve & Weishar [30]	18	O_2 delignified modified kraft	0.0567	±0.0013	±0.0037
Reeve & Weishar [30]	16	O_2 delignified kraft	0.0404	±0.0012	±0.0033
Connell et al.[31]	30	kraft	0.0363	±0.0009	±0.0021
Ragnar [25]	13.1	O_2 delignified kraft	0.0179	±0.0014	±0.0045
van Lierop et al. [13]	31.1	kraft	0.0367	±0.0006	±0.0015
van Lierop et al. [17]	24.1	kraft	0.0429	±0.0007	±0.0016
Vegega et al. [33]	16.9	O_2 delignified kraft	0.0548	±0.0014	±0.0062
Tessier & Savoie [9]	29-32	Kraft	0.0338	±0.0008	±0.0034
Suess & Davies [22]	29	Kraft	0.0549	±0.0021	Not calculated
Ragauskas [32]	22	Kraft	0.0576	±0.0012	±0.0027
Connell et al. [31]	26	Kraft	0.0399	Not calculated	Not calculated
Connell et al. [31]	23	Kraft	0.0449	Not calculated	Not calculated
McDonough et al. [35]	15.7	Low effective alkali kraft	0.0645	Not calculated	Not calculated
McDonough et al. [35]	26.3	Low effective alkali kraft	0.0527	Not calculated	Not calculated
McDonough et al. [35]	15.6	High effective alkali kraft	0.0521	Not calculated	Not calculated
McDonough et al. [35]	27.0	High effective alkali kraft	0.0436	Not calculated	Not calculated

II. Slopes of extracted k/s vs. extracted kappa relationship for various softwood pulps treated by the D_0(EO) sequence. The y-intercept of the linear regression expression was set to 0.0250.

those found in lignin. Typically, chlorine dioxide delignification of softwoods is rarely pushed to result in extracted kappa values less than 2 [1,8,12,13,15,23,30]. As a result, the extracted brightness after a chlorine dioxide delignification rarely exceeds 70% ISO brightness (i.e., $k/s \approx 0.0640$). Thus, Fig. 1 demonstrates that the extracted k/s value can be represented as linear function of the extracted kappa number with a given gradient and a limiting y-axis intercept of 0.0250. This relationship should be valid so long as the extracted kappa number is within the typical bleachable range (i.e., 2-8 kappa).

Influence of kraft pulping on the extracted k/s vs. kappa number relationship

Table II lists the calculated slopes of the extracted k/s vs. kappa for a variety of softwoods delignified by the D_0(EO) sequence. The slopes were determined with the y-intercept set to 0.0250. The slope varies significantly for the brownstocks and oxygen-delignified softwoods. No specific trend was observed that correlated the kappa number entering the D_0 stage to the slope value. The 95% CIs for the slopes were typically 5%-10% of the calculated slope value. Data from the D_0(EO) studies of McDonough et al. [35] and Connell et al. [31], which specifically investigated different loblolly pine cooking conditions, were examined to see what effects these



2. Influences of kraft pulping conditions on the slope values of extracted k/s vs. kappa relationship for loblolly pine brownstocks delignified with the D_0(EO) sequence [31,35]. Lines through the data are generalized trends, not a specified mathematical relationship. EA = effective alkali; S = sulfidity.

conditions have on the k/s vs. kappa slope value. **Figure 2** shows the results of these analyses. CIs at the 95% level could not be determined because the authors' investigations only reported results for one chlorine dioxide charge for the D_0(EO) sequence. For a given fixed set of effective alkali (EA)

applied in the digester, the slope values increased as the H-factor increased. These slope values decreased for pulps produced with higher EA vs. lower EA for similar kappa numbers. These observations might partially indicate why there are wide ranges in the slope values for brownstocks delignified by D_0(EO), or other chlorine dioxide delignification sequences (see below). The lines shown in Fig. 2 are generalized trends for the selected data sets; sufficient data were not available to ascertain mathematical relationships among the pulping variables to the slope value. The wide range seen with the extracted *k/s*-kappa slopes likely define the future brightening response of softwood pulps with chlorine dioxide [10,11,16,35,39].

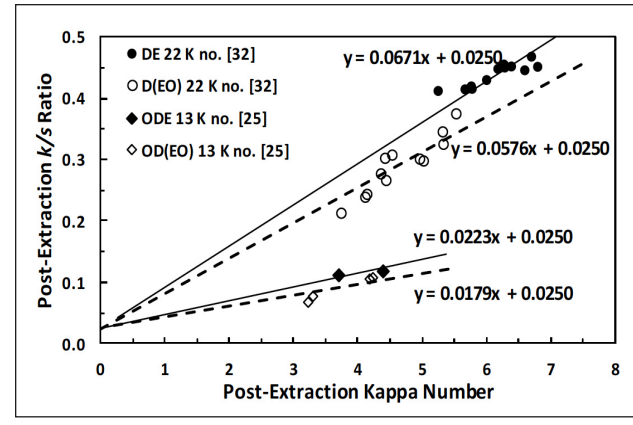
Influence of oxygen delignification on the extracted k/s vs. kappa number

Reeve and Weishar [35] investigated the chlorine dioxide delignification of a 34 kappa Canadian softwood brownstock and its corresponding 16 kappa oxygen-delignified counterpart. Figure 1 shows the *k/s* vs. kappa plots of these two pulps. Oxygen delignification caused the slope to decrease from 0.0639 to 0.0404. Experimental D_0(EO) data from McDonough et al. [36] illustrate a similar effect. These authors used oxygen delignification to reduce a 25.1 kappa brownstock to 8.8 before D_0(EO); this treatment caused the slope value to decrease from 0.0586 for the brownstock to 0.0372 for the oxygen-delignified pulp. Likewise, Strunk and co-workers [34] took a 28.5 kappa brownstock and treated it with oxygen delignification to reduce its kappa to 16.0. In this case, the slope value of the OD_0(EO) pulp was ~30% lower vs. the D_0(EO) pulp (0.0473 vs. 0.0777, respectively). Thus, it appears that oxygen delignification typically reduces the slope values of the extracted *k/s* vs. kappa relationship by roughly one-third when compared to its corresponding brownstock.

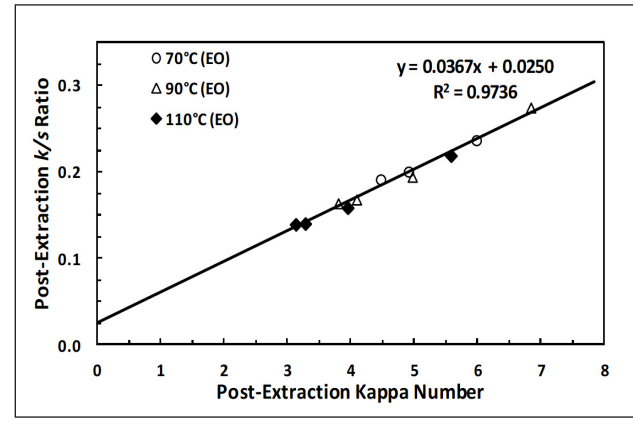
Influence of (EO) conditions on the extracted k/s vs. kappa number

Figure 3 shows how oxygen reinforcement of the extraction stage affected the *k/s* vs. kappa relationship based upon the data from two chlorine dioxide delignification studies [25,32]. The slope of the extracted *k/s* vs. kappa plot was slightly lower (~15%-20%) for the D_0(EO) pulps when compared with the D_0E_1 pulps. The slope value of the OD_0E_1 pulp was relatively close to that of the OD_0(EO) pulp (0.0179 ± 0.0045 (at 95% CI); Table II). This suggests that the extracted *k/s*-kappa relationship for D_0(EO) vs. D_0E_1 pulps become nearly indistinguishable from one another when the kappa number of the pulp before chlorine dioxide delignification is low (≤13). This finding is consistent with the studies of Suess and Davies [22]. These authors reported that when oxygen-delignified softwoods (10 kappa) were treated with D_0E_1 and D_0(EO) at the same kappa factor charge, the resulting pulps had nearly identical extracted kappa numbers and brightness levels.

The use of higher (EO) stage temperatures (90°C-110°C) has been shown to increase D_0(EO) delignification and extracted brightness vs. a lower (EO) temperature (70°C) [13,14,17,22,23,25]. However, extraction temperature does not have an effect on the *k/s* vs. kappa slope (**Fig. 4**). This result indicated that any given improvement in kappa number reduction with a more aggressive (EO) stage is accompanied by the same incremental reduction in the *k/s* value.



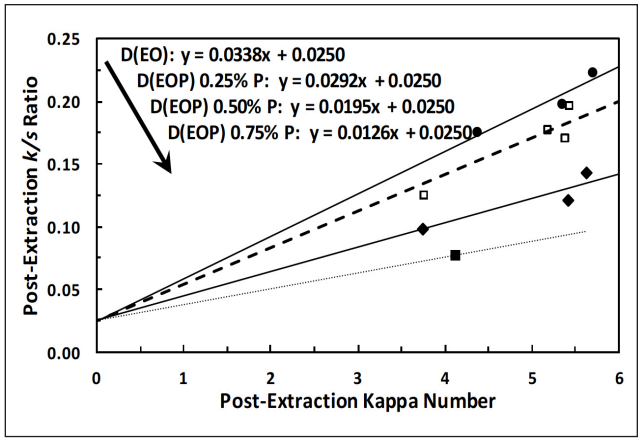
3. Plot of extracted k/s vs. kappa number for brownstocks [32] and oxygen-delignified [25] pulps treated with D_0(EO) or D_0E_1 delignification sequence.



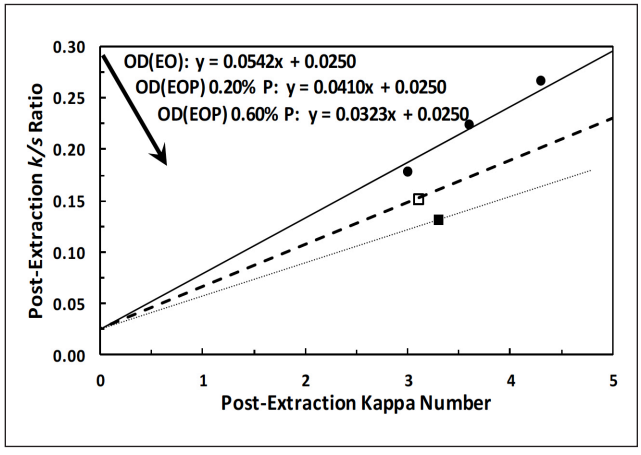
4. Plot of extracted k/s vs. kappa number for the D_0(EO) delignification of a 31.4 kappa brownstock [13] for various extraction temperatures.

Influence of peroxide reinforcement on the extracted k/s vs. kappa number

Figures 5 and **6** are selected examples illustrating how peroxide reinforcement of the D_0(EOP) sequence affects the slope of the *k/s* vs. kappa relationship based on the analysis of bleaching data from two studies [9,33]. The slope values decreased as the peroxide reinforcement in the (EOP) increased for brownstocks and for oxygen-delignified pulps. These two examples [9,33], and others [13,22,31], demonstrated that this reduction of the slope value, relative to the D_0(EO) slope value, was a linear function of the amount of peroxide employed (**Fig. 7**). Data from several other D_0(EOP) studies [22,25,34] were comparable and generally were within the 95% CIs.

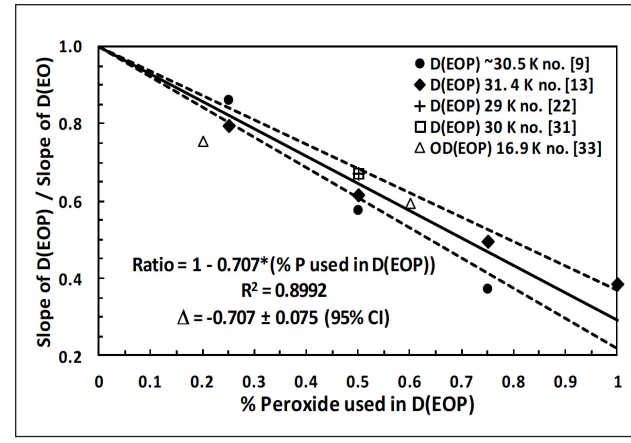


5. Plot of extracted k/s *vs. kappa number for D_0(EO) and D_0(EOP) delignification of 29 to 32 kappa brownwstocks using various peroxide dosages in the extraction stage.*



6. Plot of extracted k/s *vs. kappa number for the D_0(EO) and D_0(EOP) delignification of a 16.9 kappa oxygen-delignified pulp [33] using various peroxide dosages in the extraction stage.*

Very few softwood bleaching studies have reported both post-extraction kappa number and brightness data that compare D_0(EP) to D_0E, D_0(EO), or D_0(EOP). **Table III** lists the data analysis of the Suess and Davies [22] study that examined D_0(EP), D_0(EO), and D_0(EOP) sequences with a softwood brownstock. D_0(EP) and D_0(EOP) showed similar reductions in the *k/s* vs. kappa relationship slope at the same extraction peroxide charge. Thus, the slope value of the D_0(EP) sequence



7. Ratio of the slope value from D_0(EOP) delignification relative to D_0(EO) delignification as a function of peroxide dosage in the (EOP) stage for various pulps. CI = confidence interval.

may be approximated to that of the D_0(EOP) sequence at identical peroxide dosages. Analogous observations have been reported by Jain and co-workers [8] in their studies relating extracted *k/s* to extracted kappa number.

DISCUSSION

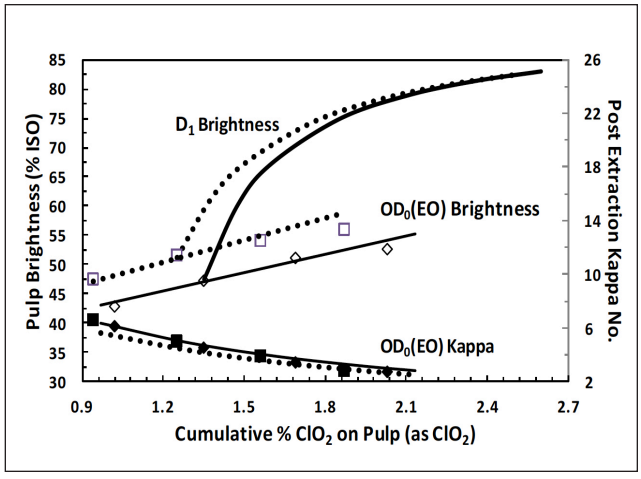
Analyses of the various chlorine dioxide delignification studies, which reported both extracted kappa numbers and extracted brightness values for numerous softwood species, chlorine dioxide charges, and oxidant reinforced extraction conditions, indicated that there is a linear relationship between these two quantities if the extracted brightness is converted to its *k/s* quotient (Eq. [1]). This expression for softwoods is:

$$\frac{k}{s} = a * (\text{Extracted Kappa No.}) + 0.0250 \qquad (2)$$

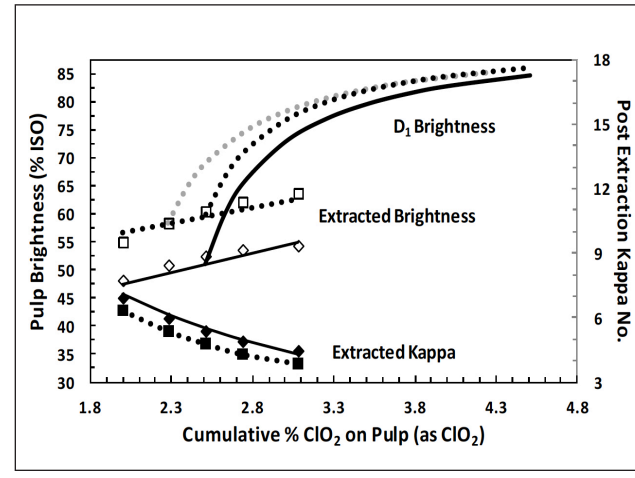
where *a* is the slope value and 0.0250 is the limiting y-intercept value (at "zero" extracted kappa). Most brownstocks and oxygen-delignified pulps that were treated by chlorine dioxide delignification could be modeled by Eq. (2), particularly if the extracted kappa numbers were between 2 and 8. Inspection of D_0(EO) delignification data revealed that the *a* values varied considerably, from 0.01 to 0.07, with most values being

Chlorine Dioxide Delignification Sequence	% Peroxide in Extraction	Slope Value	Ratio of Slope Value Relative to D_0(EO) Slope Value
D_0(EO)	0	0.0549	1
D_0(EP)	0.5	0.0365	0.665
D_0(EOP)	0.5	0.0383	0.698

III. Slopes values of the extracted k/s *vs. extracted kappa relationship for D_0(EO), D_0(EP), and D_0(EOP) sequences (29 kappa softwood brownstock) [22].*



8. Chlorine dioxide delignification model [15] and brightening model [16] predictions for extracted kappa, extracted brightness, and D_1 brightness as a function of total chlorine dioxide consumed for a 16 kappa oxygen-delignified modified kraft cook (dotted lines) and an 18 kappa oxygen-delignified conventional kraft cook (solid lines). Squares are the reported data for 16 kappa oxygen-delignified pulp [30] and diamonds are the reported data for 18 kappa oxygen-delignified pulp [30]. The a value used for Eq. (2) to calculate the D_0(EO) brightness from extracted kappa is given in Table II.



9. Chlorine dioxide delignification model [15] and brightening model [16] predictions for extracted kappa, extracted brightness and D_1 brightness as a function of total chlorine dioxide consumed for a 31.4 kappa brownstock. Dotted lines are Eq. (2) predictions for the D_0(EOP) sequence (with 0.5% peroxide), and solid lines are predictions for the D_0(EO) sequence. Squares are the D_0(EOP) data [13] and diamonds are the D_0(EO) data [13]. The a value used for Eq. (2) to calculate the D_0(EO) brightness from extracted kappa is given in Table II; the a value used for Eq. (2) to calculate the D_0(EOP) was obtained from Eq. (3) using -0.782 as the peroxide coefficient (lower 95% CI value). The gray dotted D_1 line for the D_0(EOP) pulp is where the extracted kappa is the same as that of D_0(EO) pulp; the black dotted D_1 line for the D_0(EOP) pulp is for same D_0 kappa factor as D_0(EO).

between 0.04 and 0.06. However, there were no clear relationships observed for the *a* values vs. the kappa numbers entering the chlorine dioxide delignification sequence.

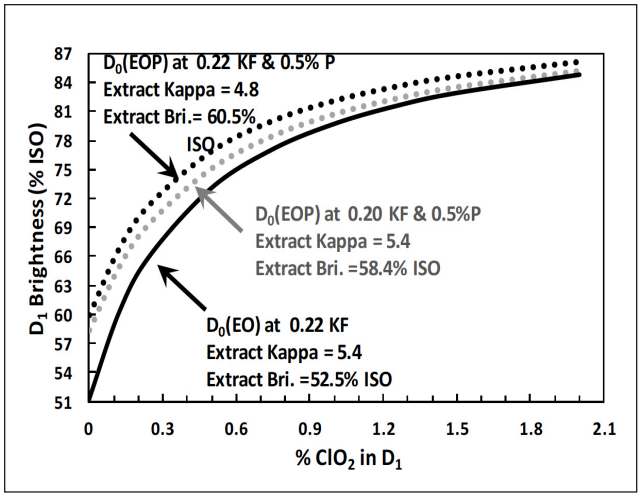
The data from the McDonough et al. [35] and the Connell et al. [31] studies, which examined the effect of kraft pulping conditions on ECF pulp bleachability, was scrutinized. The calculated *a* values appeared to be affected by the cooking EA charge and the H-factor employed. However, no specific mathematical function could be drawn from this analysis, nor from the analysis of data from later McDonough et al. studies [45,46], which examined the ECF bleachability of alkali-profiled kraft pulps. Nonetheless, it can be deduced that kraft cooking conditions can affect the *a* value of Eq. (2). This parameter appears to be a unique characteristic for a pulp delignified by a chlorine dioxide sequence (e.g., D_0[EO]); therefore, this parameter value must be determined from laboratory or mill bleaching data.

Analysis of the Reeve and Weishar [20], McDonough et al. [36], and Strunk et al. [34] bleaching data revealed that oxygen delignification reduced the *a* value for OD_0(EO) delignification by ~33% when compared to D_0(EO) delignification for the corresponding brownstock. This proportional decrease in the *a* value appeared to be constant for softwood brownstocks oxygen-delignified by 45%-65% prior to chlorine dioxide delignification.

Most of the chlorine dioxide delignification investigations analyzed in this study focused on the D_0(EO) sequence. However, the effect of other extraction stages, such as E_1, (EOP), or (EP), on the *a* value of Eq. (2) can be estimated relative to D_0(EO). The *a* value for D_0E_1 delignified pulps were ~15%-20% higher than that for D_0(EO) delignified pulps. This difference is just outside the typical 95% CI observed for D_0(EO) delignified pulp (±10% or less of the *a* value). If the kappa number entering the D_0(EO) sequence is <15, then the more similar the *a* values will be. The effect of peroxide addition to the D_0(EOP) sequence can be approximated from the D_0(EO) reference by the following equation:

$$a_{D(EOP)} = a_{D(EO)} * \left(1 - 0.707 * \left(\%\ \text{Peroxide in (EOP)}\right)\right) \qquad (3)$$

where $a_{D(EOP)}$ is the slope value from the D_0(EOP) sequence and $a_{D(EO)}$ is the slope value from the D_0(EO) sequence. The peroxide addition coefficient may vary from -0.632 to -0.782, based on the 95% CI range (Fig. 7.) Part of this variation, besides systematic experimental errors, may be attributable to peroxide decomposition catalyzed by transition metal ions and/or alkali [23,29,48]. Based on the existing literature data, the effect of peroxide addition to the D_0(EP) sequence relative to D_0(EO) can be roughly estimated from Eq. (3) by assuming that $a_{D(EP)}$ is nearly equal to $a_{D(EOP)}$. These relationships of D_0E_1, D_0(EOP), or D_0(EP) relative to D_0(EO) can be used to model the effects of alternative extraction conditions if the *a* value for the D_0(EO) sequence is known.



10. Comparisons of the predicted chlorine dioxide brightening response from the D_1 model [16] for the various chlorine dioxide delignified pulps of Fig. 9.

The generalized model proposed in this study, which relates extracted brightness to extracted kappa number for chlorine dioxide delignification sequences (Eqs. [1]-[3]), can be used to link other steady-state models for ECF delignification and brightening [1-8,10-12]. **Figure 8** shows an example of that. This illustration uses the $OD_0(EO)$ data from the Reeve and Weishar [20] study, and the $D_0(EO)$ delignification and the D_1 brightening models of Brogdon [15,16]. The predicted $OD_0(EO)$ brightness values match the experimental data for the two oxygen-delignified pulps rather well. The data calculated from Eq. (2) was then used in the D_1 brightening model [16] to forecast $OD_0(EO)D_1$ brightness for chlorine dioxide charges of 0.125%-1.25% in D_1. The combined steady-state ECF models showed that both oxygen-delignified pulps, which were produced by different kraft pulping conditions, had similar brightening responses in the D_1 stage when they were treated with the same D_0 kappa factor. This prediction from the ECF sequence simulation corroborates the findings of Björklund and co-workers [14]. These authors found only negligible differences in the total ECF bleach consumption for oxygen-delignified pulps produced by modified kraft pulping processes (e.g., alkali profiling) vs. conventional kraft process when bleaching to 87%-91% ISO brightness.

Figure 9 shows a second example of linking steady-state models to simulate an entire ECF sequence. In this example, $D_0(EO)$ and $D_0(EOP)$ data from the van Lierop et al. study [13] were used. The predicted $D_0(EOP)$ brightness values from the extracted kappa numbers (Eqs. [1-3]) were close to the values from the van Lierop investigation when the lower CI for the peroxide coefficient of Eq. (3) was used (i.e., -0.782 instead of -0.707). The forecasted brightening in the D_1 stage indicated that the $D_0(EOP)$ delignified pulps afforded higher D_1 brightness values (2 to 3 points) vs. the $D_0(EO)$ delignified pulps at identical D_0 kappa factor charges. The D_1 brightening model [16] also showed that $D_0(EO)$ and $D_0(EOP)$ delignified pulps with similar extraction kappa numbers yielded similar D_1 brightness values for the same D_1 bleach charge (**Fig. 10**). However, in this case, the cumulative chlorine dioxide consumed for the $D_0(EOP)$ pulp was lower than $D_0(EO)$ pulp to reach a targeted D_1 brightness value (Fig. 9).

CONCLUSIONS

This study proposed a linear relationship that related the pulp's extracted kappa number (~2-8) to its extracted *k/s* ratio, where *k/s* is a function of the pulp's extracted brightness by the Kubelka-Monk remission equation. Analyses of literature data where *k/s* was plotted against kappa number for chlorine dioxide delignified pulps indicated that softwood kraft pulps have a common limiting y-intercept value of 0.0250. However, the slope values for these linear expressions varied significantly. It was ascertained that the slope value was affected by oxygen delignification and by oxygen and/or peroxide reinforcement during alkaline extraction. The slopes of the *k/s*-kappa relationship for $D_0(EOP)$ decreased proportionally to the amount of peroxide used during extraction relative to $D_0(EO)$. The proposed model in this study was successfully used to couple previous ECF delignification and brightening models to simulate ECF bleach sequences for softwood kraft pulps. **TJ**

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ABOUT THE AUTHORS

An issue that one encounters when simulating an entire ECF sequence is how to take the output data from delignification models, which is the extracted kappa number, and convert it to its corresponding brightness or chromophore concentration, which is the input data for subsequent brightening models. Very few studies have investigated this topic, as I discovered when I wrote the review chapter on bleach plant models for The Bleaching of Pulp (5th edition).

The starting point was the works of Wang et al. [6] and Mothra et al. [7], who were simultaneously solving kinetic models of coupled bleaching stages. Both used linear regression relationships to convert extracted kappa number to chromophore concentration to link their kinetic models together. When I was analyzing literature data, I realized that there was a common brightness limit after extraction for softwoods treated with chlorine dioxide delignification sequences. This asymptote (the softwood is delignified near to zero kappa) is near the limits reported earlier by Rapson and Anderson [21]. This asymptotic had not been contemplated in earlier published models and should be considered during the regression analysis.

I discovered several generalized relationships that related variations of chlorine dioxide delignification, such as $D_0(EOP)$ and D_0E_1, to the referenced $D_0(EO)$ sequence. One of the tuning parameter of the model showed a wide range of values for various softwood kraft pulps; this parameter likely defines the pulp's bleachability. What I found to be most interesting was that this modified extracted kappa-to-brightness relationship could be used to couple steady-state ECF models for delignification and brightening, such as the ones I have been developing (TAPPI J. 11[3]: 31[2012] and 13[3]: 17[2014]).

Brogdon

Future work will investigate hardwood pulps to see if similar generalized relationships can be developed for chlorine dioxide delignification sequences. Also, I will examine the use of this extracted kappa-to-brightness relationship to combine chlorine dioxide delignification and brightening models to simulate an entire ECF bleach sequence. Operators, engineers, and managers can use these coupled models as a guide to optimize process conditions/targets when the cost of bleaching chemicals and energy fluctuate.

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