# Elemental chlorine-free bleaching of North American hardwood kraft pulps: Evaluation of oxidant-reinforced extraction variables on overall bleaching optimization

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**ABSTRACT:** This investigation evaluates how higher reaction temperatures or oxidant reinforcement of caustic extraction affects chlorine dioxide consumption during elemental chlorine-free bleaching of North American hardwood pulps. Bleaching data from the published literature were used to develop statistical response surface models for chlorine dioxide delignification and brightening sequences for a variety of hardwood pulps. The effects of higher (EO) temperature and of peroxide reinforcement were estimated from observations reported in the literature. The addition of peroxide to an (EO) stage roughly displaces 0.6 to 1.2 kg chlorine dioxide per kilogram peroxide used in elemental chlorine-free (ECF) bleach sequences. Increasing the (EO) temperature by Δ20°C (e.g., 70°C to 90°C) lowers the overall chlorine dioxide demand by 0.4 to 1.5 kg. Unlike what is observed for ECF softwood bleaching, the presented findings suggest that hot oxidant-reinforced extraction stages result in somewhat higher bleaching costs when compared to milder alkaline extraction stages for hardwoods. The substitution of an (EOP) in place of (EO) resulted in small changes to the overall bleaching cost. The models employed in this study did not take into account pulp bleaching shrinkage (yield loss), to simplify the calculations.

***Application:*** This paper illustrates how alkaline extraction variables affect overall chlorine dioxide consumption and bleaching costs for hardwoods. Operators, engineers, and scientists can apply this data as a guide to optimize and troubleshoot hardwood pulp bleaching operations.

Management at bleached kraft pulp mills are being pressured to lower their pulp production costs to remain competitive in today's global economy. Approximately 30% to 40% of the variable production cost of bleached pulp is directly related to chemical and energy consumption [1-7]. A major cost component of elemental chlorine-free (ECF) bleaching is chlorine dioxide ($ClO_2$). Several investigators [6-14] have examined how to balance the $ClO_2$ charges in delignification ($D_0$) and brightening ($D_1$, $D_2$) to obtain a given brightness target while minimizing the total $ClO_2$ consumed. Others [6,7,12,14-22] have evaluated the use more aggressive oxidative extraction stages (e.g., a hot [EO] or an [EOP]) as a method to minimize chemical consumption and cost with softwood pulps.

The consequences of employing more powerful oxidative extraction conditions with hardwood pulp, unlike softwood pulp [6,7,14-17], has received limited scrutiny. Generally, it has been assumed that the principles of extraction for bleaching softwoods are directly applicable to hardwoods [12,15]. This premise has been recently questioned by Süss and coworkers [15]. Their investigations emphasize that oxidant-reinforced extraction, when compared to simple extraction ($E_1$), affords marginal kappa number reductions for hardwoods; elevated extraction temperatures (90°C) likewise result in minor post-extraction kappa reductions. Similar findings have been reported in a recent literature review [23] of chlorine dioxide delignification of hardwoods. Other studies have noted that peroxide reinforcement of (EO) stages (i.e., [EOP]) can reduce total $ClO_2$ bleaching requirements for hardwood pulps by 4 to 5 kg/ton [16,20-22]. However, these investigations [16,20-22] were primarily focused on reducing $ClO_2$ usage in bleaching delignification. Generally, the extracted kappa number for hardwoods decreases by 0.1–0.2 units for each 0.1% increment of peroxide used in the $D_0$(EOP) delignification sequence [23].

The observations by Süss et al. [15], as well as Ragnar [16], regarding the impact of altering caustic extraction variables for hardwood pulps seems at variance with observations made for softwood pulps [6,7,14,17]. Can the principles of oxidant-reinforced extraction learned from softwood bleaching to lower bleaching cost be extrapolated to apply to hardwood pulps? The overall objective of this investigation is to rigorously examine how $ClO_2$ dosages in delignification and brightening stages interact with (EO) variables, such as peroxide dosage and reaction temperature, and how these interactions affect hardwood bleaching efficiency and cost.

## RESULTS AND DISCUSSION

### *Methodology*

Data from several hardwood ECF bleaching studies are analyzed in this report [8,13,24,25]. A summary of the bleaching conditions employed with these studies is given in **Table I**; the reader is referred to the hardwood studies for more specific conditions [8,13,24,25]. The impact of higher extraction temperature and/or peroxide addition (or absence) on the post-extraction kappa number was approximated from the authors' $D_0$(EO) (or $D_0$[EOP]) data. These estimations are based upon generalized trends recently reported in a literature review of chlorine dioxide delignification of hardwoods [23].

The numerical or graphical data obtained from these studies were fitted to response surface functions by statistical regression using Minitab 15 (Minitab; State College, PA, USA) [6,12]. Investigations [24,25] that reported pulp brightness as GE brightness (or TAPPI brightness) were converted to approximate ISO brightness based on the nomographs of Reeve [26] for laboratory brightness handsheets (i.e., % ISO brightness ≈ 0.98•[% GE brightness]). Extracted kappa numbers were ascertained to be linear functions of the $D_0$ kappa factor (KF), extraction temperature, and extraction peroxide dosage. Bleached brightness after the $D_1$ stage was found to be a function of extracted kappa number and $D_1$ $ClO_2$ charge, whereas brightness after the $D_2$ stage was found to be a function of $D_1$ brightness and $D_2$ $ClO_2$ charge. The response surface functions had coefficient of multiple determinations (i.e., $r^2$) values >0.90. Estimated total $ClO_2$ curves for the ECF sequences were calculated from the coupled response surface models simulating an ECF bleach sequence. The Excel Solver routine (Microsoft; Redmond, WA, USA) in the spreadsheet software was used to minimize the total overall $ClO_2$ charge for a targeted brightness [6,8].

The generated data from the coupled response surface models were also analyzed to see the economic impact of extraction conditions on hardwood ECF bleaching. Similar assumptions were employed in this economic analysis as was described in detail in the earlier softwood study [7]. Economic calculations in this study, unlike the softwood study, did not take into account pulp shrinkage (yield loss) to simplify the calculations.

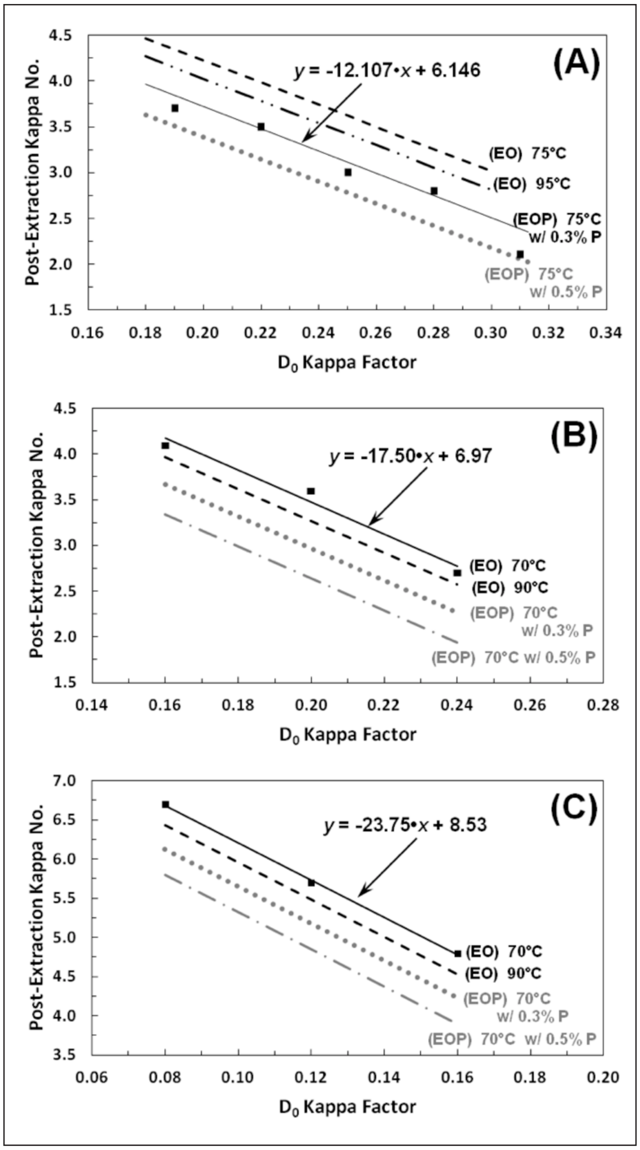
### *Impact of extraction conditions on chlorine dioxide delignification*

Data were used from three ECF bleaching studies, which used various North American hardwood species. The first study, Parathasarathy et al. [25,26], used a mixed hardwood kraft pulp (kappa no. 15) comprising white oak, red oak, and hickory (according to Pryke et al. [27]). The second study, McDonough et al. [8], investigated the bleaching of a red oak kraft pulp that had a brownstock kappa no. 14; the authors pulped the oak using 30% sulfidity, 13.6% effective alkali, and ~1,010 H-factor. The third investigation, Reeve and Weishar [13], studied a sweetgum kraft brownstock (kappa no. 18) that was oxygen delignified to kappa no. 12.1. The mixed hardwood investigation [25,26] employed a $D_0$(EOP) delignification sequence, whereas the red oak [8] and sweetgum [13] investigations employed a $D_0$(EO) delignification sequence. All the bleaching studies focused on extraction stages conducted at 70°C to 75°C, although Parathasarathy and coworkers [25,26] performed some limited experimentation at 95°C.

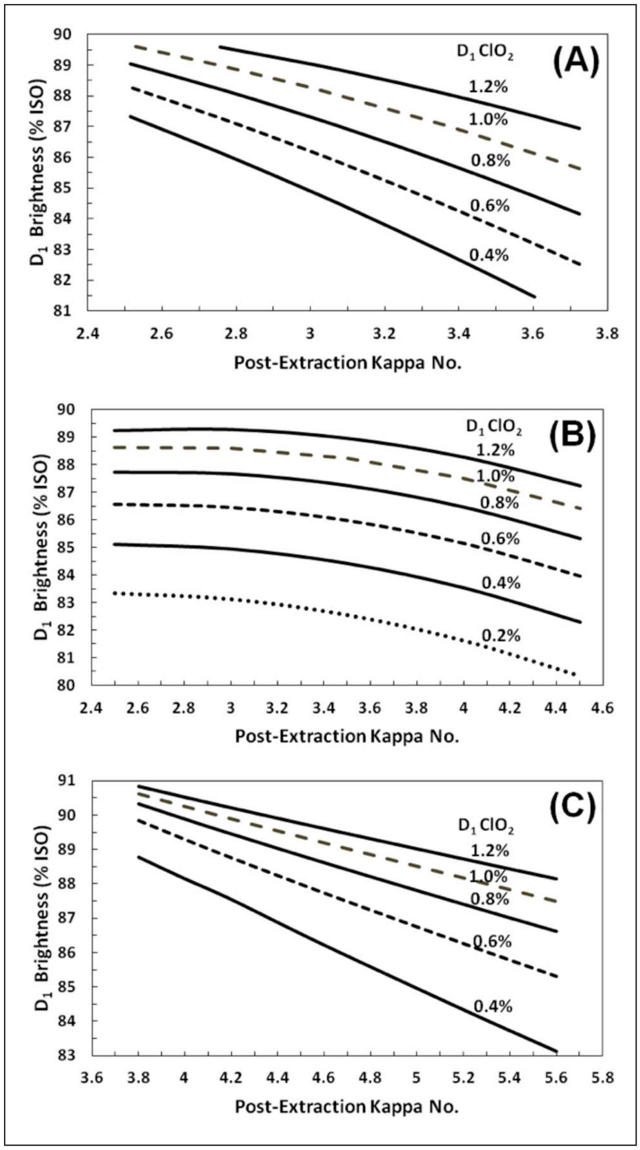
**Figure 1** illustrates the delignification responses of these pulps as a function of the $D_0$ KF. The post-extracted kappa number steadily decreased in a linear fashion as the KF increased. These trends for the hardwoods were valid for a wide range of KF charges. Similar observations have been reported for other hardwoods, such as maple [13] and eucalypt species [19]. The steady decrease in extracted kappa for hardwoods at higher KF charges (>0.25) differ significantly from soft-

| Stage Conditions | $D_0$ | (EO) or (EOP) | $D_1$ | $E_2$ | $D_2$ |
|---|---|---|---|---|---|
| Consistency (%) | 3-10 | 10-12 | 6-10 | 10 | 6-10 |
| Temperature (°C) | 45-50 | 70-90 | 70-75 | 70 | 70 |
| Time (min) | 30 | 60 | 180-300 | 60 | 180 |
| Kappa factor (KF) | 0.04-0.30 | – | – | – | – |
| $ClO_2$ (% on pulp) | 0.2-1.71 | – | 0.20-0.80 | – | 0.1-0.9 |
| $O_2$ Pressure (MPa) | – | 0.14-0.41 | – | – | – |
| $H_2O_2$ (% on pulp) | – | 0 (or 0.3 in [24,25]) | – | – | – |
| NaOH (% on pulp) | – | Variable | Variable | 0.4-0.5 | Variable |
| $H_2SO_4$ (% on pulp) | Variable | – | Variable | – | Variable |
| End pH | 1.5-2.5 | ~11+ | 3-4.5 | ~10 | ~3-5 |

***I. Summary of conditions employed in the hardwood bleaching studies [8,13,24,25] for $D_0(EO)D_1E_2D_2$ and $D_0(EOP)D_1E_2D_2$ sequences.***




***1. Bleaching delignification response of: (A) mixed hardwood pulp (kappa no. 15); (B) red oak pulp (kappa no. 14); and (C) oxygen-delignified sweetgum (kappa no. 12.1). Laboratory bleaching data from the studies [8,13,24,25] denoted by ■; the solid lines represent the linear regression of the data. Estimated effects of higher extraction temperature or of peroxide addition (or exclusion) are denoted by broken lines.***



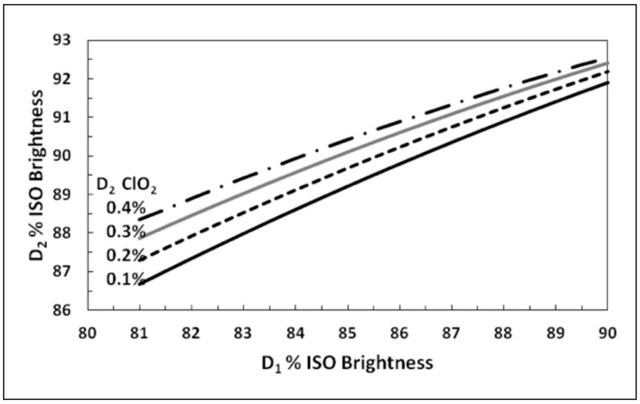

***2. Brightening response in the $D_1$ stage as a function of extracted kappa number and $D_1$ $ClO_2$ dosage for (A) mixed hardwood pulp (kappa no. 15); (B) red oak pulp (kappa no. 14); and (C) oxygen-delignified sweetgum (kappa no. 12.1). Bleach sequences of $D_0$(EO)$D_1$ and $D_0$(EOP)$D_1$.***

wood brownstocks [4,6,12,14,17], which generally approach an asymptotic kappa number.

The impacts of peroxide reinforcement or higher temperatures on the post-(EO) or post-(EOP) kappa number were estimated from the authors' data (Fig. 1; broken lines). A recent review [23] noted that a ~Δ20°C increment in (EO) or (EOP) temperature can afford a 0 to 0.2 unit drop in the extracted kappa for hardwoods (at a fixed KF charge). Likewise, the review [23] reported that the extracted kappa can decrease by 0.07 to 0.20 kappa units for each 0.1% unit increase in peroxide charge in the (EOP). For this study, it was assumed that an increase in extraction temperature from 70°C to 90°C will result in an extracted kappa number that is 0.2 units lower. It was further assumed that peroxide reinforcement will result in a 0.167 kappa unit drop per 0.1% peroxide employed.

### *Brightening response from chlorine dioxide stages ($D_1$ and $D_2$)*

**Figure 2** shows the calculated $D_1$ brightness from the response surface models for the various hardwood pulps. The mixed hardwood and the oxygen-delignified sweetgum pulps exhibited steady brightness gains for a fixed $D_1$ bleach charge as the extracted kappa number decreased. These trends are similar to the trends observed for softwoods [6,14]. The trend for the red oak pulp was somewhat different (Fig. 2B).




***3. Brightening response in the $D_2$ stage as a function of $D_1$ brightness and $D_2$ $ClO_2$ dosage for red oak pulp (kappa no. 14). Bleach sequences of $D_0$(EO)$D_1E_2D_2$ and $D_0$(EOP)$D_1E_2D_2$.***

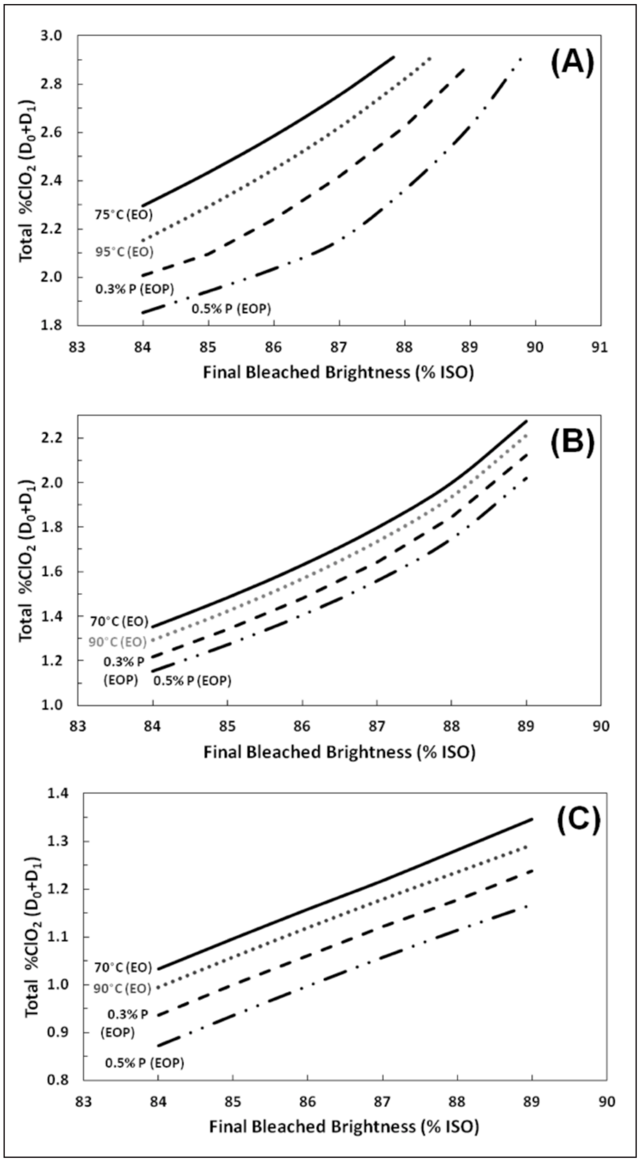
Decreasing the extracted kappa of the red oak pulp from 4.5 to 3.5 resulted in brightness increases for a fixed bleach charge in the $D_1$. However, decreasing the extracted kappa below 3.5 did not afford additional post-$D_1$ brightness gains for a given fixed bleach charge. The brightening models for all three hardwood pulps indicated that $D_1$ brightness increased as the bleach charge was increased over the ranges shown in Fig. 2.

**Figure 3** shows results from the response surface model for $D_2$ brightening of the red oak kraft pulp from the McDonough et al. study [8]. As expected, the $D_2$ brightness increased as the $ClO_2$ charge is increased at a given post-$D_1$ brightness. Likewise, the $D_2$ brightness increased as the post-$D_1$ brightness increased for a fixed bleach charge. Response surface models for $D_2$ brightening for the mixed hardwood pulp and oxygen-delignified sweetgum pulp could not be determined. Parathasarathy et al. [25,26] only examined the $D_0$(EOP)$D_1$ bleaching for the mixed hardwood pulp, whereas Reeve and Weishar [13] summarized and reported limited data regarding $D_2$ brightening of the sweetgum pulp.

### *Analysis of extraction conditions on bleach consumption of short ECF sequences*

The statistical regression models for chlorine dioxide delignification and brightening for each of the hardwood pulps were coupled together to simulate $D_0$(EO)$D_1$ and $D_0$(EOP)$D_1$ sequences. The combined models were used to investigate how extraction stage conditions affected the total amount of $ClO_2$ consumed by short-sequence bleaching. The results from these analyses where the total amount of $ClO_2$ consumed was minimized for various fixed brightness targets are illustrated in **Fig. 4**.

Increasing the (EO) reaction temperature by Δ20°C (e.g., 70°C-90°C) resulted in reductions of overall $ClO_2$ consumption by 0.4 to 1.5 kg/ton pulp. Bleach consumption by the red oak (Fig. 4B) and sweetgum (Fig. 4C) pulps were the least affected by boosting the extraction temperature (0.4 to 0.6 kg $ClO_2$/ton pulp). The $D_0$(EOP) treatment with 0.3% peroxide afforded $ClO_2$ reductions of 1.0 to 3.3 kg/ton pulp versus




***4. Minimum total $ClO_2$ consumption for hardwood kraft pulps for various brightness targets: (A) mixed hardwood pulp (kappa no. 15); (B) red oak pulp (kappa no. 14); and (C) oxygen-delignified sweetgum (kappa no. 12.1). Bleach sequences of $D_0$(EO)$D_1$ and $D_0$(EOP)$D_1$. Data calculated from Figs. 1 and 2.***

$D_0$(EO). Increasing the peroxide charge to 0.5% resulted in savings of 1.7 to 5.2 kg $ClO_2$/ton pulp when compared to an (EO) stage. Employing an (EOP) stage yielded higher overall $ClO_2$ reductions for the mixed hardwood pulps (Fig. 4A) than for either single-specie pulp. In general, the short bleach sequence models for the various hardwood pulps illustrate that a 90°C to 95°C (EO) is roughly equivalent to a 70°C to 75°C (EOP) using 0.15% peroxide.

The distribution of overall $ClO_2$ between the $D_0$ and the $D_1$ varied for $D_0$(EO)$D_1$ and $D_0$(EOP)$D_1$ sequences and for the various hardwood kraft pulps (**Table II**). Increasing the (EO) temperature reduced the $ClO_2$ needed in $D_1$ stage for the mixed hardwood pulp without impacting the $D_0$, whereas the

| Hardwood Pulp | Bleach Sequence | Extraction Stage | % $ClO_2$ (on Pulp) | | %Total $ClO_2$ (on Pulp) | Proportion of Total % $ClO_2$ in $D_0$ | Final Brightness |
|---|---|---|---|---|---|---|---|
| | | | $D_0$ | $D_1$ | | | |
| Mixed hardwood [25,26] | $D_0$(EO)$D_1$ | 75°C/0% P | 1.71 | 0.72 | 2.43 | 70.3 | 85% ISO |
| | $D_0$(EO)$D_1$ | 95°C/0% P | 1.71 | 0.58 | 2.29 | 74.6 | 85% ISO |
| | $D_0$(EOP)$D_1$ | 75°C/0.3% P | 1.69 | 0.40 | 2.09 | 80.9 | 85% ISO |
| | $D_0$(EOP)$D_1$ | 75°C/0.5% P | 1.54 | 0.40 | 1.94 | 79.4 | 85% ISO |
| Mixed hardwood [25,26] | $D_0$(EO)$D_1$ | 75°C/0% P | 1.71 | 1.04 | 2.75 | 62.1 | 87% ISO |
| | $D_0$(EO)$D_1$ | 95°C/0% P | 1.71 | 0.91 | 2.62 | 65.3 | 87% ISO |
| | $D_0$(EOP)$D_1$ | 75°C/0.3% P | 1.69 | 0.40 | 2.09 | 80.9 | 87% ISO |
| | $D_0$(EOP)$D_1$ | 75°C/0.5% P | 1.71 | 0.44 | 2.15 | 79.5 | 87% ISO |
| Red oak [8] | $D_0$(EO)$D_1$ | 70°C/0% P | 0.86 | 0.62 | 1.48 | 58.0 | 85% ISO |
| | $D_0$(EO)$D_1$ | 90°C/0% P | 0.80 | 0.62 | 1.42 | 56.2 | 85% ISO |
| | $D_0$(EOP)$D_1$ | 70°C/0.3% P | 0.80 | 0.54 | 1.34 | 59.6 | 85% ISO |
| | $D_0$(EOP)$D_1$ | 70°C/0.5% P | 0.80 | 0.47 | 1.27 | 62.8 | 85% ISO |
| Red oak [8] | $D_0$(EO)$D_1$ | 70°C/0% P | 0.95 | 0.85 | 1.80 | 52.8 | 87% ISO |
| | $D_0$(EO)$D_1$ | 90°C/0% P | 0.89 | 0.85 | 1.74 | 48.6 | 87% ISO |
| | $D_0$(EOP)$D_1$ | 70°C/0.3% P | 0.80 | 0.85 | 1.65 | 59.6 | 87% ISO |
| | $D_0$(EOP)$D_1$ | 70°C/0.5% P | 0.80 | 0.76 | 1.56 | 51.2 | 87% ISO |
| Oxygen-delignified sweetgum [19] | $D_0$(EO)$D_1$ | 70°C/0% P | 0.70 | 0.40 | 1.10 | 63.5 | 85% ISO |
| | $D_0$(EO)$D_1$ | 90°C/0% P | 0.66 | 0.40 | 1.06 | 62.2 | 85% ISO |
| | $D_0$(EOP)$D_1$ | 70°C/0.3% P | 0.60 | 0.40 | 1.00 | 60.0 | 85% ISO |
| | $D_0$(EOP)$D_1$ | 70°C/0.5% P | 0.54 | 0.40 | 0.94 | 57.3 | 85% ISO |
| Oxygen-delignified sweetgum [19] | $D_0$(EO)$D_1$ | 70°C/0% P | 0.82 | 0.40 | 1.22 | 67.2 | 87% ISO |
| | $D_0$(EO)$D_1$ | 90°C/0% P | 0.78 | 0.40 | 1.18 | 66.1 | 87% ISO |
| | $D_0$(EOP)$D_1$ | 70°C/0.3% P | 0.72 | 0.40 | 1.12 | 64.3 | 87% ISO |
| | $D_0$(EOP)$D_1$ | 70°C/0.5% P | 0.66 | 0.40 | 1.06 | 62.1 | 87% ISO |

***II. Optimum distribution of $ClO_2$ in $D_0$ and $D_1$ for the various hardwood pulps treated with different extraction stage conditions.***

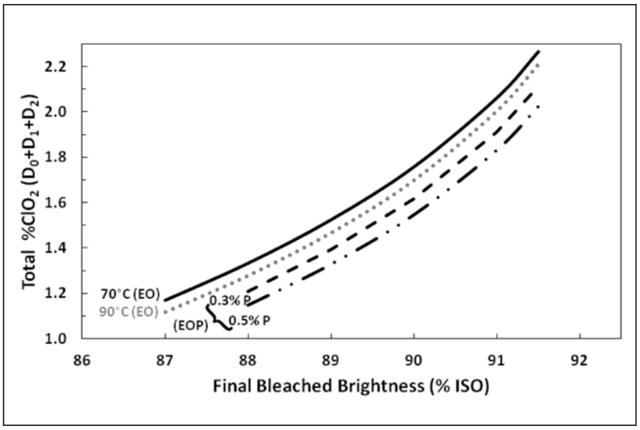
oxygen-delignified sweetgum exhibited the opposite propensity and the red oak pulp had bleach reductions for both stages. The observed trends for these hardwood pulps with increasing (EO) temperature were similar to replacing the (EO) stage with (EOP).

### *Analysis of extraction conditions on bleach consumption of extended ECF sequences*

A similar analysis was performed with the $D_0$(EO)$D_1$ and $D_0$(EOP)$D_1$ models for red oak pulp incorporating the $D_2$ stage model to simulate $D_0$(EO)$D_1E_1D_2$ and $D_0$(EOP)$D_1E_1D_2$. **Figure 5** shows the total amount of $ClO_2$ consumed by the five-stage bleach sequence to obtain a targeted final brightness.

Expanding a three-stage bleach sequence to a five-stage sequence lowered the total amount of $ClO_2$ need to reach 87% to 89% ISO brightness by 6 to 7.5 kg/ton pulp. Nearly identical findings were reported by Reeve and Weishar [8] for red oak (7 kg $ClO_2$/ton pulp). These authors also observed bleach savings of 4 to 5 kg $ClO_2$/ton pulp for maple and sweetgum when the $D_0$(EO)$D_ND_2$ sequence was used as opposed to $D_0$(EO)$D_1$.

Adjusting the (EO) temperature from 70°C to 90°C only afforded 0.5 to 0.6 kg/ton pulp savings of $ClO_2$ when bleaching to 87% to 91.5% ISO brightness. This amount of bleach reduction is nearly identical to that observed earlier for the short sequence $D_0$(EO)$D_1$. Likewise, substituting an (EOP) in place of (EO) decreased $ClO_2$ requirements by 1.4 to




***5. Minimum total $ClO_2$ consumption for a red oak kraft pulp (kappa no. 14) for various brightness targets. Bleach sequences of $D_0(EO)D_1E_2D_2$ and $D_0(EOP)D_1E_2D_2$. Data calculated from Figs. 1–3.***

2.1 kg/ton pulp for peroxide charges of 3 to 5 kg/ton (0.3% to 0.5% on pulp). The $ClO_2$ that was displaced by employing a higher (EO) temperature or by replacing an (EO) with an (EOP) occurred in the delignification and brightening stages.

Other hardwood studies [15,16,18,20-22] have examined extended ECF bleaching sequences using (EO) and (EOP). These studies generally did not contain enough reported data to develop statistical response surface models. However, the data given in these studies can be used for comparison to the model predictions seen with the red oak pulp. Strunk et al. [20,21] examined $D_0(EO)D_1E_2D_2$ and $D_0(EOP)D_1E_2D_2$ sequences for bleaching a kappa no. 16.5 mixed hardwood pulp to >90% ISO brightness. The authors noted that 0.3% peroxide with an (EOP) reduced the overall $ClO_2$ demand by 2.4 kg/ton pulp. Mathur and Dawe [22] investigated $D_0(EO)D_1D_2$ and $D_0(EOP)D_1D_2$ bleaching of an oxygen-delignified mixed tropical hardwood pulp. The results from their study are summarized in **Table III**. When 0.3%-0.7% peroxide was used, it displaced 2 to 10 kg $ClO_2$/ton pulp depending upon the final brightness. The $ClO_2$ savings from these bleach studies are comparable to the observations made from the presented $D_0(EOP)D_1$ model for the mixed hardwood pulp from the previous section.

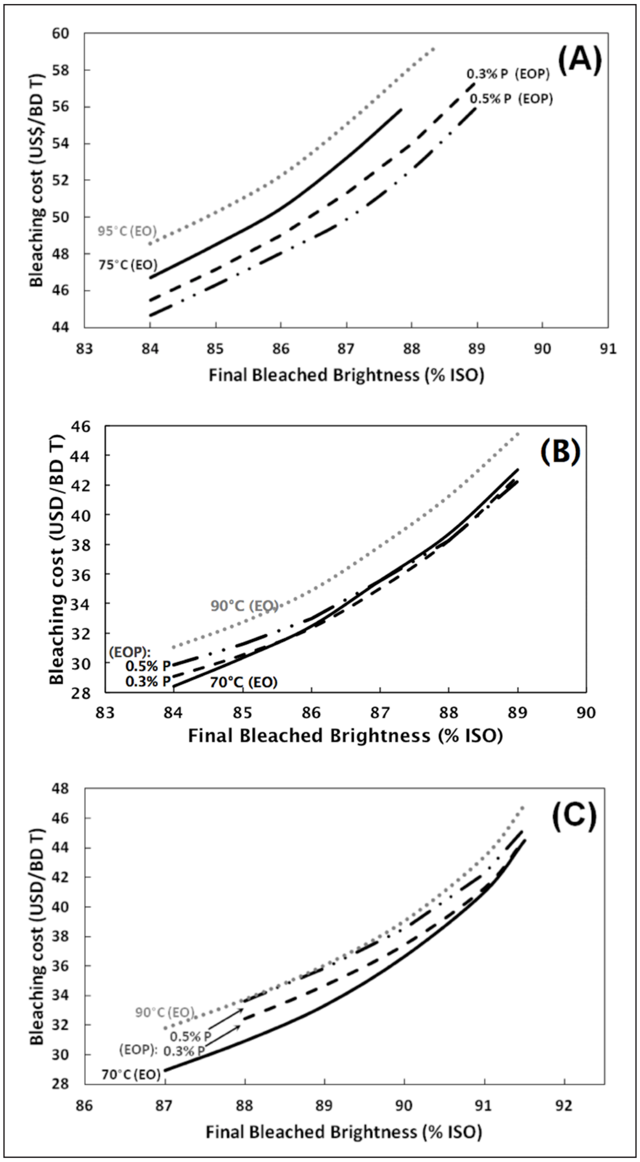
### *Economic analysis*

The bleach consumption models for the mixed hardwood and red oak pulps were used to evaluate the impact of extraction conditions on bleaching costs. The analysis employed the following hypothetical cost inputs for chemicals and energy [28]: chlorine dioxide ($ClO_2$) US\$1.30/kg, hydrogen peroxide ($H_2O_2$) US\$0.80/kg, sodium hydroxide (NaOH) \$0.55/kg, oxygen ($O_2$) US\$0.05/kg, sulfuric acid ($H_2SO_4$) US\$0.13/kg, and steam US\$11.00/kkg (1000 kg) or US\$5.00/klb (1000 lb). Other assumptions used in these economic calculations were similar to those in the softwood study [7]. The results are summarized in **Fig. 6**.

Increasing the extraction temperature of the (EO) stage of a three-stage bleach sequence generally increased the bleaching cost by ~\$1.80/ton for the mixed hardwood pulp (Fig. 6A) and by ~\$2.45/ton for the red oak pulp (Fig. 6B). A similar trend was also observed for the five-stage bleaching of the red oak (Fig. 6C). The substitution of an (EOP) for an (EO) stage yielded various results. Bleaching cost for the mixed hardwood pulp decreased by \$1.20/ton to \$1.90/ton when 0.3% peroxide was used and by \$2/ton to \$3/ton when 0.5% peroxide was used. On the other hand, switching an (EO) with an (EOP) for the short-sequence bleaching of the red oak had little impact on bleaching costs. If the red oak bleach se-

| Sequence | % $H_2O_2$ in (EOP) | Final Brightness (% ISO) | Total $ClO_2$ (% on Pulp) | $ClO_2$ Displaced (% on Pulp) |
|---|---|---|---|---|
| $D_0(EO)D_1D_2$ | 0 | 88 | 1.8 | - |
| $D_0(EOP)D_1D_2$ | 0.3 | 88 | 1.6* | 0.2 |
| $D_0(EOP)D_1D_2$ | 0.5 | 88 | 1.4 | 0.4 |
| $D_0(EOP)D_1D_2$ | 0.7 | 88 | 1.3 | 0.5 |
| $D_0(EO)D_1D_2$ | 0 | 89 | 2.2 | - |
| $D_0(EOP)D_1D_2$ | 0.3 | 89 | 1.9* | 0.3 |
| $D_0(EOP)D_1D_2$ | 0.5 | 89 | 1.6 | 0.6 |
| $D_0(EOP)D_1D_2$ | 0.7 | 89 | 1.4 | 0.8 |
| $D_0(EO)D_1D_2$ | 0 | 90 | 2.6* | - |
| $D_0(EOP)D_1D_2$ | 0.5 | 90 | 1.9 | 0.6 |
| $D_0(EOP)D_1D_2$ | 0.7 | 90 | 1.6 | 1.0 |

***III. Impact of substituting an (EOP) for an (EO) on total $ClO_2$ consumption for an oxygen-delignified mixed hardwood pulp with $D_0(EO)D_1D_2$ or $D_0(EOP)D_1D_2$. Mixed Indonesian tropical hardwood pulp with a kappa no. 10.3. (EO) or (EOP) conducted at 70°C. Data from Mathur and Dawe [22]. Values marked with * are estimated from authors' graphical data.***




***6. Estimated ECF bleaching cost per moisture-free ton for hardwood pulps using different bleach sequences: (A) $D_0$(EO)$D_1$ and $D_0$(EOP)$D_1$ for mixed hardwoods (kappa no. 15); (B) $D_0$(EO) $D_1$ and $D_0$(EOP)$D_1$ for red oak (kappa no. 14); and (C) $D_0$(EO)$D_1E_2D_2$ and $D_0$(EOP)$D_1E_2D_2$ for red oak (kappa no. 14). Estimations are based on the following costs: $ClO_2$ US$1.30/kg; $H_2O_2$ US$0.80/kg; NaOH US$0.55/kg; $O_2$ US$0.05/kg; $H_2SO_4$ US$0.13/kg; and steam US$11.00/kkg (US$5.00/klb). Caustic in (EO) or (EOP) was calculated: % NaOH = 0.5*($D_0$ KF)*(pulp kappa number); $H_2O_2$ in (EOP) at 0.3% or 0.5%; and $O_2$ in (EO) or (EOP) at 0.5%. Calculations similar to the earlier study [7] but do not account for pulp shrinkage (yield loss).***

quence was expanded to five stages, the use of an (EOP) generally yielded bleaching costs that were between a 70°C and a 90°C (EO).

### General discussion

The results of these analyses suggest that hardwood bleaching significantly differs from softwood bleaching. An earlier investigation indicated that a hot 90°C (EO) stage was very effective at lowering bleaching cost for a Southern US softwood utilizing a $D_0$(EO)$D_1$ sequence [7]. However, the amount of bleach that is saved with a hot (EO) for hardwoods (0.4 to 1.5 kg/ton pulp) is outweighed by the steam costs. If steam costs are negligible (~$0/kkg steam), then the cost of extraction at 90°C to 95°C is almost identical to 70°C–75°C. This finding corroborates the conclusions of Süss et al. [15], who questioned the value of aggressive extraction stages for hardwood pulps. Such a stage may have greater value for hardwood bleach plants that have limited retention times and could benefit from accelerated extraction kinetics.

Although not specifically scrutinized in this study, the use of oxygen in an (EO) could also be questionable [15]. A recent review indicated that an (EO) only lowers the post-extraction kappa number by 0 to 0.2 units versus a simple $E_1$ stage for hardwoods [23]. This reduction in kappa number for the pulps examined in this study would roughly save 0.6 to 1.2 kg $ClO_2$/ton pulp. This would translate approximately to $0.50 to $1.30/ton pulp difference in bleaching cost (which takes into account the cost of oxygen). A hardwood bleaching study performed by Ragnar [16] suggested that replacing an $E_1$ with an (EO) saved ~1.1 kg $ClO_2$/ton pulp with a three-stage sequence. Although (EO) and $E_1$ stages are nearly identical, environmental factors would favor the (EO) because it affords a low-cost alternative to reduce extraction effluent color [29].

In most of the previously mentioned cases, the use of an (EOP) stage in place of an (EO) stage resulted in small changes in bleaching cost, especially considering that the historical costs of peroxide range from 60% to 140% of the cost of $ClO_2$ [7]. Under these circumstances, chlorine dioxide and peroxide can be used interchangeably. Replacing chlorine dioxide with peroxide might be advantageous if reduced color and/or adsorbable organic halogens in the ensuing effluents is desired [14,18,24]. The hardwood modeling results indicated that 1 kg of peroxide in (EOP) displaces 0.6 to 1.2 kg of $ClO_2$ needed for ECF bleaching. This replacement ratio is comparable to the eucalypt bleaching investigation by Ranger and Dahllöf [30]. However, it differs from what is seen with softwoods [6], where 1 kg of peroxide in (EOP) displaces 1.4 to 2.6 kg of $ClO_2$ during ECF bleaching.

The recent literature review of hardwood extraction stages [23] indicated that $D_0$(EOP) and $D_0$(EP) sequences yield nearly identical extracted kappa numbers when the KF charges in $D_0$ and the peroxide charges in extraction (≥0.2%) are the same. Thus, this observation would imply that replacing the $D_0$(EOP) sequence with the $D_0$(EP) sequence should result in indistinguishable differences in overall bleaching costs.

The differences in the bleaching of hardwoods versus softwoods are probably attributable to several factors. Hardwood kraft pulps generally contain lower lignin content when compared to softwoods. These structures consume $ClO_2$, oxygen, and peroxide during a bleach sequence [31]. A second difference between the wood species is the hexenuronic acid (HexA) content of the pulps. Hardwood pulps typically contain significant levels of HexA (~30-60 mmol/kg pulp) than softwoods (<30 mmol/kg pulp) [32-34]. Hexenuronic acids can contribute to one-third to two-thirds of the measured kappa number for hardwood pulps as opposed to <20% for softwoods. These unsaturated structures consume $ClO_2$ but are virtually inert toward oxygen, peroxide, or alkali [32,33].

## CONCLUSIONS

This study reanalyzed the data from three hardwood bleaching studies to illustrate how elevated extraction temperatures or peroxide reinforcement of (EO) stages can effect total $ClO_2$ consumption in three- and five-stage ECF sequences. Higher (EO) temperatures resulted in small reductions of total $ClO_2$ usage (0.04%–0.15% on pulp). Applications of peroxide to a 70°C (EO) can displace 0.6–1.2 kg $ClO_2$ per kg peroxide used. An aggressive (EO) stage (i.e., ≥90°C) does not afford significantly lower hardwood bleaching cost as has been observed for softwoods. Replacing an (EO) with an (EOP) stage resulted in small changes in overall bleaching cost. The results from this analysis demonstrate that hardwoods respond differently to ECF bleaching when compared to softwoods, particularly regarding aggressive oxidant-reinforced extraction stages. **TJ**

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## ABOUT THE AUTHORS

This paper is an accompanying article to the earlier ones I wrote on softwood brownstocks in *TAPPI Journal* 9(8): 27(2010) and 9(9): 47(2010), which examined how oxidant-reinforced extraction affects the overall ECF bleach sequence optimization. I wanted to do a similar study for hardwood; that is, to examine how extraction affects hardwood bleaching economics from a holistic viewpoint. In the past, it was assumed that hardwood and softwood bleach similarly; however, recent studies have noted distinct differences in how these species respond to extraction conditions.

A challenge with this investigation, similar to the softwood study, was constructing a steady-state model of a hypothetical bleach plant. These models are predicated on laboratory data published in the literature. Several hardwood studies have systematically investigated the $ClO_2$ delignification and brightening stages of various ECF sequences; however, most of the studies only employed a fixed set of extraction conditions. This obstacle was overcome by approximating the effects of oxygen and/or peroxide reinforcement, as well as reaction temperature, on extraction performance. These estimated effects were based on generalized trends reported in a review of $ClO_2$ delignification of hardwoods in *TAPPI Journal* 12(2): 17(2013).

This investigation demonstrates how peroxide reinforcement or higher extraction temperatures affect total $ClO_2$, as well as the allocation of $ClO_2$ in the D-stages. The findings from the various scenarios indicated that increasing oxidant-reinforced extraction temperature (e.g., 70°C–90°C) has little impact on total bleach consumption and generally results in slightly higher bleaching costs. The use of peroxide in extraction can displace an approximately equal amount of $ClO_2$. These findings differ significantly from those reported earlier for the softwood studies.

*Brogdon*

Operators, engineers, and managers can use this information as a guide to altering process conditions/targets when the cost of bleaching chemicals and energy fluctuate. Also, the information can serve as a generalized reference for the bleaching of North American hardwood pulps.

I am currently working on some improvements and broader generalizations of the ECF brightening models, and how to couple these models to the ECF delignification models. The softwood models look promising, and I presented these findings at the 2013 TAPPI PEERS Conference in Green Bay, WI.

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