

USING BLEACHING STAGE MODELS FOR BENCHMARKING HARDWOOD ECF BLEACH PLANTS

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ABSTRACT

Steady-state models estimated the performance of the D_0 (EOP) D_1 bleach sequence at two mixed hardwood bleach plants in the southern US. At Mill 1, the full sequence's chlorine dioxide charge was monitored for two weeks, which brightens the pulp to ~84% ISO. Mill 2 considered the partial sequence for nearly four weeks that brightens the pulp to ~86% ISO. Elevated levels of chlorine dioxide were linked to increased washer carryover in brownstock and extraction areas. For Mills 1 and 2, an extra 0.24% and 0.33% chlorine dioxide was consumed in the D_0 stage. This extra bleach demand was equivalent to an additional 4.8 and 5.5 kappa load to the brownstock, respectively. Some differences were observed for the D_1 stage. Mill 1 had extraction carryover that averaged 1.1 units higher than was measured. It contributed an extra 0.22% chlorine dioxide being used. Mill 2 had extraction carryover that averaged between zero and 0.7 kappa units and consumed up to 0.13% more chlorine dioxide. Another data set from Mill 2 showed high brownstock and extraction carryover, leading to ~0.90% total chlorine dioxide usage to brighten to 84% ISO. Overall, this investigation illustrated that the models could be employed as benchmarks.

INTRODUCTION

In North America, mixed hardwood bleach plants constantly determine ways to lower production expenses. Roughly 55% to 70% of the variable costs are related to the wood used [1-3]. Next, pulping and bleaching chemicals comprise 15% to 25% of variable costs with the bulk related to chlorine dioxide usage. The rest of the costs are steam and electricity (energy).

Various factors influence the chlorine dioxide usage and efficiency throughout hardwood ECF bleaching. These issues have been covered with North American softwood kraft pulps [4-15]. Like the softwood pulps, familiar inadequacies for bleaching hardwood pulps include the elevated chemical usage because of washer carryover, such as brownstock (or post-oxygen delignification) and first extraction stage. Many mills have examined this carryover coming into the D_0 stage. However, most mills infrequently measure the carryover to D_1 stage.

Recently, a computer model was employed for softwood bleach sequences [16]. Global steady-state models for ECF delignification and brightening were used. The benefits of such models are they can delineate how bleaching delignification or incoming brownstock kappa number is altered, or how D_1 brightness is influenced by the bleach applied and extracted kappa number of the pulp. Additional modifications allow the models to inspect how washer carryover influence chlorine dioxide charge D_0 and D_1 , besides how pulp bleaching is altered.

For this study, the in-line sensor data gathered from two US hardwood bleach plants are examined. These kraft mills bleach the brownstocks using the D_0 (EOP) D_1 as their sequence. Models for delignification and brightening are used to assess the effectiveness of chlorine dioxide. The models are also used to estimate how much brownstock and extraction washer carryover are occurring. These assessments will show how the models can identify and measure problems in the hardwood bleach plant.

METHODOLOGY

Daily average data were gathered from two southern US hardwood bleach plants (*i.e.*, Mill 1 and 2). These mills used automated in-line sensors to assess various stream properties (*e.g.*, kappa number, pulp brightness, pH, *etc.*) to control the process. Throughout the data compilation, the bleach plants functioned at comparatively constant production rates. It was presumed that the sensors were calibrated and maintained. Earlier articles [16-20] cover the specifics of the D_0 (EOP) delignification and D_1 brightening models.

The mixed hardwood bleaching delignification model is given by:

$$[Kappa_1] = [Kappa_0] * \left(1 - 1/n \cdot \ln \left(\frac{[x_0] + 2.77 \cdot e^{-n}}{2.77 \cdot e^{-n}} \right) \right) \quad \text{Eq. (1)}$$

where $Kappa_0$ is the brownstock kappa number, x_0 (% ClO_2 on oven-dried pulp) is the chlorine dioxide used in the D_0 stage, and $Kappa_1$ is the post-extracted kappa number. The value of n is a linear function of hydrogen peroxide charge (P) [18,19]:

$$n = 1.61 \cdot P + 3.77 \quad \text{Eq. (2)}$$

The D_1 mixed hardwood brightness model is given by:

$$B_{D1} = c_{01} - \frac{\beta_1}{x_1 + \frac{\beta_1}{c_{01} - B_E}} \quad \text{Eq. (3)}$$

where x_1 (% ClO_2 on oven-dried pulp) is the chlorine dioxide used in the D_1 stage, B_E (% ISO) is the post-extracted pulp brightness, and B_{D1} (% ISO) is the post- D_1 brightness [20]. The constant c_{01} (% ISO) is the estimated brightness limit for kraft pulp (i.e., 93.4% ISO for Mill 1 or 92.5% ISO for Mill 2). This value is evaluated from the Kubelka-Munk remission function, which is based on the unbeaten light scattering (ca. 42.9 m²/kg for Mill 1 and 32.9 m²/kg for Mill 2) and absorption (ca. 0.10 m²/kg) coefficients for the hardwood pulp. The tuning parameter, β_1 (% ClO_2 •% ISO), is established from the post-extracted kappa number entering the D_1 by the expression:

$$\beta_1 = a \cdot [Kappa_1] - b \quad \text{Eq. (4)}$$

The values of a and b are 4.36 and 4.84 for Mill 1, and 1.68 and 1.98 for Mill 2.

Table I. Computations of predicted variables based on various model inputs from daily-averaged bleach plant data with similarities of the predictions to the mill values to estimate washer carryover.

Bleaching Model	Inputs (Averaged Mill Data)	Calculated Variable (Prediction)	Calculated vs. Averaged Mill Value
D_0 (EOP) Delignification (Eqs. 1 & 2)	$P, x_0, Kappa_0$	$Kappa_1$	Brownstock carryover (C.O.) to D_0 if Calculated $Kappa_1 < \text{Mill's } Kappa_1$
	$P, Kappa_0, Kappa_1$	x_0	Difference represents ClO_2 consumed by C.O.
	$P, x_0, Kappa_1$	$Kappa_0$	Difference represents C.O. (as kappa units)
D_1 Brightening (Eqs. 3 & 4)	$Kappa_1, x_1, B_E$	B_{D1}	Extraction C.O. to D_1 if Calculated $B_{D1} > \text{Mill's } B_{D1}$
	$Kappa_1, B_E, B_{D1}$	x_1	Difference represents ClO_2 consumed by C.O.
	x_1, B_E, B_{D1}	$Kappa_1$	Difference represents C.O. (as kappa units)

Equations 1 to 4 were initially used to calculate $Kappa_1$ and B_{D1} (Table I). These values were based on daily-averaged $Kappa_0$, x_0 , B_E , and x_1 values, as well as the peroxide used in (EOP). Once determined, these values were compared to the mill's daily-averaged extracted kappa and post- D_1 brightness to determine if washer carryover is affecting stage performance. When the predictions for $Kappa_1$ and B_{D1} were better than the mill's extracted kappa and post- D_1 brightness, then further tests were performed on the model's daily-averaged mill data.

Equations 1 to 4 were then used to explain other predicted quantities in Table 1, like x_0 or $Kappa_0$ for bleaching delignification, and x_1 or $Kappa_1$ for D_1 brightening. These values were compared to the daily-averaged mill data to approximate the entering washer carryover as wet kappa units, or chlorine dioxide consumed by D_0 or D_1 [16]. Model uncertainties for the hardwood estimates (Table II) are determined using the propagation of errors method [21].

Table II. Estimated uncertainty in the calculated variables from the bleaching models.

Hardwood Bleaching Model	Calculated Variable (Prediction)	Estimated Uncertainty
D ₀ (EOP)Delignification (Eqs. 1 & 2)	$Kappa_1$	±0.07 to ±0.20 kappa units
	x_0	±0.07% to ±0.09% ClO ₂ on o.d. pulp
	$Kappa_0$	±1.3 to ±2.7 kappa units
D ₁ Brightening (Eqs. 3 & 4)	B_{D1}	±0.4% to ±1.2% ISO points
	x_1	±0.06% to ±0.16% ClO ₂ on o.d. pulp
	$Kappa_1$	±0.15 to ±0.40 kappa units

Approximations of hardwood brownstock carryover are founded upon the extra chlorine dioxide used; these excesses were similar to softwood pulps [16]. It was estimated that one kg saltcake (Na₂SO₄)/t pulp carryover consumed 0.3 kg chlorine dioxide/t pulp (or one kg chemical oxygen demand (COD)/t pulp consumed 0.2 kg chlorine dioxide/t pulp). Predicted hardwood extraction carryover (expressed as COD) was estimated from its filtrate kappa number much in the same way as with softwoods [16]:

$$\text{Model's Extraction Filtrate COD (kg/t pulp)} = 4.5 \cdot (\text{Model's Filtrate Kappa on pulp}) + 2.4 \quad \text{Eq. (5)}$$

RESULTS

Overview

The model computed data from two southern US hardwood bleach plants that used the D₀(EOP)D₁ bleach sequence. For Mill 1, the full sequence produced an 84% ISO brightness pulp. It was from a mixture of gums (black and sweet), southern oaks, ashes, and poplars that used a modified kraft process. Mill 2 employed this partial sequence to obtain an 86% ISO pulp, which was predominantly from gums and southern oaks (75% to 90% by mass). This mill used a conventional kraft process. In both mills, the D₀ stage operated with zero chlorine dioxide residuals. The D₁ stages operated with trace vat residuals (*ca.* ≤ 0.05 g ClO₂/L).

Mill 1: D₀(EOP)D₁ Full Sequence

Figure 1 provides the daily averages from the full D₀(EOP)D₁ bleach plant for Mill 1. Furthermore, the plot presents the calculated data from D₀(EOP) delignification and D₁ brightening models. During this two-week period, Mill 1 has brownstock kappa numbers that varied between 14.6 and 16.5 kappa number with an overall averaged of 15.4. Mill 1 uses a kappa factor (KF), which is the amount of chlorine dioxide consumed (as active chlorine) on o.d. pulp per brownstock kappa, that is between 0.17 and 0.23. This results in D₀(EOP) kappa numbers that ranged from 2.9 to 3.9 (Fig. 1A and B). The delignification model predicts that the pulp should have extracted kappa numbers of 2.6 to 3.5 (Fig. 1B). When the excess KF charge is determined, the KF is approximately 0.02 units higher for days 1, 2, 3 and 14, and approximately 0.04 to 0.06 units higher for the other days. It is assumed that brownstock carryover influences the D₀ stage in the later cases. On days 6 to 12, the model-determined carryover is exhausting roughly 0.31% more ClO₂ on pulp. These amounts are beyond the delignification uncertainty errors (*i.e.*, 0.07% ClO₂ on pulp).

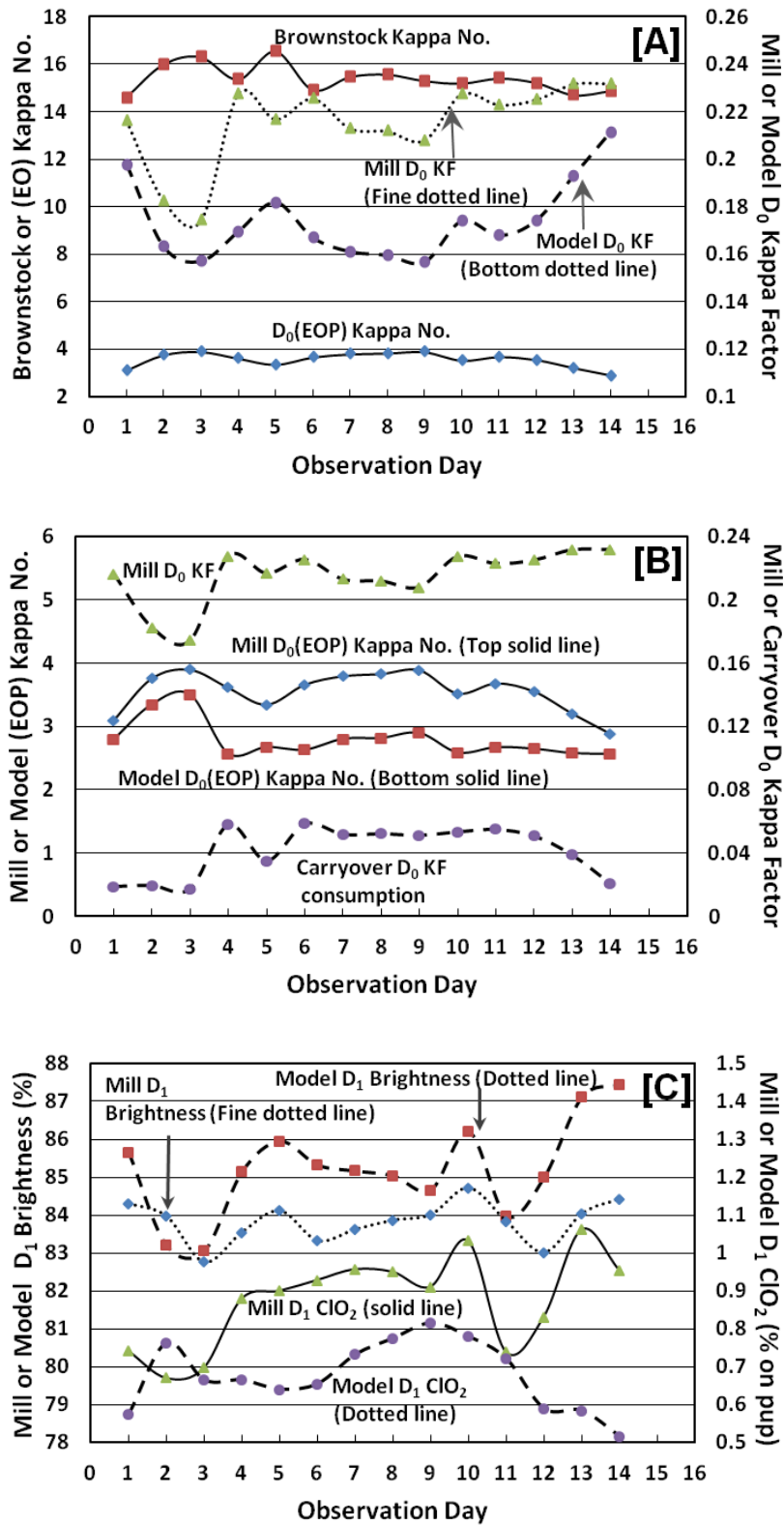


Figure 1. Comparing the daily averages of the D₀(EOP)D₁ full sequence of Mill 1 to the D₀(EOP) delignification model (A and B) and the D₁ brightening model (C).

Figure 1C allows one to compare the actual D_1 stage to the brightening model data for Mill 1. Throughout this assessment, the final mixed hardwood brightness stays around 84.0% ISO. The model's D_1 brightness fluctuates between 83% and 87% ISO brightness with the preponderance of days higher than the mill. When the mill data of extracted kappa ($Kappa_1$) and D_1 brightness (B_{D1}) are placed into Eq. 3, the amount of extra chlorine dioxide spent on the bad days (days 4 to 7, 10, 12, 13 and 14) amounts to 0.25% to 0.48% on pulp. These values are outside the uncertainty errors of the brightening model (*i.e.*, $\pm 0.10\%$ ClO_2 on pulp).

Mill 2: D_0 (EOP) D_1 Partial Sequence

The daily averages for Mill 2's partial D_0 (EOP) D_1 sequence are shown in **Figure 2**, along with predicted data from delignification and brightening models. This mill allowed for daily data to be collected for nearly four weeks (with a gap at day 14). Mill 2 has brownstock kappa numbers that ranged between 11.4 and 15.5 with an overall averaged of 13.2. The mill uses a KF of 0.20 to 0.29 to obtain D_0 (EOP) kappa numbers between 3.4 and 4.0 (Fig. 2A and B). Usually, the model predicts kappas between 2.0 and 3.3, which are about 1.1 kappa units lower. Further calculations indicate that the brownstock washer carryover is consuming 0.05 to 0.13 KF charge, with the overall average being around 0.07 KF. This shows that D_0 stage is using an extra 0.33% ClO_2 on pulp, which is well past the model's uncertainty errors (*i.e.* $\pm 0.07\%$ ClO_2 on pulp).

Figure 2C lets one see the actual D_1 stage *versus* the brightening model data for Mill 2. The mill bleaches the mixed hardwood between 85% and 87% ISO brightness. Typically, the model's D_1 brightness oscillates between 85.5% and 87.9% ISO brightness. It is observed with the first half trial that the model's D_1 brightness values averaged 1.1 points higher than the actual values, whereas in the second half, the brightness values of both are the same. When the mill extracted kappa and D_1 brightness are used, the excess chlorine dioxide used on the bad days (days 6, 7, 9 and 10) is between 0.28% and 0.43% on pulp. On these days, the quantities are beyond the brightening model's uncertainty errors (*i.e.*, $\pm 0.10\%$ ClO_2 on pulp).

Mill 2: Brownstock Washer Carryover

Mill 2, unlike Mill 1, monitored the brownstock washer carryover into D_0 stage daily. Washer losses, when expressed as the sensor's saltcake (Na_2SO_4), are provided in **Figure 3** along with the delignification model predictions. The standard error of the daily sensor's values is estimated to be ± 5.7 kg Na_2SO_4 /t pulp [22], whereas the model's uncertainty is expected to be ± 2.3 kg Na_2SO_4 /t pulp. Almost all the data are within the errors prescribed.

DISCUSSION

In the examination, it was found that the hardwood bleaching models could measure the effectiveness of chlorine dioxide in the mill's D_0 and D_1 stages. Similar to the kraft softwoods [16], both mixed hardwoods commanded an additional 0.24% and 0.33% chlorine dioxide *versus* the delignification model. The delignification model implied the extra bleach used is attributed to brownstock washer carryover, which is a common problem at most of US mills. If this is the case, then the two mills had carryover levels between 8 and 11 kg Na_2SO_4 /t pulp. Put in another way, the carryover levels were exerting an additional 4.8 and 5.5 kappa load on the incoming brownstock. One trial value was corroborated with Mill 2. This mill saw an overall average sensor carryover of 11.8 kg Na_2SO_4 /t pulp (or 16.7 kg COD/t pulp). The brownstock carryover observed in these two southern US mills is common to Canadian hardwood mills [23].

By using the D_1 brightening model, it was possible to approximate the chlorine dioxide used for brightening. It also determined the amount of extraction carryover, which increased the chlorine dioxide demand. For Mill 1, the D_1 stage spent an additional 0.2% to 0.4% chlorine dioxide on pulp on days 4 through 7, 10 and 12 through 14 to obtain ~84% ISO. The calculations showed that Mill 1 had a daily D_0 (EOP) kappa that was roughly 1.1 units higher than determined (3.4 measured vs. 4.5 calculated). The D_1 stage operated better for Mill 2. Here, the mill ran with chlorine dioxide charges close to the predicted values. Only on days 6, 7, 9 and 10 did the D_1 stage use 0.3% to 0.5% more chlorine dioxide than the brightening model to reach ~86% ISO. During the first half of the trial, the D_0 (EOP) kappa averages ran ~0.7 units higher than was measured. For the second half of the trial, the D_0 (EOP) kappa

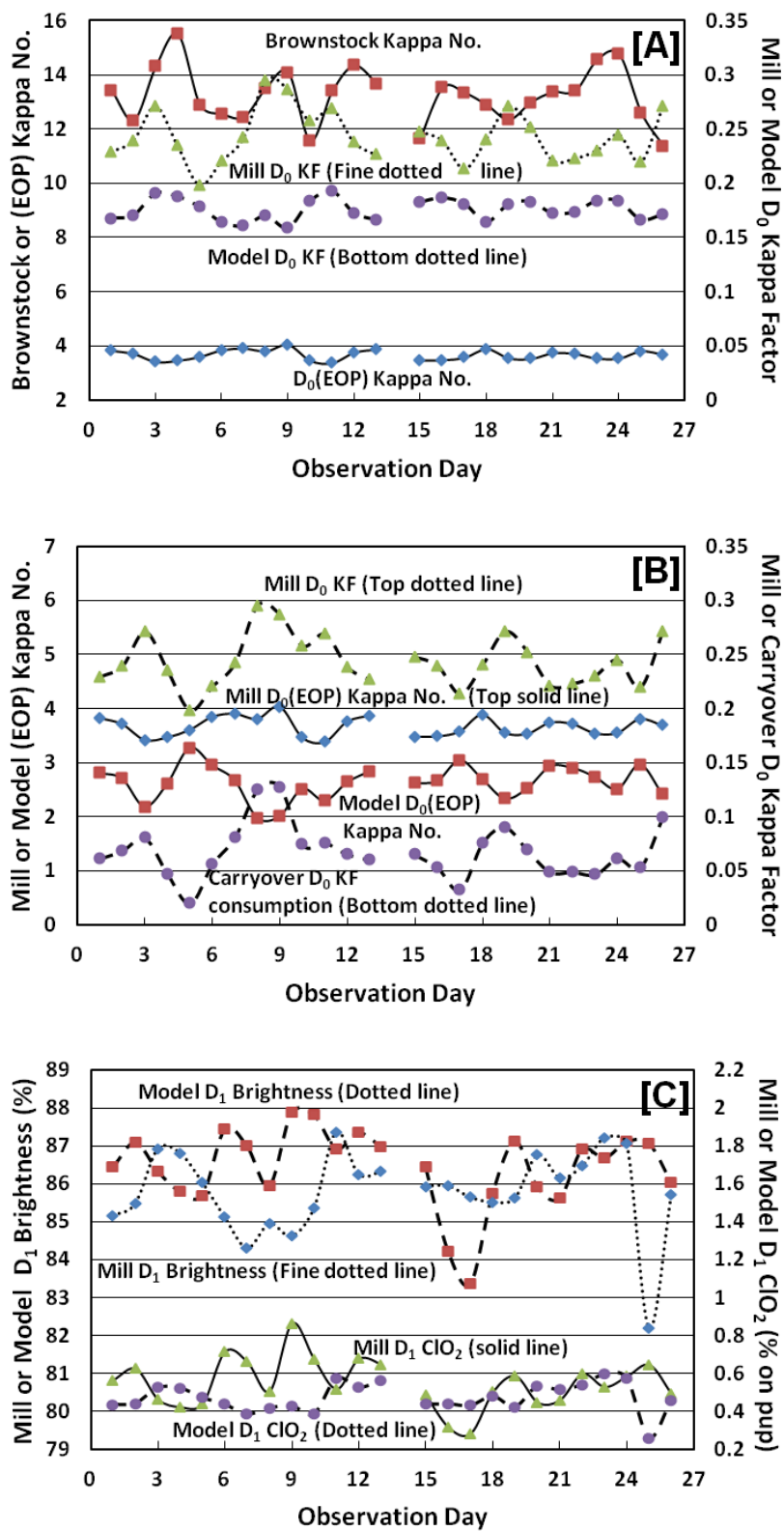


Figure 2. Comparing the daily averages of the D₀(EOP)D₁ partial sequence of Mill 2 to the D₀(EOP) delignification model (A and B) and the D₁ brightening model (C).

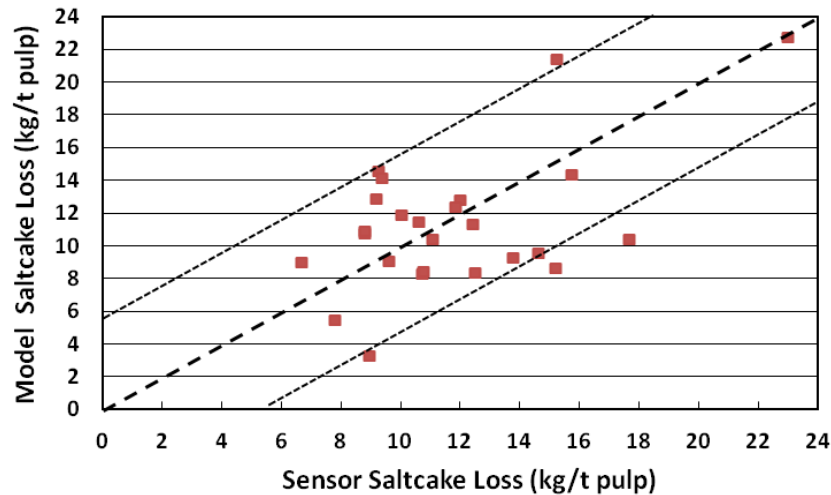


Figure 3. Daily averages of the sensor to the delignification model saltcake (Na_2SO_4) loss for Mill 2. The middle dotted line represents where y is equal to x ; the fine dotted lines are the sensor's uncertainty errors ($\pm 5.7 \text{ kg Na}_2\text{SO}_4/\text{t pulp}$ [22]).

averages were much closer to the model values ($\sim \Delta 0$ kappa units). The extra COD load exerted by the carryover was more or less $7.4 \text{ kg COD/t pulp}$ for Mill 1 and $3.9 \text{ kg COD/t pulp}$ for Mill 2. These carryovers tended to be on par with Canadian hardwood mills [14], which run between 5 and 12 kg COD/t pulp .

Overall chlorine dioxide usage in the two US hardwood bleach plants was examined and compared to the bleaching models. In Mill 1, the total chlorine dioxide used was about 0.27% to 0.69% more than what the models predicted. The total chlorine dioxide inefficiency for Mill 2 ranged from 0.10% to 0.65% on pulp. Most of this extra bleach usage (*i.e.*, >50%) was attributed to delignification rather than the first brightening stage. As with the softwood pulps [16], it is unlikely in these hardwood cases that brownstock washing could be improved further.

Figure 4 illustrates an example of where pulp washing was inadequate. Here, Mill 2 did not perform well in delignification and brightening when targeting for 84% ISO intermediate brightness. These data were collected approximately two months earlier than the first case. The $D_0(\text{EOP})$ kappa numbers were much higher than what the delignification model predicted (*i.e.*, 3.8 vs. 2.3 kappa). It was estimated that an extra 0.10 KF is being used (*ca.* 0.51% extra chlorine dioxide), which equated to $17.1 \text{ kg Na}_2\text{SO}_4/\text{t loss}$. Likewise, D_1 stage required an additional 0.35% chlorine dioxide to reach the target brightness. This was comparable to an extracted pulp with an additional 1.9 kappa load (*i.e.*, 5.7 kappa number). Nearly 0.90% extra chlorine dioxide is being used to bleach the pulp, which is roughly 72% more than what the models predict.

CONCLUSIONS

Bleaching models were employed to verify how well the $D_0(\text{EOP})D_1$ sequence was working at two southern hardwood US bleach plants that used chlorine dioxide. Daily in-line sensor measurements were acquired. These data were analyzed and compared to the predictions of the delignification and brightening models. Mill 1 was discerned to have standard levels of brownstock ($\sim 8 \text{ kg Na}_2\text{SO}_4/\text{t pulp}$) and somewhat elevated levels of extraction washer carryover (1.1 kappa units or $7.0 \text{ kg COD/t pulp}$) during the trial. Mill 2 possessed comparable levels of brownstock carryover as Mill 1 ($11 \text{ kg Na}_2\text{SO}_4/\text{t pulp}$), which was verified by sensor data. Unlike Mill 1, this mill had lower forecasted extraction carryover (≤ 0.7 kappa units or $\leq 5.5 \text{ kg COD/t pulp}$). Both mills operated with an extra 4 to 5 kg/t pulp total chlorine dioxide, and within the typical levels of Canadian bleach plants. An earlier data set from Mill 2 demonstrated very high levels of brownstock ($17.1 \text{ kg Na}_2\text{SO}_4/\text{t pulp}$) and extraction stage carryover (1.9 kappa units or $11.0 \text{ kg COD/t pulp}$). This investigation illustrated that the bleaching models can gauge how effective the chlorine dioxide is being used for hardwood bleaching.

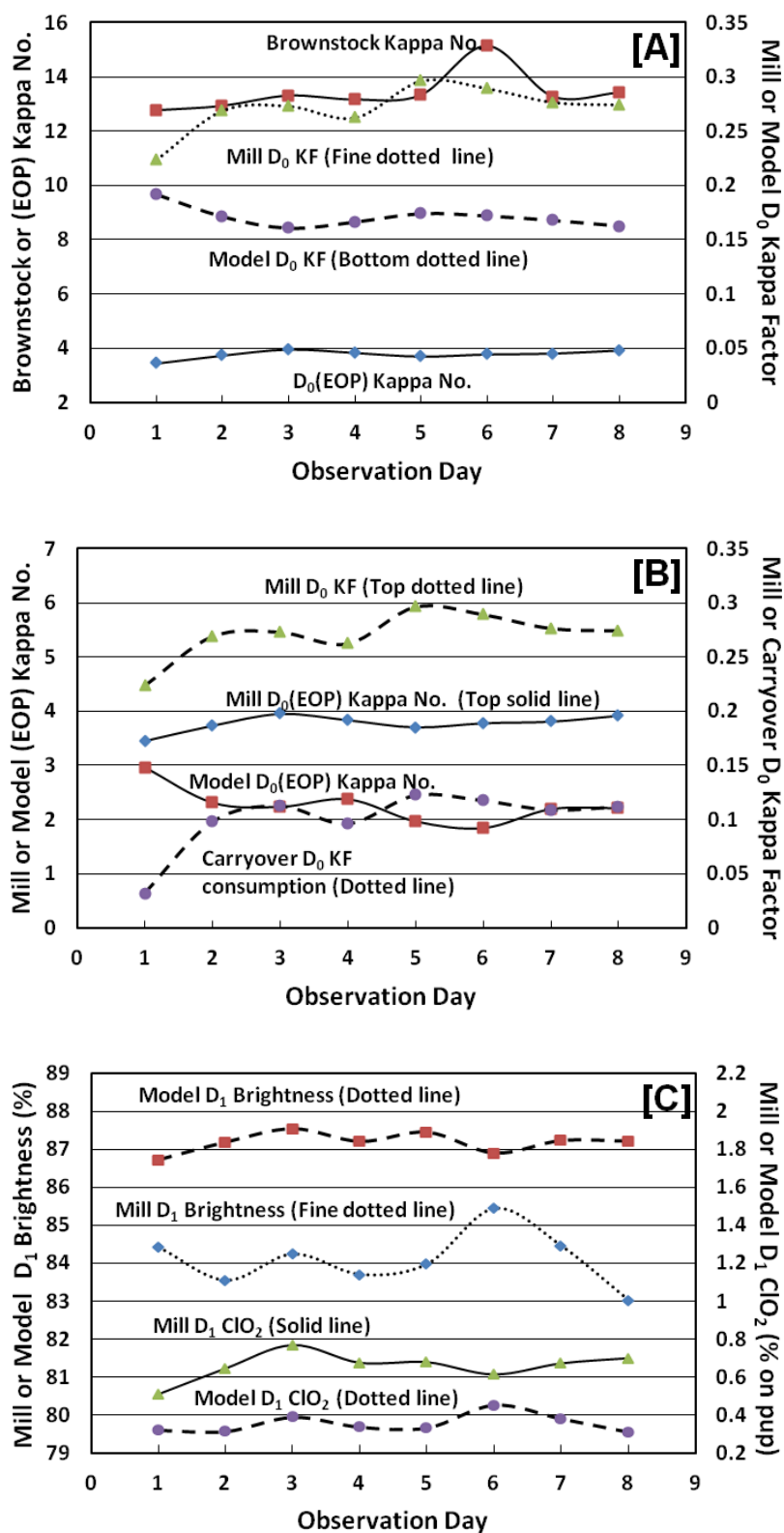


Figure 4. Comparing the daily averages of the D_0 (EOP) D_1 partial sequence of Mill 2 to the D_0 (EOP) delignification model (A and B) and the D_1 brightening model (C) on a bad bleaching week.

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