Optimization of ECF bleaching of kraft pulp: II. Effects of acid prehydrolysis on hardwood pulp bleachability

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ABSTRACT: Earlier studies [1] have shown that when a hardwood kraft pulp is bleached in the $D_0(EO)D_1ED_2$ sequence, the brightness of the pulp emerging from the D_2 stage can be accurately predicted from the brightness of the pulp entering that stage. The entering brightness, in turn, is a well-defined function of the ratio of the D_1 stage ClO_2 charge to the (EO) stage kappa number. In this study, we use the same model, together with the results of pulping and bleaching experiments on southern U.S. red oak chips, to compare the bleachability characteristics of a conventional kappa number 15 pulp with that of an acid-prehydrolyzed pulp having, after 25% kappa number reduction by prehydrolysis, a similar kappa number. After the (EO) stage, the prehydrolyzed pulp had a lower extracted kappa number, but its brightness was lower than that of the control pulp. Both observations may be interpreted in terms of the relative amounts of residual lignin and hexenuronic acid present in the pulps. The full-sequence model described in our previous paper accurately described bleaching of the prehydrolyzed pulp. The model was used to evaluate the effects of the prehydrolysis on the optimized performance of the D_1 and D_2 stages. The brightness disadvantage of the prehydrolyzed pulp after the $D_0(EO)$ stages persisted over the lower range of D_1 charge multiples but diminished as the multiple was increased, eventually disappearing. The prehydrolyzed pulp required slightly less ClO_2 than the control pulp when bleaching to high brightness in five stages.

Application: Bleach plant operators can use the findings of this study to improve operations by adjusting chemical charges. Additionally, those who have access to laboratory facilities can use the approach illustrated by this study to optimize bleaching processes by identifying the most advantageous distribution of chemicals among the various stages.

An earlier study [1] made the case for deriving and using steady-state models of multistage pulp bleaching sequences. Such models are based on the fact that, for each stage, there is a relationship between the entering pulp properties, the conditions prevailing within the stage, and the properties of the pulp leaving it. It is possible to describe this relationship by a mathematical model, the output of which can serve as one of the necessary inputs to a similar model of the following stage. A collection of such models, one for each stage of the sequence, constitutes a predictive model of the entire sequence.

A more complete description of the bleaching process would be provided, at least in principle, by models that account for the effects of the composition of the entering pulp, the composition of the liquid phase mixed with the pulp, flow patterns within the mixer and bleaching tower, concentration gradients throughout the system, temperature, and retention time. However, this is not a practical alternative, since such models would be exceedingly complex and virtually impossible to derive. Other more fundamental approaches [2,3] have involved simplifying assumptions to get around this problem. Because they incorporate kinetic expressions and flow pattern assumptions, models of this kind are, in principle, capable of simulating the dynamic behavior of the bleach plant, a desirable feature for process control applications. However, this capability comes at a price: a high degree of complexity, a large number of parameters, and a demanding requirement for tuning and validation. Keski-Säntti and coworkers [4] addressed this problem by using neural networks to infer the needed relationships from mill operating data. This method results in a model that accurately describes the particular installation on which it is based and does not rely on the availability of laboratory-derived kinetic relationships and assumptions concerning their applicability in the field. On the other hand, the predictive ability of the resulting model is limited to the ranges of the operating variables represented in the operating data used, making it possible, and perhaps even likely, that optimal operating conditions lie outside these ranges. Such models are therefore limited in their ability to optimize the system.

For applications where it is not necessary to simulate process dynamics, much simpler steady-state models suffice. Among the applications of steady-state models is the determination of optimum set points for chemical dosage controllers, which is equivalent to optimizing the allocation of chemicals to the different stages of the sequence for any desired final brightness. Another application of steady-state bleach plant models is as a basis for comparison of the bleachability char-

acteristics of different types of pulp in terms of their minimum chemical requirement to attain a given set of final product properties, such as fully bleached brightness, content of nonfibrous contaminants, brightness stability, etc.

In an early study [5], we identified a broadly applicable equation that describes brightness development in ClO_2 bleaching stages. Subsequently [6], we incorporated it into a full-sequence model for the $D_0(EO)D_1ED_2$ bleaching of a hardwood kraft pulp. The latter work showed that when the pulp was bleached with a D_0 stage kappa factor (KF) of 0.20, the brightness of the pulp emerging from the D_2 stage can be accurately predicted from the brightness of the pulp entering that stage. The entering brightness, in turn, was shown to be a well-defined function of the ratio of the D_1 stage ClO_2 charge to the (EO) stage kappa number. The model incorporating these relationships was used to determine the optimum allocation of ClO_2 to the D_1 and D_2 stages and the minimum total ClO_2 requirement for any desired final brightness. Hart and Connell [7] have used this model, with suitable adjustment of its parameters, to optimize unbleached kappa number with respect to the combined costs of wood and bleaching chemicals for various brightness targets.

In the recent study cited above [1], we extended the model to account for the effect of changing the D_0 KF and used it to assess the effect of digester alkali charge on hardwood kraft pulp bleachability. We also showed how this approach can be used to unambiguously characterize pulp bleachability, minimize the total ClO_2 requirement for any desired final brightness and optimize the allocation of ClO_2 to the three D stages of the D(EO)DED sequence or the two D stages of the D(EO)D sequence.

In the research for this paper, we used the same modeling approach to study the effect of acid prehydrolysis on hardwood kraft pulp bleachability, as well as to determine optimum conditions for bleaching prehydrolyzed pulp in three- and five-stage ECF sequences. Prehydrolysis conditions were chosen to mimic those used in some commercial operations to remove hexenuronic acids that would otherwise consume bleaching chemicals. Previous studies of effects of prehydrolysis on bleachability, as exemplified by the recent work of Costa and Colodette[8], have used a single set or narrow range of bleaching conditions and focused primarily on bleachability in the D_0 stage. In the current study, use of the modeling approach together with experiments employing a wide range of chemical charges in each of the three D stages allowed unambiguous comparison of the bleachabilities of prehydrolyzed and control pulps of similar kappa numbers (14-15) under conditions that were optimum for each pulp type.

EXPERIMENTAL

A southern U.S. mill provided red oak chips. We prepared pulps in an M/K Systems 10-liter laboratory digester, using 30% sulfidity liquor and a temperature schedule that consisted of a 110-min rise from ambient temperature to a maximum cooking temperature of 170°C. Synthetic pulping liquors were prepared from sodium hydroxide and sodium sulfide. Pulp with a kappa number of 14 was prepared with an effective alkali (EA) charge of 17.9%, expressed as Na_2O based on o.d. wood weight. Another pulp was prepared under the same conditions, except that the cook was terminated earlier, giving a kappa number of 20.3. The pulps were screened on a laboratory flat screen having 0.008" slots. The kappa number 20.3 pulp was then acid hydrolyzed with dilute H_2SO_4 at 90°C and pH 3 for 4 hours, resulting in pulp with a kappa number of 14.9. Both pulps were bleached with widely varied chemical charges as described below.

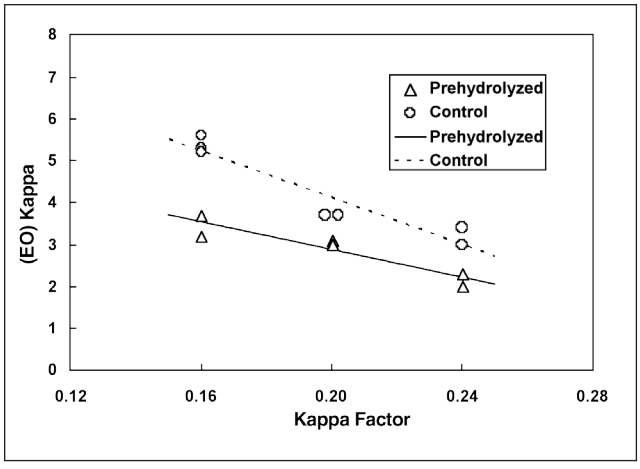
The bleaching sequence was $D_0(EO)D_1ED_2$. We washed the pulp thoroughly between stages. The ClO_2 charge in the D_0 stage was chosen to give one of three specified KFs: 0.16, 0.20, or 0.24. For example, when the KF was 0.20, the amount of ClO_2 charged was equivalent to a chlorine charge numerically equal to 20% of the kappa number of the unbleached pulp. The first stage was carried out for 30 min at 45°C in a Quantum mixer, with an exit pH in the range 1.8 – 2.3. The (EO) stage was conducted at 70°C and 10% consistency in a horizontal shaft peg mixer rotating at 200 rpm and lasted for 60 min. The oxygen pressure, initially at 60 psig, was decreased by 12 psig every five min during the first 30 min, and the alkali charge was equal to 50% of the active chlorine charge in the D_0 stage, giving an exit pH of 11 or higher. The D_1 and D_2 stages were conducted for 180 min at 70°C, and the E_2 stage was at 70°C for 60 min, with an NaOH charge of 0.4%. After the (EO) stage, each pulp was divided into three equal portions, which were then bleached in the D_1 stage with 0.2, 0.6, and 1.8% ClO_2. Each of the three resulting D_1 pulps was then extracted with caustic and further subdivided for bleaching with 0.1, 0.3, and 0.9% ClO_2 in the D_2 stage.

Measurements included pH and residual chemical at the end of each stage, the kappa number after the (EO) stage, and the brightness after the D_1 and D_2 stages. Kappa number and ISO brightness were determined according to TAPPI Test Methods.

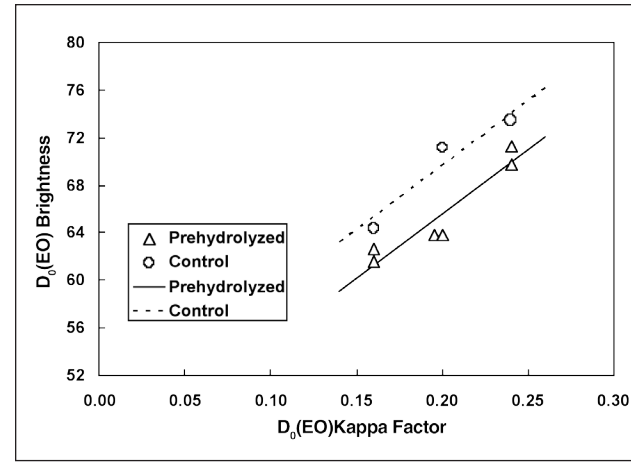
RESULTS AND DISCUSSION

D_0 stage model

Figure 1 presents the results of $D_0(EO)$ bleaching of the two pulp types. Despite the well-known curvilinear dependence of extracted kappa number on KF, the relationship was adequately represented by a linear regression relationship over the range of KFs studied in the present case. The figure shows that the extracted kappa number of the prehydrolyzed pulp was significantly lower than that of the control pulp, especially at the lower end of the range of KFs employed. This observation is readily explained in terms of the relative kappa number compositions of the two unbleached pulps. It is now well established that both residual lignin (RL) and hexenuronic acids (HexA) contribute to the kappa number of unbleached kraft pulps, especially hardwood pulps, and that acid hydrolysis can remove most or all of the HexA. It has also been shown that, in a D_0 stage, chlorine dioxide does not react with HexA [8,9]. Any HexA removal that does result



1. Dependence of (EO) kappa number on D_0 stage kappa factor.



2. D_0(EO) brightness-kappa number relationships.

from a D_0 stage is attributable to chlorine and hypochlorous acid that are byproducts of the reactions with lignin. The results of Fig. 1 can thus be interpreted as follows: the prehydrolyzed and control pulps, although initially having the same kappa number, have different kappa number compositions. In the case of the prehydrolyzed pulp the kappa number reflects primarily RL, while the control pulp's kappa number is due to both HexA and RL. Since chlorine dioxide does not efficiently remove HexA in D_0, the extracted kappa number of the control pulp remains relatively high, owing to its relatively high content of residual HexA. As the KF is increased the difference between the two extracted kappa numbers decreases, as the greater amount of chlorine dioxide present generates larger amounts of HexA-removing chlorine and hypochlorous acid.

When interpreting the results shown in Fig. 1, it is also relevant to consider the possible effect of acid hydrolysis on the structure of the RL present in the pulp. Gellerstedt [10], for example, has shown that acid hydrolysis forms new phenolic hydroxyl groups in RL. Such groups would presumably render the lignin more readily removable in the D_0 and (EO) stages. It is therefore possible that the prehydrolyzed pulp, as well as having a smaller proportion of (ClO_2 resistant) HexA, has RL that is more susceptible to removal by ClO_2 than the RL in the control pulp.

The following equation describes the curves shown in Fig. 1:

$$y_0 = b_{00} - b_{10} \cdot f \quad (1)$$

in which

y_0 = kappa number after the D_0 and (EO) stages

and

f = D_0 stage KF.

The constants in this equation, as well as in the other equations of this paper, are named according to following rule: The first subscript identifies the order of the constant within the equation and the second is the same as that of the stage it refers to (e.g., 0 for D_0, 1 for D_1).

For the prehydrolyzed and control pulps, regression analysis gave b_{00} values of 6.13 and 9.69, respectively. The value of b_{10} was 16.25 for the prehydrolyzed pulp and 27.91 for the control pulp.

The D_0(EO) control pulps, although of higher kappa number, were much brighter than their prehydrolyzed counterparts. After extraction, the prehydrolyzed pulps were not as bright as the control pulps. The brightness disadvantage was ten points at constant kappa number and four points at constant KF (**Fig. 2**). The disadvantage at constant KF was smaller because the prehydrolyzed pulps had lower kappa number after extraction. This result also may be explained in terms of kappa number composition. After D(EO), the kappa number of the control pulp reflects both HexA and RL, while that of the prehydrolyzed pulps may be assumed to be due primarily to RL, the HexA having been removed before bleaching. If, as it seems reasonable to assume, RL is more highly colored than HexA, the higher RL content of the prehydrolyzed pulps at any given extracted kappa number results in lower brightness.

D_1 stage model

The results of experiments in which the prehydrolyzed and control pulps were fully bleached are presented in **Tables I** and **II**, respectively.

The brightness after the D_1 and E stages correlates closely with the ClO_2 charge in the D_1 stage divided by the kappa number of the pulp entering the D_1 stage. This quotient may be referred to as the "D_1 multiple." Note that the ClO_2 charge is expressed as ClO_2, not as equivalent chlorine, when calculating the D_1 multiple.

The relationship between the brightness after the D_1 and E stages and the D_1 multiple may be represented by the equation:

$$y_1 = c_{01} - c_{11} / (m + c_{21}) \quad (2)$$

in which

y_1 = brightness after the D_1 and E stages

and

m = D_1 stage ClO_2 charge multiple.

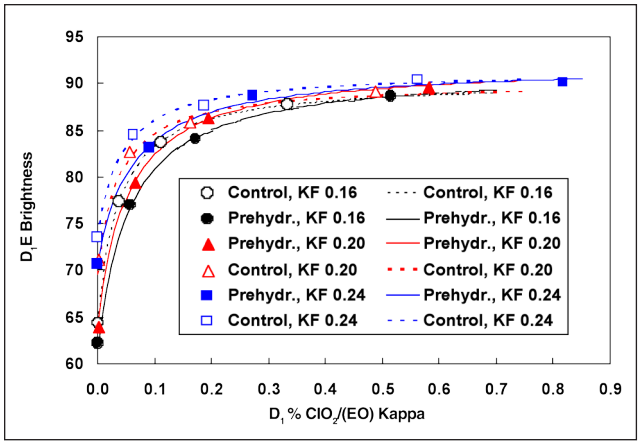
The constant c_{01} is the ultimate brightness ceiling. The

After D_0(EO)			After D_1E			After D_2		
KF	Brightness	kappa	"ClO_2, %"	D_1 End pH	Brightness	"ClO_2, %"	End pH	Brightness
0.16	62.2	3.5	0.2	4.4	77.0	0.1	4.4	84.8
						0.3	3.9	87.6
						0.9	3.7	90.3
			0.6	4.5	84.1	0.1	4.4	89.2
						0.3	4.2	90.6
						0.9	4.0	91.4
			1.8	3.8	88.7	0.1	4.8	91.2
						0.3	4.7	92.3
						0.9	4.6	92.3
0.20	63.9	3.1	0.2	3.9	79.4	0.1	4.2	86.6
						0.3	4.1	88.4
						0.9	3.7	90.7
			0.6	3.7	86.4	0.1	4.7	89.8
						0.3	4.3	90.4
						0.9	4.3	91.5
			1.8	3.4	89.7	0.1	4.9	92.0
						0.3	4.6	92.5
						0.9	4.4	92.6
0.24	70.6	2.2	0.2	3.9	83.1	0.1	4.6	88.8
						0.3	3.8	90.8
						0.9	6.4	90.6
			0.6	3.5	88.7	0.1	4.4	91.8
						0.3	4.4	91.7
						0.9	5.4	92.3
			1.8	3.9	90.1	0.1	4.5	92.1
						0.3	4.8	92.6
						0.9	6.0	92.8

I. Bleaching data for prehydrolyzed pulp.

After D_0(EO)			After D_1E			After D_2		
KF	Brightness	kappa	"ClO_2, %"	D_1 End pH	Brightness	"ClO_2, %"	End pH	Brightness
0.16	64.4	5.4	0.2	4.8	77.4	0.2	4.5	84.2
						0.6	3.2	86.7
						1.8	-	87.9
			0.6	3.9	83.7	0.2	4.3	89.0
						0.6	2.8	90.5
						1.8	4.5	91.1
			1.8	4.0	87.8	0.2	4.2	91.2
						0.6	3.8	91.2
						1.8	4.5	91.3
0.20	71.2	3.7	0.2	4.5	82.8	0.2	4.0	87.4
						0.6	3.7	90.5
						1.8	3.5	91.1
			0.6	4.0	86.0	0.2	4.1	91.3
						0.6	4.7	91.8
						1.8	5.8	92.1
			1.8	4.1	89.2	0.2	4.5	92.0
						0.6	4.6	91.9
						1.8	4.9	92.5
0.24	73.5	3.2	0.2	4.7	84.5	0.2	4.3	89.1
						0.6	3.3	90.5
						1.8	3.9	92.0
			0.6	3.7	87.6	0.2	4.2	91.6
						0.6	4.1	91.9
						1.8	4.7	92.4
			1.8	4.4	90.4	0.2	4.5	91.7
						0.6	4.6	92.7
						1.8	4.8	92.8

II. Bleaching data for the control pulp.



3. D_1E brightness values as functions of D_1 multiple. The top curve is the regression model applicable to the high alkali pulps after a 0.24 kappa factor D_0 stage and the bottom one is the model for the high alkali pulps after a 0.16 kappa factor D_0 stage. The middle curve models all other combinations of alkali and kappa factor studied.

constants c_{11} and c_{21} together determine the brightness of the pulp entering the stage and the dependence of the slope of the response curve on the charge multiple. The brightness of the pulp entering the stage is $c_{01} - c_{11}/c_{21}$. Differentiating Equation (2) gives the slope as a function of m. At a charge multiple of zero, the slope is c_{11}/c_{21}^2 and at any charge the slope is $c_{11}/(m+c_{21})^2$.

Figure 3 shows the D_1E brightness results as a function of D_1 ClO_2 charge multiple, together with the corresponding regression curves based on equation (2). The control pulps behaved as described earlier [1], exhibiting moderately higher D_1E brightness at higher KF for a given D_1 multiple. The prehydrolyzed pulps had lower brightness than the corresponding controls after the $D_0(EO)$ stages and this disadvantage persisted over the lower range of D_1 multiples but diminished as the multiple was increased, eventually disappearing. It is not surprising that the prehydrolyzed pulp curves in this figure fall below those of the corresponding control pulps, in view of the fact that, in the case of the control pulps, whose kappa number reflects both RL and HexA, the "true" D_1 charge multiple, the ratio of ClO_2 charge to that portion of the kappa number that is due to RL, is higher than the "apparent" multiple plotted in Fig. 3. In the case of the prehydrolyzed pulps, the multiple more accurately reflects the ratio of oxidant to RL. Note, however, that substantial HexA removal occurs in the D_1 stage [9], so it is likely that some ClO_2 is consumed by HexA as well as by RL.

	Kappa Factor	c_{01}	c_{11}	c_{21}
Prehydrolyzed	**0.16**	91.54	1.666	0.05681
	0.20	92.16	1.475	0.05216
	0.24	91.94	1.295	0.06058
Control	**0.16**	90.35	0.9669	0.03728
	0.20	90.10	0.7405	0.03596
	0.24	91.32	0.7372	0.04141

III. Values of the fitted constants for equation (2).

The fitted values of c_{01}, c_{11} and c_{21} for the six curves of Fig. 3 are shown in **Table III**. It is perhaps significant that the values of c_{01}, the ultimate D_1E brightness ceiling, average 1.3 points higher for the prehydrolyzed pulps than for the control pulps. This may indicate the presence of difficultly removable lignin-carbohydrate complexes in the control pulps. Such complexes may be at least partially removed by prehydrolysis.

D_2 model

The D_2 stage can be accurately represented by the model used in the earlier studies[1,5]. The relevant equation is:

$$y_2 = b_{02} + b_{12} \cdot [1 - \exp(-b_{22} \cdot x)] \quad (3)$$

in which

y_2 = brightness after the D_2 stage,

and

x = ClO_2 charge in the D_2 stage.

The constants b_{02}, b_{12}, and b_{22} may be interpreted as, respectively, the brightness of the pulp entering the stage, the maximum brightness gain achievable in the D_2 stage, and a constant characteristic of the relative rate of approach to this maximum as the chemical charge is increased. The D_2 stage response curve exhibits a well defined and rapidly approached brightness ceiling, given by $b_{02}+b_{12}$.

Both b_{12} and b_{22} depend on the brightness of the pulp entering the D_2 stage. Consequently the model must include mathematical descriptions of the relationships between these parameters and the entering brightness. These descriptions were obtained by regression analysis of the experimental bleaching data.

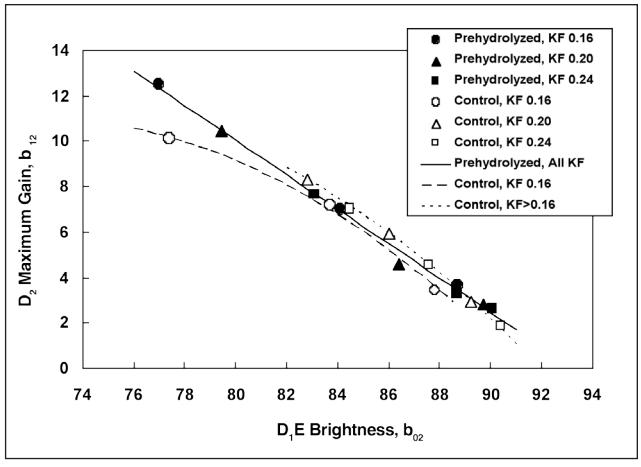
Figure 4 shows the resulting correlations between b_{12} – the maximum possible D_2 brightness gain – and the entering pulp brightness. A single relationship was evident for all of the prehydrolyzed pulps, regardless of D_0 stage KF. For entering brightness values between 82 and 89, the maximum possible D_2 brightness gain of the prehydrolyzed pulps was close to, and intermediate between, that of the 0.16 D_0 KF control pulps and the slightly higher maximum possible gain of the 0.20 and 0.24 KF control pulps. For final brightness values in the range 89 to 91, the prehydrolyzed pulps were capable of undergoing a greater D_2 brightness gain than the control pulps.

The equations of the lines shown in Figure 4 are of the form:

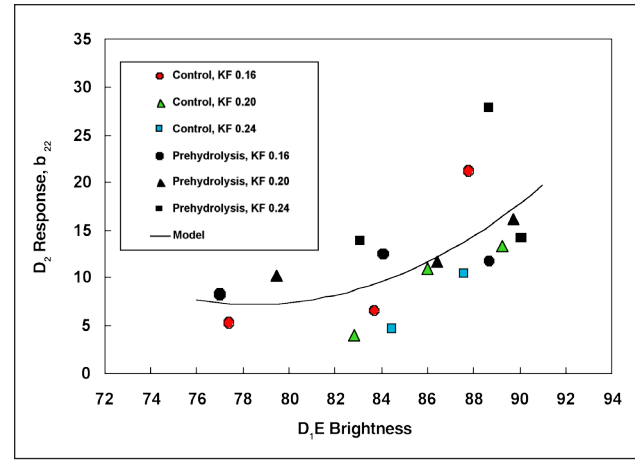
$$b_{12} = b_{120} + b_{121} \cdot y_1 - b_{122} \cdot y_1^2 \quad (4)$$

in which

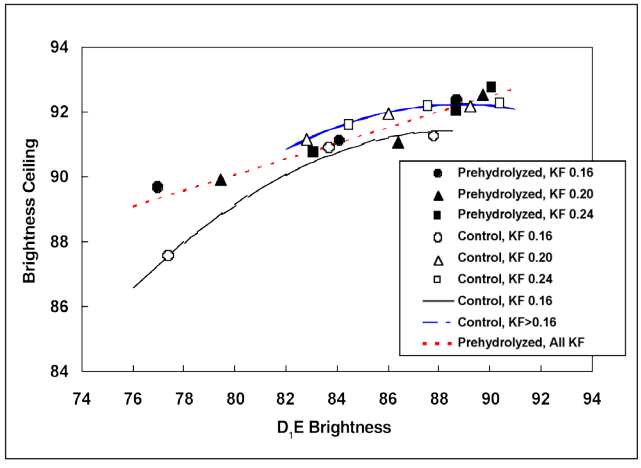
b_{12} = maximum possible brightness gain in the D_2 stage



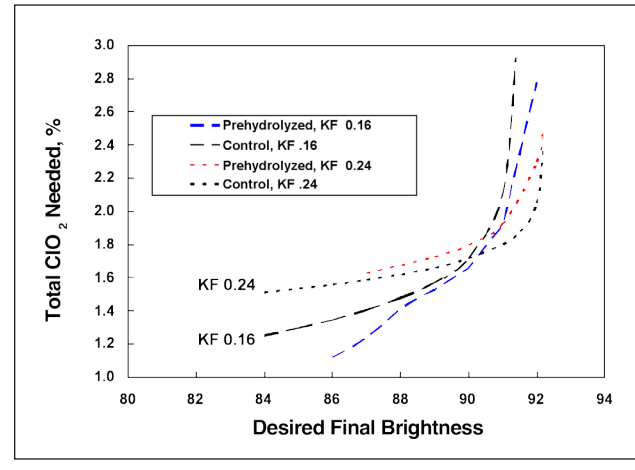
4. Maximum possible brightness gain in the D_2 stage vs. the brightness of the pulp entering the stage.



6. Dependence of the D_2 stage model parameter b_{22} on entering pulp brightness.



5. D_2 stage brightness ceiling dependence on entering pulp brightness.



7. Minimum ClO_2 requirement vs. final brightness target. D(EO)DED sequence.

(a parameter in Eq. 3),

y_1 = brightness after the D_1 and E stages,

$b_{120}, b_{121}, b_{122}$ = regression coefficients.

The values of b_{120}, b_{121} and b_{122} for the prehydrolyzed pulps are 70.64, -0.7573, and 0. For the low-KF control pulp they are -142.08, 4.26, and 0.0296. For the higher-KF control pulps they are -141.33, 4.26, and 0.0296.

A higher value of b_{12} (i.e., a higher maximum possible D_2 brightness gain) at a given entering brightness is equivalent to a higher brightness ceiling. The brightness ceiling of the prehydrolyzed pulps is compared to those of the control pulps in **Fig. 5**, which shows the estimated ceiling value as a function of entering brightness for each pulp condition. The prehydrolyzed pulps are capable of being bleached to a higher brightness when the brightness of the pulp entering D_2 is below 82 or above 89.

The other input required by the D_2 stage model is the parameter b_{22} of equation (3). It can also be predicted from the brightness of the pulp entering the stage, although with somewhat less precision than b_{12}, as shown in **Fig. 6**. This lack of precision is not serious, since the response curve is relatively insensitive to this parameter, except at unrealistically low ClO_2 charges.

The equation of the line shown in Fig. 6 is of the form:

$$b_{22} = b_{220} - b_{221} \cdot y_1 + b_{222} \cdot y_1^2 \quad (5)$$

in which

b_{22} = maximum possible brightness gain in the D_2 stage [a parameter in Eq. (3)],

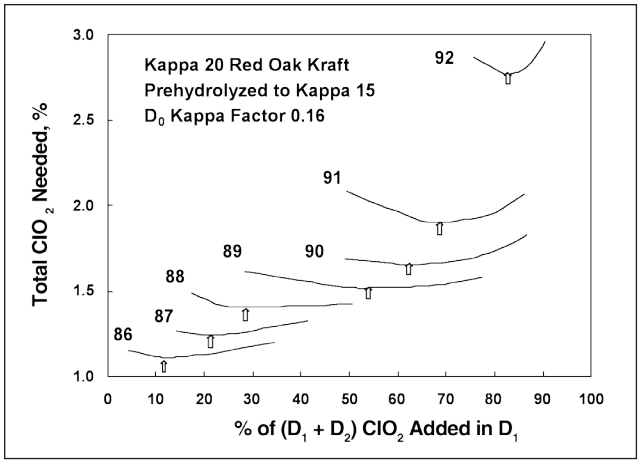
y_1 = brightness after the D_1 and E stages,

$b_{220}, b_{221}, b_{222}$ = regression coefficients.

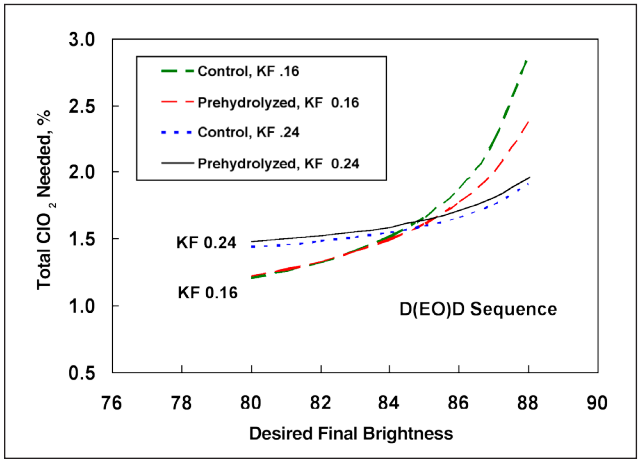
The values of b_{220}, b_{221}, and b_{222} are 504.9, 13.06, and 0.0853.

Applications of the model

A major motivation for deriving a model of a full bleaching sequence is that it allows the bleachability of a given pulp to be unambiguously characterized, in terms of a curve showing the minimum chemical requirement for any desired final brightness target. Other methods, such as laboratory bleaching with constant conditions in all but the last stage and vary-



8. Total D(EO)DED sequence ClO_2 requirement vs. relative allocation of chemical to the D_1 and D_2 stages for D_0 stage kappa factor 0.16 and various final brightness values. Prehydrolyzed pulp. Arrows indicate minimum ClO_2 requirements.



9. Minimum ClO_2 requirement vs. final brightness target. D(EO)D sequence.

ing the chemical in that stage, fail to show each pulp to its best advantage and may well result in incorrect rankings of pulps with respect to their bleachabilities.

The curves in **Fig. 7** were generated by using the model together with the Solver routine of Microsoft Excel® to minimize the ClO_2 requirement to reach various final brightness targets. These curves are characteristic of the bleachabilities of the four pulp types represented. For final brightnesses up to 90, the model predicts that pulping to kappa number 20 followed by prehydrolysis to kappa number 15 gives a pulp that requires slightly less ClO_2 than pulping to kappa number 15 without prehydrolysis, provided that the D_0 stage KF is not too high. When the D_0 stage KF is 0.16, bleaching in five stages to brightness 86 requires 16% less ClO_2 in the former (prehydrolysis) case. The savings decreases to 3% as the target brightness is increased to 89 and then increases to 9% at 91. At a KF of 0.24, prehydrolysis increases the ClO_2 requirement for all brightness targets.

Figure 8 addresses the question of how to optimally allocate ClO_2 to the different D stages in the sequence in terms of percent of the combined D_1 and D_2 charges that should be allocated to the D_1 stage to minimize total chemical requirement when bleaching the prehydrolyzed pulp. For minimum total chemical consumption, the percentage of the total D_1+D_2 ClO_2 that should be added in the D_1 stage ranges from 11% when the brightness target is 86 to 83% when the brightness target is 92. As in the case of the control pulp[1], the required percentage is higher when the brightness target is higher, and higher brightness targets are less forgiving of departures from the optimum allocation. In the case of the prehydrolyzed pulp, however, allocating larger fractions to the D_2 stage is favored.

Three-stage bleaching

The model can also be used to predict the behavior of the pulps studied when the bleaching sequence has only three stages. This involves the assumption that the pulp brightness changes little during the second extraction stage, since the model is based on measurements of D_1E brightness, not D_1 brightness. Experience suggests that this assumption is a valid one.

Figure 9 shows the results of optimization to minimize total ClO_2 requirement for prehydrolyzed and control pulps at two different values of D_0 KF. Prehydrolysis offers no advantage when the KF is 0.24, but at KF 0.16, prehydrolysis decreases the chemical requirement, especially for high brightness targets. However, these brightness targets are more economically achieved by increasing the D_0 KF without prehydrolysis.

CONCLUSIONS

Compared to one made with no prehydrolysis, a kappa 15 red oak kraft pulp made by prehydrolysis of kappa 20 pulp has a lower kappa number after the first two stages of the $D_0(EO)D_1ED_2$ bleaching sequence. A possible interpretation is that, since chlorine dioxide does not efficiently remove HexA, the extracted kappa number of the control pulp remains relatively high, owing to its relatively high content of residual HexA.

After the D_0 and (EO) stages, the prehydrolyzed pulp had a lower brightness at any given D_0(EO) kappa number. A possible interpretation is that, while the kappa number of the control pulp reflects both HexA and RL, that of the prehydrolyzed pulps may be assumed to be due primarily to RL, the HexA having been removed before bleaching. The higher RL content of the prehydrolyzed pulps at any given extracted kappa number might reasonably be assumed to result in lower brightness.

When bleaching hardwood kraft pulps represented by the pulps studied here, the behavior of the D_1 stage can be precisely modeled by an equation of the form, $y_1 = c_{01} - c_{11} / (m + c_{21})$ in which y_1 = brightness after the D_1 and E stages and m = D_1 stage ClO_2 charge multiple (the ClO_2 charge in the D_1 stage divided by the kappa number of the pulp entering the D_1 stage). The brightness disadvantage of the prehydrolyzed pulp after the D_0(EO) stages persisted over the lower range

of D_1 charge multiples but diminished as the multiple was increased, eventually disappearing. The prehydrolyzed pulp exhibited higher values of the constant c_{01}, which corresponds to the ultimate D_1E brightness ceiling. A possible interpretation of this observation is that prehydrolysis removes a recalcitrant colored pulp component.

The D_2 stage can be accurately represented by the model used in earlier studies. The relevant equation is $y_2 = b_{02} + b_{12} \cdot [1 - \exp(-b_{22} \cdot x)]$ in which y_2 = brightness after the D_2 stage, and x = ClO_2 charge in the D_2 stage. The constants b_{02}, b_{12}, and b_{22} may be interpreted as, respectively, the brightness of the pulp entering the stage, the maximum brightness gain achievable in the D_2 stage, and a constant characteristic of the relative rate of approach to this maximum as the chemical charge is increased. The D_2 stage response curve exhibits a well defined and rapidly approached brightness ceiling, given by $b_{02}+b_{12}$. The values of b_{12} and b_{22} are functions of the entering pulp brightness and can therefore be predicted from that brightness.

Examination of brightness ceilings showed that the prehydrolyzed pulp was capable of being bleached to a higher brightness than the corresponding control pulp when the brightness of the pulp entering D_2 is below 82 or above 89.

Pulping to kappa number 20 followed by prehydrolysis to kappa number 15 yields a pulp that requires slightly less ClO_2 than pulping to kappa number 15 without prehydrolysis, provided that the D_0 stage KF is not too high. When the D_0 stage KF is 0.16, bleaching in five stages to brightness 86 requires 16% less ClO_2 in the former (prehydrolysis) case. The savings decreases to 3% as the target brightness is increased to 89 and then increases to 9% at 91. Prehydrolysis, as applied in this study, offered no advantage when bleaching in the three-stage D(EO)D sequence.

For minimum total chemical consumption when bleaching the prehydrolyzed pulp, approximately 10% to 85% of the ClO_2 added after the D_0 stage should be added in the D_1 stage. Except at the highest brightness targets, these percentages are lower than the optimum percentages for the control pulp. The required D_1 percentage is higher when the brightness target is higher, and higher brightness targets are less forgiv-

INSIGHTS FROM THE AUTHORS

Although elemental chlorine-free (ECF) bleaching is now in general use in the industry, it is likely that significant cost savings can be realized by optimizing the allocation of chemicals to the individual bleaching stages.

Our research builds on our earlier work to describe mathematically the brightness development in individual stages and their interdependence. We extended that work to the case of hardwood pulps that have been prehydrolyzed to improve their response to bleaching. Our approach differs from previous modeling efforts by more accurately and comprehensively predicting steady-state behavior without attempting to model the dynamics of the process.

The most difficult aspect of our research was accurately characterizing the bleach response of each stage. This demanded judicious experimental design, especially with regard to choice and spacing of chemical levels, and careful execution of the bleaching experiments.

The unbleached prehydrolyzed pulp had the same kappa number as the unbleached pulp that had not been hydrolyzed (the control pulp) and therefore had a higher content of colored residual lignin. As a result, the prehydrolyzed pulp had a lower brightness after the first two bleaching stages. It was interesting to us that, despite this initial brightness disadvantage, the prehydrolyzed pulp could be bleached to a higher final brightness.

Mills might use the information on the bleaching behavior of prehydrolyzed pulps to evaluate the possible benefits of using a prehydrolysis stage. Even if prehydrolysis is not a possibility, it is likely that mills could achieve significant bleaching chemical cost reductions by conducting site-specific studies employing the approaches we demonstrated here and in the previous paper in this series to determine their own optimal allocations of bleaching chemicals.

We have used the approach illustrated in this paper to study the effects on bleachability of several other process variables, including black liquor addition to the pulping step, inclusion of an oxygen stage and changes in the type of wood pulped. Our next step will be to analyze the resulting data and publish the results.

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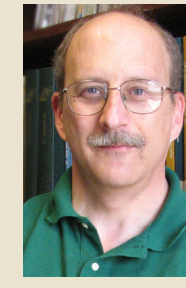
Courchene

ing of departures from the optimum allocation.

When bleaching in the three-stage sequence $D_0(EO)D_1$, prehydrolysis offers no advantage when the KF is 0.24, but at KF 0.16, prehydrolysis decreases the chemical requirement, especially for high brightness targets. However, these brightnesses are more economically achieved by increasing the D_0 KF without prehydrolysis. **TJ**

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