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ORIGINAL ARTICLE

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Empirical modeling of chlorine dioxide delignification of oxygen-delignified hardwood kraft pulp

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Abstract Due to the complexity of delignification, it is still not accurate enough to describe the whole chlorine dioxide delignification system with mechanistic models such as kinetic studies. The simple aim of predicting and optimizing the process requires the use of economical empirical models, few of which are in the literature. In this study, principal component analysis was used to classify various bleaching response variables, including end pH, kappa number, viscosity, and optical properties such as brightness, into different categories. Statistical methods, including factorial design, multiple regression, and response surface methodology, were then used successfully to screen the importance of bleaching factors and their interactions. Models to control, predicate, and optimize the bleaching responses were established. In most cases, the results of empirical modeling coincided well with those from conventional research methods, but the empirical methodology was more economic or less laborious. The empirical models are robust enough to predicate and optimize the bleaching responses to chlorine dioxide delignification of oxygen-delignified hardwood kraft pulp.

Key words Delignification · Chlorine dioxide · Empirical modeling · Mechanistic modeling · Bleaching

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Introduction

In a modern pulp mill that produces elementally chlorine-free (ECF) pulp, the D_0 delignification stage plays a critical role in determining the end results such as final brightness and pulp strength. It is very important to have accurate and robust models that can be used in controlling and optimizing this process.[1] Generally, there are two methods, classified as mechanistic modeling and empirical modeling, used for modeling studies.

Mechanistic modeling tries to determine the mechanism of the process under study. Thus, mechanistic models can contribute to scientific understanding and provide a basis for extrapolation. In the field of chlorine dioxide delignification and bleaching, many studies have been attempted from mechanistic points of view.[2–18] However, the D_0 delignification stage is a very complicated system, heterogeneous in nature, with a huge number of reactions taking place simultaneously and rapidly around the polymeric structure of lignocelluloses. However, it is difficult to characterize the individual reactions involved as well as the change of lignocellulosic structures as such. Because of this, it is difficult to generalize the whole delignification system by mathematical expressions such as differential equations in chemical kinetics. Even if a very complicated model is possible, it is too difficult for it to be used in a model-based control strategy.

On the other hand, empirical modeling is based on factorial designs and polynominal regressions from laboratory or mill data. These models are adequate for many purposes, and the advantages of such empirical models lie in the simplicity of the calibration procedure and the efficiency in studying complex interactions. It has been reported that empirical models are widely used in commercial bleaching plants.[12] However, there are few studies available in the literature concerning the empirical modeling of chlorine dioxide bleaching. Thus, in this study, modern statistical methods including factorial design, multiple regression, and response surface methodology were used to screen the importance of bleaching factors and their interactions. Models

to control, predict, and optimize the bleaching responses were then established.

Experimental

Materials

The pulp used in this study was an oxygen-delignified hardwood kraft pulp made by TongHae Pulp, South Korea. Its kappa number was 10.7, ISO brightness 41.0%, and viscosity 23.7 cP. Chlorine dioxide solution was prepared by dissolving chlorine gas into chilled sodium chlorite solution. The ClO_2 concentration was 8.85 g/l with no detectable chlorine by CPPA standard method J.14P.

Methods

Four bleaching process variables, ClO_2 charge [0.5%–2.0% on oven-dried pulp (weight)], acid charge [1.0%–4.0% on oven-dried pulp (weight)], temperature (40°–95°C), and retention time (10–90 min), were considered in the bleaching experiments using response surface design generated by Modde 5.0 software provided by Umetrics AB, Sweden. A total of 25 experiments, shown in Table 1, were carried out with the center point replicated three times. The pulp consistency in the chlorine dioxide delignification experiments was 3%. Alkali extraction (pulp consistency 3%, alkali addition 0.7% on oven-dried pulp, reaction temperature 70°C, and reaction time 60 min) was carried out after chlorine dioxide delignification.

Optical properties such as brightness, whiteness, tint, CIE L a b values, yellowness, opacity, light scattering, and absorption coefficient were measured with an Erlepho 3000 spectrophotometer (Datacolor). Kappa number was measured according to TAPPI method T 236 cm-85, and pulp viscosity according to TAPPI method T 230 om-89. All the data are shown in Table 2.

Software Simca 8.0 was used for principal component analysis (PCA) and Modde 5.0 was used for multiple regression analysis. Both products are from Umetrics AB, Sweden.

Results and discussion

Classification of bleaching response variables

Before carrying out the modeling analysis, it is good to obtain an overview of the data and to reduce the number of response variables required for mathematical modeling. This was mainly carried out by PCA. The results, shown in Fig. 1, are described as follows:

1. Yellowness, kappa number, CIE a, CIE b, light absorption coefficient *K*, and opacity can be classified as type I response variables. These variables have positive correlations between each other and higher values indicate poorer delignification.
2. Whiteness, tint, brightness, and CIE L can be classified as type II response variables. These variables also have positive correlations between each other and higher values indicate better delignification.

Table 1. Experimental design of ClO_2 delignification of oxygen-delignified kraft pulp

Experiment	Dioxide	Temperature (°C)	Time (min)	Acid
1	0.50 (−1)	40.0 (−1)	10.0 (−1)	1.0 (−1)
2	0.50 (−1)	40.0 (−1)	90.0 (+1)	1.0 (−1)
3	0.50 (−1)	40.0 (−1)	10.0 (−1)	4.0 (+1)
4	2.00 (+1)	40.0 (−1)	10.0 (−1)	4.0 (+1)
5	0.50 (−1)	95.0 (+1)	10.0 (−1)	4.0 (+1)
6	0.50 (−1)	40.0 (−1)	90.0 (+1)	4.0 (+1)
7	2.00 (+1)	40.0 (−1)	90.0 (+1)	4.0 (+1)
8	0.50 (−1)	95.0 (+1)	90.0 (+1)	4.0 (+1)
9	0.50 (−1)	95.0 (+1)	36.7 (−1/3)	1.0 (−1)
10	0.50 (−1)	76.7 (+1/3)	90.0 (+1)	1.0 (−1)
11	2.00 (+1)	40.0 (−1)	36.7 (−1/3)	1.0 (−1)
12	2.00 (+1)	95.0 (+1)	10.0 (−1)	2.0 (−1/3)
13	2.00 (+1)	95.0 (+1)	90.0 (+1)	3.0 (+1/3)
14	2.00 (+1)	95.0 (+1)	63.3 (+1/3)	1.0 (−1)
15	2.00 (+1)	95.0 (+1)	36.7 (−1/3)	4.0 (+1)
16	2.00 (+1)	76.7 (+1/3)	10.0 (−1)	1.0 (−1)
17	2.00 (+1)	58.3 (−1/3)	90.0 (+1)	1.0 (−1)
18	1.00 (−1/3)	95.0 (+1)	10.0 (−1)	1.0 (−1)
19	1.50 (+1/3)	95.0 (+1)	90.0 (+1)	1.0 (−1)
20	0.50 (−1)	67.5 (0)	50.0 (0)	2.5 (0)
21	1.25 (0)	40.0 (−1)	50.0 (0)	2.5 (0)
22	1.25 (0)	67.5 (0)	50.0 (0)	4.0 (+1)
23	1.25 (0)	67.5 (0)	50.0 (0)	2.5 (0)
24	1.25 (0)	67.5 (0)	50.0 (0)	2.5 (0)
25	1.25 (0)	67.5 (0)	50.0 (0)	2.5 (0)

Chemical doses expressed as wt% on oven-dried pulp. Data in parenthese expressed as scaled and centered data

Table 2. Data of response variables after D_0E bleaching

Experiment name	D_0 End pH	Kappa no.	Yellowness	Whiteness	Tint	Brightness (%)	Viscosity (cps)	CIE L	CIE a	CIE b	S (m^2/kg)	K (m^2/kg)	Opacity (%)
DE1	3.79	6.59	20.57	5.47	−8.37	55.48	20.86	86.28	1.90	12.60	49.50	3.34	93.87
DE2	4.41	6.91	20.87	4.13	−8.53	54.96	21.89	86.06	1.93	12.77	47.96	3.36	93.59
DE3	1.90	6.94	22.43	−3.09	−9.54	52.27	22.16	84.99	2.22	13.66	46.11	3.77	92.71
DE4	1.69	4.3	19.72	10.04	−7.77	57.52	21.05	87.18	1.73	12.16	46.10	2.68	92.71
DE5	2.00	6.13	22.36	−2.54	−9.68	52.54	19.93	85.14	2.30	13.64	49.71	3.98	94.84
DE6	1.89	6.21	21.85	0.10	−9.16	53.69	21.87	85.67	2.12	13.37	48.99	3.62	93.97
DE7	1.71	3.67	17.03	23.21	−6.06	63.12	23.56	89.34	1.22	10.61	51.84	2.03	91.93
DE8	2.00	4.03	21.31	1.24	−9.23	53.43	17.99	85.3	2.21	12.97	49.41	3.87	94.98
DE9	4.65	6.34	20.97	2.91	−8.77	54.16	20.26	85.63	2.04	12.80	46.08	3.44	93.91
DE10	4.84	6.48	21.14	1.51	−8.86	53.34	19.52	85.17	2.06	12.81	51.07	4.09	94.97
DE11	2.38	4.03	17.45	21.50	−6.27	62.50	21.22	89.17	1.26	10.89	48.13	1.93	91.63
DE12	2.00	3.13	15.03	32.53	−5.08	67.14	19.42	90.77	0.98	9.44	50.16	1.45	89.55
DE13	1.81	2.11	14.38	35.00	−4.91	67.90	16.63	90.91	0.99	9.03	50.90	1.43	88.99
DE14	2.54	3.47	17.60	19.59	−6.63	61.20	18.1	88.49	1.46	10.89	47.35	2.18	91.23
DE15	1.76	2.89	15.13	32.59	−5.08	67.41	19.2	90.95	0.97	9.54	49.57	1.37	89.64
DE16	2.40	3.59	15.63	28.62	−5.59	64.92	21.26	89.80	1.16	9.42	50.95	1.82	90.31
DE17	2.19	2.78	14.27	37.25	−4.41	69.71	21.96	91.80	0.83	9.04	39.29	1.10	88.45
DE18	3.35	5.65	18.94	13.70	−7.26	58.98	21.08	87.73	1.59	11.70	48.38	2.56	92.65
DE19	2.58	2.93	16.90	23.17	−6.24	62.81	19.67	89.13	1.34	10.51	49.84	2.04	91.95
DE20	2.33	6.48	21.34	2.18	−8.85	54.33	21.51	85.87	2.02	13.06	48.63	3.48	93.72
DE21	2.02	4.63	17.76	20.03	−6.37	62.30	22.71	88.99	1.28	11.08	48.35	2.03	91.17
DE22	1.77	3.73	16.86	23.78	−5.98	63.31	22.41	89.40	1.21	10.52	46.52	1.80	91.13
DE23	2.08	4.9	17.49	20.54	−6.38	61.82	22.62	88.80	1.32	10.88	48.37	2.11	92.16
DE24	2.09	5.23	17.25	21.49	−6.39	62.12	21.14	88.88	1.36	10.72	49.62	2.13	91.48
DE25	2.05	4.71	17.54	19.97	−6.54	61.41	21.99	88.59	1.40	10.88	50.22	2.28	91.28

End pH is pH after D_0 bleaching

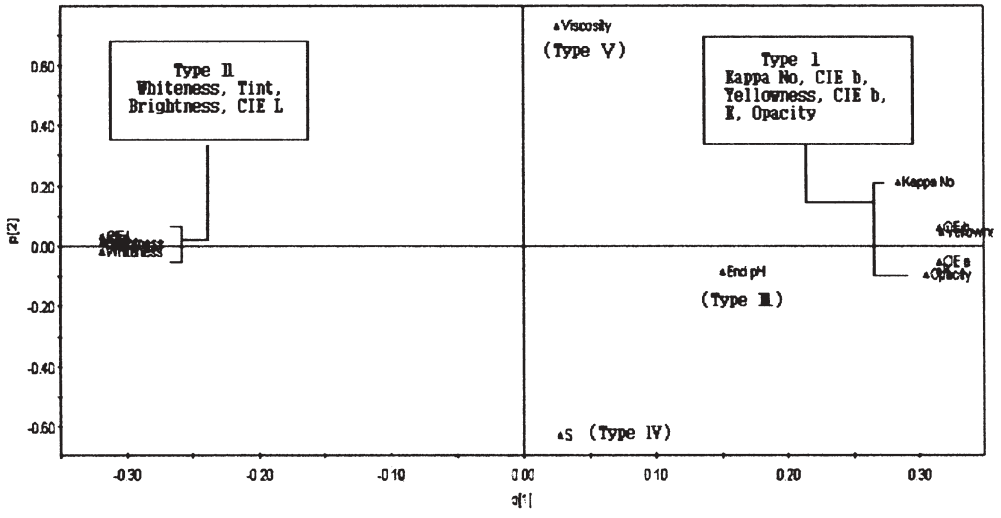

Fig. 1. Loading plot of principal component analysis on the response variables

3. End pH is classified as a type III response variable. Its correlation coefficients with other response variables are generally low but some of them are significant if the level of significance is extended to 10%. This indicates that acidity has some influence on the other response variables.
4. Light-scattering coefficient S and pulp viscosity are included as type IV and V response variables, respectively. They have no correlation with type I, II, or III variables, and they are not correlated with each other.
5. Although kappa number has positive correlations with the type I variables and negative correlations with the type II variables, the absolute values of the correlation coefficients are low. This indicates that lignin content, as described by kappa number, accounts for only a part of the colored structure in chlorine dioxide delignification.

Effect of bleaching factors on end pH of D_0 delignification

Equation 1 is the refined model of end pH after multiple regression analysis. This model is expressed in the scaled and centered form. Its determination (R^2) coefficient and predication coefficient (Q^2) were 0.9400 and 0.9070, respectively.

$$\text{End pH} = 2.1046 - 0.5156D - 0.7369A + 0.4717A^2 + 0.4606D \times A \quad (1)$$

where D (dioxide) and A (acid) are expressed as scaled and centered data in Table 1.

Only acid and ClO_2 charges were included in the model. This is consistent with Wartiovaara's statement that the effect of the volume of acidic chlorine dioxide solution is the most important when adjusting the reaction pH.[19]

Effect of delignification factors on D_0E brightness development

Equation 2 is the scaled and centered model of D_0E brightness (R^2 0.860, Q^2 0.741).

$$D_0E \text{ brightness} = 62.18 + 5.4570D + 0.5199Tp - 0.4331A - 0.2972D^2 + 1.3450Tp \times A \quad (2)$$

where Tp is temperature.

It is seen that chlorine dioxide charge and temperature had the most prominent effect on D_0E brightness. Increasing the chlorine dioxide increases brightness dramatically at the initial stage but levels off as the chlorine dioxide charge becomes higher. Increasing the temperature increases the D_0E brightness slightly but significantly. Lachenal and Chirat[20,21] performed chlorine dioxide bleaching on oxygen-delignified mixed hardwood with kappa number 8.9 and suggested that high-temperature bleaching at 95°C is more efficient than a conventional D stage performed at 45°C. This is because hexenuronic acid can be eliminated more efficiently in the acidic bleaching conditions when the bleaching temperature is high.

Another significant factor is the interaction of temperature and acid charge. When the reaction temperature is low, increasing the acid charge decreases brightness; but when the temperature is high, increasing the acid charge increases brightness. The combination of low acid charge and low temperature, or that of high acid charge and high temperature favors brightness development, while the combination of low acid charge and high temperature or that of high acid charge and low temperature deteriorates brightness development.

The reaction time, which ranged from 10 to 90 min in this study, had no great influence on brightness, indicating that brightness development is achieved very quickly during chlorine dioxide delignification of oxygen-delignified hardwood kraft pulp.

Effect of bleaching factors on D_0E kappa number

Equation 3 is the scaled and centered model of D_0E kappa number (R^2 0.901, Q^2 0.835).

$$D_0E \text{ kappa no.} = 4.73 + 1.456D - 0.506Tp - 0.440Ti - 0.249A \quad (3)$$

where Ti is time.

It was found that chlorine dioxide, reaction time, and temperature are very significant factors in decreasing the kappa number, while the effect of acid addition was much smaller. Several studies have shown chlorine dioxide delignification to be insensitive to pH from a final pH of less than 2 to 4 for 28 kappa pine kraft pulp, 17 kappa oxygen-delignified pine kraft pulp, 33 kappa softwood kraft pulp,[22] 16 kappa eucalyptus pulp,[23] 13.8 kappa oxygen-delignified eucalyptus pulp,[24] and 24 kappa southern pine pulp.[25]

In the case of reaction time, one study reported that kappa number is not adversely affected by extending the reaction time well beyond the time needed to exhaust the residue in either chlorine dioxide[22] or chlorine delignification.[26] However, in another study with an oxygen-delignified mixed hardwood kraft pulp with initial kappa number of 8.9, it was shown that chlorine dioxide was entirely consumed after a few minutes, and, despite that, the kappa number continued to decrease when the reaction time was increased. The kappa number decrease was ascribed to the acidic conditions prevailing during the D stage.[20,21,27]

Effect of bleaching factors on D_0E pulp viscosity

Equation 4 is the scaled and centered model of D_0E pulp viscosity (R^2 0.892, Q^2 0.783).

$$D_0E \text{ viscosity} = 22.13 - 0.09276D - 1.5121Tp - 0.3478Ti - 0.9544D^2 - 0.8742Tp^2 - 0.9362Tp \times T_i \quad (4)$$

It is seen that acid addition from 1.0% to 4.0% on oven-dried pulp has no significant influence on viscosity, but chlorine dioxide charge, reaction temperature, and reaction time have. The model also shows that maximum viscosity values occur with a medium charge of chlorine dioxide. High temperature and long reaction time leads to decreases in viscosity.

Effect of bleaching factors on the efficiency of chromophore removal

We introduce an expression called the efficiency of chromophore removal (ECR) that is very similar to the delignification efficiency used extensively by Germgård.[28] It is defined as the units of K/S change divided by the chlorine dioxide charge, where K/S is the ratio of light absorption coefficient to the scattering coefficient:

$$\text{ECR} = \Delta(K/S)/\text{ClO}_2 \text{ charge} = \left[(K/S)_{\text{Unbleached Pulp}} - (K/S)_{\text{Bleached Pulp}}\right]/ClO_2 \text{ charge} \quad (5)$$

Here the ClO_2 charge is used instead of the real ClO_2 consumption, because we think the recovery of residual chlorine dioxide is not possible.

Equation 6 is the scaled and centered model of ECR (R^2 0.995, Q^2 0.986).

$$ECR = 24.79 - 14.38D - 0.172Tp + 0.592Ti - 0.748A + 5.975D^2 + 0.811D \times Tp - 0.744D \times A - 0.969Tp \times A + 0.690T_i \times A \quad (6)$$

This shows that the efficiency of chromophore removal decreases with increasing chlorine dioxide dosage. The second most significant effect is the interaction between reaction temperature and acid charge. At lower acidic dosages, increasing the temperature decreases ECR; however, at higher acidic dosages, higher reaction temperature increases ECR. This indicates that at low acidity, increasing temperature creates some chromophores, while at high acidity, increasing the temperature eliminates chromophore structures.

Prediction and optimization of chlorine dioxide delignification stage

Optimizing the bleaching process is not an easy task. The first problem is to select the principles used to determine the optimal conditions. As was pointed out by Pryke and Reeve,[29] the following criteria might be used in optimization: (1) minimizing cost, (2) maximizing delignification, (3) maximizing pulp quality, and (4) minimizing environmental impact.

In this study, the following set conditions were used to determine the corresponding bleaching conditions based on the models obtained above:

1. At constant kappa factor (i.e., constant chlorine dioxide charge) to achieve the maximum brightness without considering other properties;
2. At constant kappa factor (i.e., constant chlorine dioxide charge) to achieve the minimum kappa number without considering other properties;
3. To achieve maximum brightness, maximum viscosity, maximum color removal efficiency, and minimum kappa number.

Under the above premises, the statistical software Modde 5.0 used a simplex method to achieve the optimum conditions,[30] which are listed in Table 3. Figure 2 shows the predicted data and the observed data for D_0E brightness, D_0E kappa number, D_0E viscosity, and the efficiency of chromophore removal. Apparently the models are robust enough to give relatively good prediction.

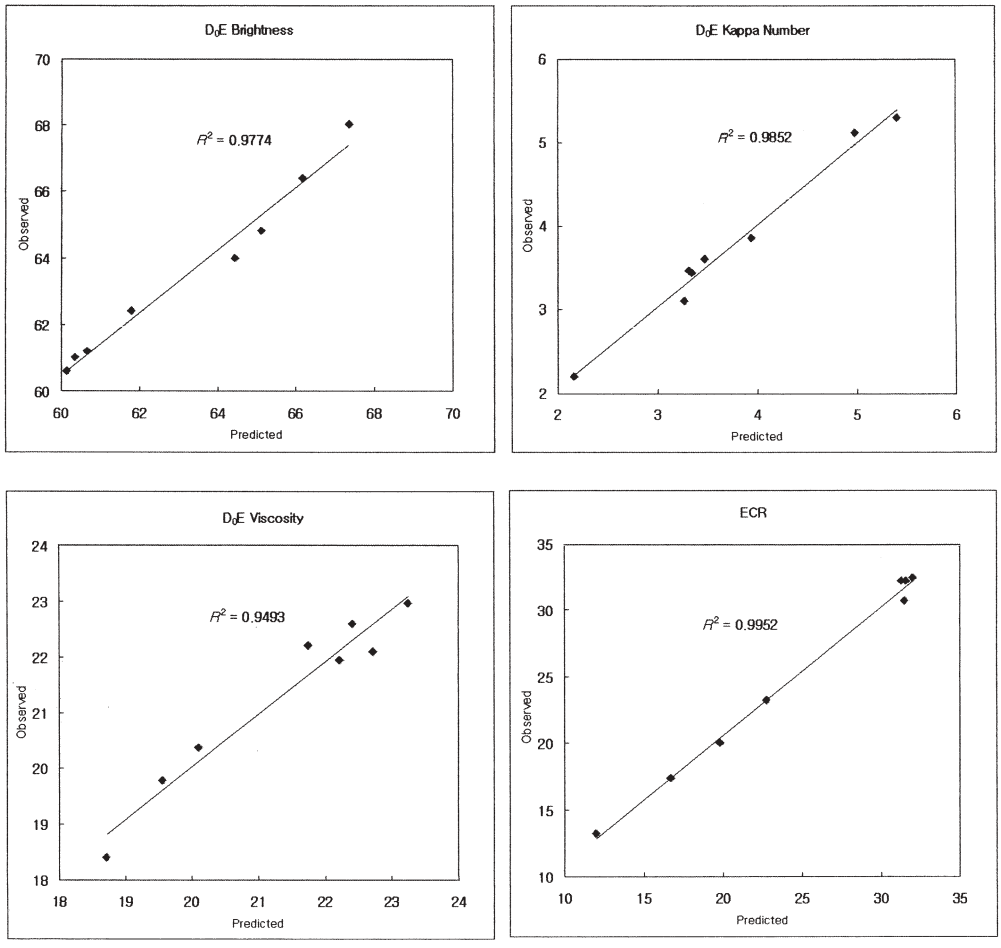

Fig. 2. Predicted versus observed data on D_0E brightness, D_0E kappa number D_0E viscosity, and efficiency of chromophore removal (ECR)

Table 3. Experimental and predicted results for eight Experiments designed under three premises

Premise	Experiment no.	ClO_2 (%)	Tp (°C)	Ti (min)	Acid (%)	End pH	Brightness (%)	Kappa no.	Viscosity (cps)	ECR
1	1	1.00	75.40	10.01	2.01	2.60	60.36	5.42	21.75	32.2
	2	1.00	54.59	90.00	2.35	2.55	61.80	4.99	22.42	32.4
2	3	1.00	95.00	90.00	3.61	1.89	60.16	3.32	18.72	32.2
	4	1.00	88.49	90.00	4.00	1.67	60.69	3.27	19.56	30.7
3	5	1.89	79.60	89.94	4.00	1.54	67.38	2.17	20.11	17.4
	6	1.81	48.90	90.00	1.00	2.44	66.19	3.48	22.22	20.0
	7	2.00	43.91	90.00	4.00	1.70	65.14	3.35	23.25	13.2
	8	1.38	56.31	90.00	3.24	1.79	64.45	3.95	22.72	23.2

ECR, efficiency of chromophore removal

Conclusions

1. Predicting and optimizing the chlorine dioxide delignification process are economically feasible by empirical studies with the combination of factorial design, regression analysis, and response surface methodology.
2. Modern multiple regression methods are successful in screening the importance and lack of importance of various bleaching factors (process variables).
3. In most cases, the results by empirical modeling coincide well with those from conventional research methods, but the empirical methodology is more economic or less laborious.
4. The empirical models are robust enough to predicate and optimize the bleaching responses of chlorine dioxide delignification of oxygen-delignified hardwood kraft pulp.

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