A Method for Integrated Optimization of Chlorine Dioxide Delignification of Bagasse Pulp

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Chlorine dioxide bleaching is an important component of elemental chlorine-free bleaching. A method is introduced in this work to optimize process conditions for chlorine dioxide delignification based on nonlinear programming and response surface analysis. An energy consumption model for chlorine dioxide bleaching is established, as well as statistical models for the brightness, viscosity, and absorbable organic halogen content with the process conditions. The results from the model predict that the cost can be reduced compared to the optimization results of the response surface analysis and experiments.

Keywords: Chlorine dioxide bleaching; Optimization; Bagasse; Nonlinear programming

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INTRODUCTION

Chlorine and hypochlorite bleaching is becoming increasingly restricted because of the environmental requirements for the emissions of carcinogenic compounds (Nie *et al*. 2014; Yao *et al*. 2017). Elemental chlorine-free (ECF) bleaching and total chlorine-free (TCF) bleaching are the current economically viable and environmentally friendly bleaching technologies used on wood pulp (Bajpai 2012; Nie *et al.* 2017). ECF bleaching is a technology choice used with sustainable pulp and paper manufacturing because of the higher yield, higher strength, pulp whiteness stability, and lower production costs (Reeve 1995; Rooks 2001). In 2012, ECF-bleached pulp commanded the highest worldwide market share at greater than 93%, and totaled 94 million tons. The ECF market share continues to grow in all of the pulp producing regions. This trend is expected to continue, as all new planned production will incorporate ECF bleaching (AET 2015).

Absorbable organic halogen (AOX) is an important persistent organic pollutant in pulp bleaching. Some of these compounds are highly toxic, lipophilic, and can accumulate in organisms (Nie *et al*. 2014, 2015). Chlorine dioxide (ClO_2) is the primary bleaching agent applied in ECF bleaching processes for delignification or obtaining a higher brightness. It has a high selectivity and low environmental impact. The AOX content in chlorine dioxide bleaching wastewater is only one fifth of that in chlorine bleach wastewater for the same effective chlorine consumption (Bajpai 2012). ECF bleaching is an effective bleaching method to reduce the AOX content in wastewater. There are still a few AOX compounds that can be detected in the ECF bleaching process because of the participation of chlorine dioxide (Stratton 2001; Nakamata *et al*. 2010). Chlorine dioxide is used both in the delignifying (pre-bleaching) stage (D_0) and brightening stages (D_1 and D_2). This work focuses on the D_0 stage.

A typical pulp mill is operated to optimize its production level, operating costs, pulp quality, and environmental impacts. A general description of this goal is to deliver pulp with the lowest Kappa number to a bleach plant that still maintains the required pulp strength and avoids sharply dropping the pulp yield (Pikka *et al*. 2000). It is necessary to establish an integrated optimization model for the chlorine dioxide bleaching process to achieve this goal.

Reaction kinetics is currently a popular topic in modeling research. The presently available chlorine dioxide bleaching models typically employ one or two empirical correlations to predict the kinetics in the Kappa number development, brightness, or chlorine dioxide charge (Savoie and Tessier 1997; Tessier and Savoie 2000; Barroca *et al*. 2002; Yoon *et al*. 2004; Benattar *et al*. 2007). The empirical models used were established by other researchers to control or predict the AOX content of the chlorine dioxide bleaching process from previous models (Hatam *et al*. 2008; Tarvo 2010; Tarvo *et al*. 2010; Nie *et al*. 2014). Similarly, kinetics models that determine the Kappa number, brightness, or chemical oxygen demand or AOX content for other bleaching agents have been developed (Lenz *et al*. 2005; Fisera and Holler 2006; Susilo and Bennington 2007). The bleaching system models were developed based on gray-box identification technology, neural networks, fuzzy systems, and genetic algorithms to predict the whiteness or other properties of the pulp after bleaching and to control the bleaching system (Sayda and Taylor 2003; Paiva *et al*. 2004; Raghavan *et al*. 2005; Achiche *et al*. 2007).

Most models are focused on the study of one or multiple properties of the bleached pulp, such as the Kappa number, viscosity, whiteness, and AOX content. There are few studies available on the integrated optimization of the bleaching process. Though Major *et al*. (2005) proposed a method to minimize the bleaching operation cost, the environmental effects were not considered.

The response surface analysis software was used to optimize the operating conditions in the co-authors' previous work (Nie *et al*. 2013), but the result is a product of weighing the brightness, viscosity, and AOX content. Maybe this better condition is not necessary, because the D_0 stage is just an intermediate process of the entire bleaching system. Especially the cost of chlorine dioxide production is high and AOX is still produced. This situation suggests that it may be possible to reduce the entire bleaching production cost by weakening the effect of D0 and increasing the subsequent bleaching effect under the premise of the same performance of pulp.

There has been a lack of studies on integrated optimization models of the chlorine dioxide bleaching process that consider the chemical consumption, energy consumption, and environmental effects. This study of chlorine dioxide bleaching mainly focuses on the bleaching process flow, operating conditions, and environmental impacts. The lowest cost is the goal of this integrated optimization model, which is more important to the enterprise. The purpose of this work is to provide a research method to develop an integrated optimization model based on modern statistical methods, including multiple regression, response surface methodology, and nonlinear programming.

EXPERIMENTAL

Materials

The bleaching experiments were carried out with unbleached bagasse pulp that came from Guangxi Guitang Group Co., LTD (China). Results of those tests were used to obtain the constraint functions discussed below. Three major bleaching process variables, the chlorine dioxide charge, pH value, and temperature, were considered in the bleaching experiments using the response surface design generated by the Design-Expert 8.0 software (Stat-Ease, Minneapolis, USA) under a specific pulp consistency and retention time. The brightness and viscosity of the pulp and the AOX content of the bleaching effluent were chosen as the dependent response variables to assess the bleaching effect because of the importance of these three different responses in practice when bleaching bagasse pulp. The details can be found in the authors' previous work (Nie *et al*. 2013).

Methods

Mathematical modeling

In the previous work, the co-authors did a lot of single-factor experiments to find out that chlorine dioxide charge, pH, and bleaching temperature are the major impact factors of the pulp's properties and environmental. Therefore, the optimization study is based on the results of previous experiments designed by response surface software, and only those three variables were considered.

Here, pulp at an approximately 10% consistency was blended with a chlorine dioxide agent in a mixer and pumped to a bleach tower, where it was retained for several hours at a temperature of approximately 30 °C to 90 °C. The dynamic behavior of the bleaching process is very complex and nonlinear because many variables affect the process dynamics, such as the chemical dosages, pulp alkalinity (pH), pulp consistency, retention time, production rate, and temperature.

In order to better understand the influence of the selected variables to the pulp properties, the process of chlorine dioxide bleaching can be simplified as shown in Fig. 1. The relationship between the pulp properties after bleaching and those variables could be expressed by Eqs.1, 2, and 3. Also, the heat consumption can be indicated easily by Eq. 4.

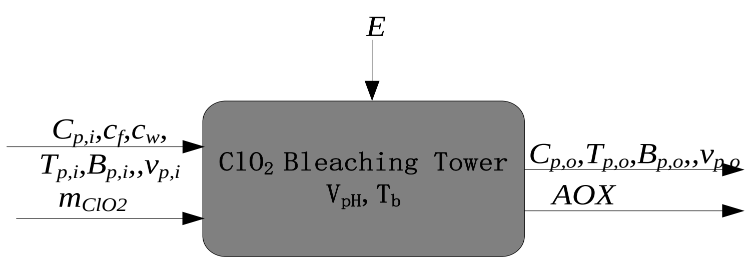

Fig. 1. Module of chlorine dioxide bleaching

$$B_{p,o} = p_3(B_{p,i}, m_{ClO_2}, V_{pH}, T_b) \quad (1)$$

$$\nu_{p,o} = p_2(\nu_{p,i}, m_{ClO_2}, V_{pH}, T_b) \quad (2)$$

$$AOX = p_3(m_{ClO_2}, V_{pH}, T_b) \quad (3)$$

$$E = p_4(C_{p,i}, c_f, c_w, T_{p,i}, T_b) \quad (4)$$

Optimizing the bleaching process is not an easy task. First, the target of optimization should be to determine the optimal conditions. The authors hoped to be able to minimize the cost, maximize delignification, maximize the pulp quality, and minimize the environmental impacts of the bleaching system. This objective is shown by Eq. 5,

$$\text{Min}\, F(x) = \sum_i C_i x_i,\ s.t.\, p(x) \geq 0 \quad (5)$$

where *F(x)* is the objective function, that is to say the total operation cost of a unit of production (Chinese Yuan /t of dry pulp), C_i is the unit price of consumed component *i* (Chinese Yuan /kg), including the chemical agent and energy costs for chlorine dioxide bleaching, x_i is the consumption of consumed component *i* of a unit of production (kg/ t of dry pulp), and $p(x)$ is the constraint functions. The constraints include the output constraint, which was determined by measuring the pulp properties after bleaching in an actual operation process, the statistical relationship between the performance of the pulp and contaminants, and the operating conditions of the process. The operating conditions were inferred using the Design-Expert 8.0 software (Stat-Ease, Minneapolis, USA) based on the results from the systematic experiments, which included the brightness (Eq.1), viscosity (Eq.2), AOX (Eq.3), and energy consumption models (Eq.4). Because the behavior of the bleaching process is nonlinear, the Fmincon function in Matlab (MathWorks, R2010, Natick, USA) was adopted to solve the models.

RESULTS AND DISCUSSION

Determining the pulp properties after chlorine dioxide bleaching was not the final target because chlorine dioxide delignification is an intermediate process of the whole bleaching system. The optimization strategy was to minimize the operating cost of chlorine dioxide bleaching at the specific brightness and viscosity determined from the experiments, with an AOX content below the value based on the current performance of the process equipment used in this study. The corresponding objective function and constraints are discussed in the rest of the paper.

Constraints and Objective Function

In general, the objective was minimize the operation cost, *via* the nonlinear optimization approach, under the constraints of AOX emission, brightness, and viscosity. The decision variables were the operating conditions from the experimental production process. The objective functions and constraints are described below.

The objective function was the total operation cost according to the above section, which included the chemical agent and energy costs. Chlorine dioxide is the main chemical used in delignification. Because of the small amount of alkali used to adjust the pH value of the pulp, the costs of the other chemicals were considered to be constant. Therefore, it was only necessary to calculate the cost of the chlorine dioxide to determine the cost of the chemicals. Additionally, because of the development of high temperature chlorine dioxide, the additional steam consumption should be added to the bleaching process and other energy consumption could be ignored, such as electricity and compressed air. As such, the objective function was expressed by Eq. 6,

$$\text{Min}\, F(x) = \sum_i C_i x_i = C_{ClO_2} x_{ClO_2} + C_{steam} x_{steam} \quad (6)$$

where the unit costs for chlorine dioxide (C_{ClO2}) and steam (C_{steam}) were set at 10 Chinese Yuan /kg and 0.150 Chinese Yuan /kg, respectively.

Constraints

It was seen that there were two types of constraints, one of which was the statistical models of the pulp performance and main process conditions that can be inferred by analyzing the experimental results, and the second was the quality requirements after delignification that could be determined through the analysis of the chlorine dioxide bleaching process. The energy consumption to keep the specific temperature of the bleaching process also be calculated based on energy conservation law.

In this work, the statistical models of the pulp performance, including the brightness, viscosity, and AOX content, were established and shown to be very reliable in the authors' previous research work (Nie *et al*. 2013). The models for the brightness, viscosity, and AOX content were expressed by Eqs. 7, 8, and 9, respectively,

$$B = 4.83 + 8.9x_1 + 0.997x_2 + 4.77x_3 - 0.0508x_1x_2 + 0.0438x1x_3 - 0.0204x_2x_3 - 0.493{x_1}^2 - 0.00458{x_2}^2 - 0.558{x_3}^2 \quad (7)$$

$$v = 1219 - 49.4x_1 - 6.87x_2 - 37.3x_3 + 0.508x_1x_2 + 0.156x_1x_3 + 0.165x_2x_3 - 0.138{x_1}^2 + 0.0272{x_2}^2 + 4.23{x_3}^2 \quad (8)$$

$$AOX = -23.8 + 6.34x_1 + 0.67x_2 + 5.85x_3 - 0.0192x_1x_2 - 0.256x_1x_3 - 0.0221x_2x_3 - 0.0625{x_1}^2 - 0.003x_2 - 0.529{x_3}^2 \quad (9)$$

where x_1 is the chlorine dioxide charge (%), x_2 is the bleaching temperature (°C), and x_3 is the pH value.

Energy Consumption Model

The change in the pulp quality in the bleaching process could be ignored because the loss of fiber was small. It was assumed that the heat loss of the bleaching tower could be ignored because the sensible heat and reaction release heat of the chlorine dioxide and other additives changed the temperature of the pulp very little. The energy consumption model was easily inferred based on the law of energy conservation, and was as expressed as follows,

$$E = p_4(C_{p,i}, c_f, c_w, T_{p,i}, T_b) = (c_f + c_w * \frac{1 - C_{p,i}}{C_{p,i}})(T_b - T_{p,i}) \quad (10)$$

where the specific heat of the fiber (c_f) is 1.423 kJ/(kg*K), the specific heat of the water (c_w) is 4.1868 kJ/(kg*K), the concentration of the pulp (C_p) is 10%, and the temperature of the input pulp (T_0) is 25 °C.

Output Constraints

The authors' previous study showed that the optimized results from the Deign-Expert 8.0 software are a brightness of 52.5, viscosity of 929 mL/g, and AOX content of 14.7 mg/L under a chlorine dioxide charge of 3.7%, pH value of 8.8, and temperature of 76.1 °C (Nie *et al*. 2013). For comparison, similar outputs were considered to be Scenario 1 to establish the optimization results of the models, as shown in Eq. 11:

$$B_{p,o} \geq 52;\ v_{p,o} \geq 920;\ AOX \leq 15 \quad (11)$$

It was determined from the experimental results that the viscosity decreased as the brightness increased. Therefore, the whiteness value was at a low level from the experimental results to maintain a high viscosity value. The following set of conditions (Scenario 2) were used to determine the corresponding bleaching conditions based on the models obtained above by analyzing the results of the experiments from the authors' previous study (Nie *et al*. 2013). The more details of the experiments can be seen in the appendix.

$$B_{p,o} \geq 60;\ v_{p,o} \geq 800;\ \text{AOX} \leq 10 \quad (12)$$

Comparison Before and After Optimization

It should be noted that with Eq. 6 the chlorine dioxide and energy (second term) costs were calculated per kg of dry pulp, and the various contributions for energy use were calculated by Eq. 10. Equation 6 was solved to minimize the total operating cost subject to the constraints in Eqs. 6 to 11 or 12. Equations 7, 8, and 9 involved nonlinear terms, which contributed to the nonlinearity of the mathematical model. A nonlinear programming model was formulated and solved using Matlab to determine the optimum conditions, which are listed in Table 1. The authors' previous work established that the models are robust enough to give a relatively good prediction (Nie *et al*. 2013).

Table 1. Comparison of the Results Before and After Optimization of the Two Scenarios

Constraint	Scenario 1			Scenario 2	
	Before Optimization	After Optimization		Before Optimization	After Optimization with Optimization Model
		Analyzed with Design-Expert	Analyzed with Optimization Model		
Chlorine dioxide charge (%)	5.0	3.7	1.94	1	1.5
pH value	9.0	8.8	1.0	5	4.3
Temperature (°C)	60	76.1	41.3	90	63.9
AOX content (mg/L)	15.4	14.7	13.2	21.1	21.9
Brightness (%ISO)	52.5	52.4	53	62.3	62
Viscosity (mL/g)	933	929	900	823	830
Chemical costs	500	370	194	100	149
Energy costs (Chinese Yuan/t of dry pulp)	64	98	24	128	72
Total operation cost (Chinese Yuan/t of dry pulp)	564	468	218	228	221

The results of experiment No. 6 (Table S1) had a total operating cost of 564 Chinese Yuan/t of dry pulp, although to a certain extent the reduction in the operating cost resulted from the optimization program of the Design-Expert 8.0 software. The cost reduction was only 17.0%. The cost was remarkably reduced using the optimization model established in this work. The optimization resulted in a 61.3% with a better brightness, a small drop in the viscosity, and a lower AOX content under a chlorine dioxide charge of 1.94%, pH value of 1.0, and temperature of 41.3 °C.

For Scenario 2 (Experiment No. 11 in Table S1), a higher brightness was achieved compared with Scenario 1 with a reduced viscosity. The cost decreased from 228 Chinese Yuan /t to 221 Chinese Yuan /t of dry pulp by increasing the chlorine dioxide charge from

1% to 1.5%, reducing the pH from 5 to 4.3, and decreasing the temperature from 90 °C to 63.9 °C, and keeping the pulp properties and environmental impacts constant.

The results of optimization model displayed that a remarkable savings were achieved under the specific pulp properties in the delignifying (pre-bleaching) stage (D_0). For future works, similar models can be developed for other bleaching processes, and then an integrated optimization model for the whole bleaching system can be generated based on those models.

CONCLUSIONS

1. A method and nonlinear programming optimization model were developed in this work to optimize the operation costs for chlorine dioxide delignification in the pulping process, which considered the chemical consumption, energy consumption, and environmental effects.
2. Remarkable savings were achieved for both the energy and chemical costs with a low environmental effect, compared to the optimization results of response surface methodology.

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NOMENCLATURE

AOX the AOX content produced by chlorine dioxide bleaching, mg/L
$B_{p,i}$ the brightness of input pulp, %ISO
$B_{p,o}$ the brightness of output pulp, %ISO
c_f the specific heat capacity of fiber, kJ/(kg*K)
c_w the specific heat capacity of water, kJ/(kg*K)
$C_{p,i}$ the concentration of input pulp, %
$C_{p,o}$ the concentration of output pulp, %
E the heat consumption of chlorine dioxide bleaching, kJ
m_{ClO2} the chlorine dioxide charge, %
T_b the temperature of bleaching, ℃
$T_{p,i}$ the temperature of input pulp, ℃
$T_{p,o}$ the temperature of output pulp, ℃
V_{pH} the value of pH , -

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APPENDIX

Experimental design and response results of chlorine dioxide delignification from the authors' previous work (Nie *et al*. 2013).

Table S1. Results of Experiments Designed by the Response Surface Methodology

Experiment No.	Chlorine Dioxide Charge (%)	Temperature (°C)	pH Value	Brightness (%ISO)	Viscosity (mL/g)	AOX Content (mg/L)
1	1.0	60	1.0	57.9	841	15.9
2	3.0	90	9.0	47.2	951	10.1
3	3.0	60	5.0	65.6	821	26.2
4	1.0	60	9.0	41.9	976	8.3
5	5.0	90	5.0	71.2	778	35.9
6	5.0	60	9.0	52.5	933	15.4
7	1.0	30	5.0	42	968	8.5
8	3.0	60	5.0	65.7	817	26.3
9	3.0	60	5.0	65.6	819	26.3
10	3.0	30	9.0	43.1	979	8.7
11	1.0	90	5.0	62.3	823	21.1
12	5.0	30	5.0	63.1	801	27.9
13	3.0	90	1.0	67.2	803	27.1
14	3.0	60	5.0	65.8	820	26.2
15	3.0	30	1.0	53.3	910	15.1
16	3.0	60	5.0	66	816	26.5
17	5.0	60	1.0	67.	793	31.2