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Modeling and Optimizing Brightness Development in Peroxide Bleaching of Thermomechanical Pulp

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ABSTRACT

Alkaline peroxide bleaching of chemi-mechanical pulp is a very complicated system where various process factors affect the bleaching performance and pulp properties. Traditional onefactor-at a time method is ineffective and costly in finding the optimal bleaching conditions. In this study, statistical experimental design and multiple regression method were used to investigate the interactions among various bleaching factors and to find out the possible maximal brightness development during one stage alkaline peroxide bleaching of TMP. The TMP was made from 10% Korean red pine and 90% Korean spruce and had an initial brightness of 54.5% ISO. The TMP was pretreated with EDTA (0.5% on O. D. pulp, 3% pulp consistency, 30°C for 60 minutes) and bleached in a 2 L Mark V Quantum Reactor at 750 rpm, 7.5% of bleaching consistency and with 0.05% magnesium sulfate addition. The ranges of chemical factors studied, based on oven-dried pulp, were 1-5% for hydrogen peroxide, 1-4% for sodium hydroxide and 1-4% for sodium silicate. The ranges of reaction temperature and time were 50-90°C and 40-180 minutes respectively. Interactions of hydrogen peroxide with alkali, time with temperature, alkali with time and silicate with temperature were found to be significant which means that hydrogen peroxide bleaching will be favored at stable concentration of perhydroxyl ion, relatively short time and low temperature, and high level of silicate. Mathematical model which has good predictability for target brightness in one stage peroxide bleaching can also be established easily. Base on the model, maximal brightness of 70% ISO was found to at 50°C and 50 minutes by chemical additions of 5% for hydrogen peroxide, 3.2-3.4% for sodium hydroxide and 4% for silicate based on O. D. pulp. However, this result might not be suitable for situations where furnishes are different from ours, or different pretreatment is used, or bleaching carried out at different pulp consistency. In these cases it will be good to re-investigate the process by a similar methodology as was used in this study.

1. Introduction

In an increasingly competitive economic climate, pulp and paper producers are looking for new means of reducing costs and improving product quality. Unfortunately most pulping and paper making processes are quite complex and identifying optimal operation conditions is easier said than done.[1] Alkali peroxide bleaching of chemimechanical pulp is one of such cases. Factors influence alkaline peroxide bleach-

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ing performance include furnish type, preceding pulping process, pretreatment, bleach liquor stability, bleaching consistency, bleaching agent charge, total alkalinity level, retention time, temperature, etc. Many of these factors are interrelated.

Many experimental studies are still carried out by the so-called one-factor-at-a-time method, i.e., changing the setting of one process variable at a time and recording the results.[2-4] Despite that it is easy to be used and understood in getting basic information, this method is not only extremely inefficient in its use of resources, but also very difficult for the user to study synergistic effects or interactions both in this peroxide bleaching case and many other cases commonly found in pulping and papermaking processes.

The object of this study is to develop models that can describe the impact of one-stage alkaline peroxide bleaching on the brightness development of thermomechanical pulp. The study demonstrates how statistical multiple regression analysis and response surface methodology can be an efficient tool in identify statistically significant factors as well as their interactions, and provide predicative models necessary to simulate and optimize the bleaching process.

2. Material and Methods

TMP used in this study was made from 10% Korean red pine and 90% Korean spruce. The original brightness of TMP was 55.4% Elrepho. The pulp was first pre-treated with 0.5% DTPA based on over-dried pulp at 3% pulp consistency, 30°C, and for 60 minutes. Then the pre-treated pulp was dewatered to 30% pulp consistency by centrifugation. The bleaching reactions were carried out in a Quantum Mark V Reactor. The pulp bleaching consistency was kept to 7.5% and the treatment of magnesium sulfate at 0.05% based on oven-dried pulp. Other factors, including chemical charge of hydrogen peroxide, sodium hydroxide and sodium silicate, reaction time and reaction temperature were varied according to Table 1 for screening experiments and Table 2 for RSM (Response Surface Modeling) experiments. When bleaching time was over, of the pulp was neutralized to pH 5.5 by 15% sodium bisulfate. Then handsheets were made according to Tappi standard and brightness measured with an Elrepho 3000 spectrophotometer.

A Modde 4 statistical software by Ulmetri AB (Sweden) was used in this study in

Table 1. Experimental design in screening stage and its corresponding brightness responses

Exp. Name	P (%)	Ak (%)	Si (%)	Ti (min)	Tp (OC)	Br (%)
N1	1	0.5	0.5	40	95	61.33
N2	5	0.5	0.5	40	50	62.41
N3	1	4	0.5	40	50	61.30
N4	5	4	0.5	40	95	64.20
N5	1	0.5	4	40	50	62.95
N6	5	0.5	4	40	95	62.83
N7	1	4	4	40	95	52.12
N8	5	4	4	40	50	69.16
N9	1	0.5	0.5	180	50	61.77
N10	5	0.5	0.5	180	95	51.94
N11	1	4	0.5	180	95	46.62
N12	5	4	0.5	180	50	69.06
N13	1	0.5	4	180	95	58.46
N14	5	0.5	4	180	50	64.39
N15	1	4	4	180	50	62.88
N16	5	4	4	180	95	59.17
N17	2.25	2.25	2.25	110	72.5	64.38
N18	2.25	2.25	2.5	110	72.5	63.92
N19	2.25	2.25	2.5	110	72.5	65.91

Note: P - peroxide; Ak - alkali, sodium hydroxide; Si - silicate; Ti - time; Temp - Temperature; Br - Brightness

Table 2. Experimental design in RSM stage and its corresponding brightness responses

Exp. Name	P (%)	Ak (%)	Si (%)	Br (%)
N1	5	2	2	68.79
N2	2	4	2	67.36
N3	5	4	2	69.66
N4	2	2	4	66.92
N5	5	2	4	69.41
N6	2	4	4	67.61
N7	5	4	4	69.67
N8	2	2	2.67	67.02
N9	5	2.67	2	67.53
N10	3	2	2	67.47
N11	5	3	3	69.50
N12	3.5	4	3	68.92
N13	3.5	3	4	69.22
N14	3.5	3	3	69.25
N15	3.5	3	3	69.48
N16	3.5	3	3	69.03

experimental designs and multiple regression calculations.

3. Results and Discussion

3. 1 Effects of bleaching factors on brightness development in screening stage

3. 1. 1 Modeling of brightness development in screening stage

Using multiple regression analysis, a model with acceptable determination coefficient (R^2=0.877, R^2_{adj}=0.754) and prediction coefficient (Q^2=0.6645) was developed (See Table 3). The insignificant effects whose p-values were bigger than the 0.05 were eliminated from the full model in a backward method so that R^2 does not decrease much while Q^2 increases to its maximum. Some factors, like alkali and silicate, though having p-values bigger than 0.05, were not removed from the model according to the hierarchy rule since their interaction with other factors were very significant. The interactions Si*Tp and Ak*Ti, also had p-values over 0.05, were kept in the modeling because eliminating these effects would lead to big decrease in both the R^2 and Q^2. Thus the scaled and centered model can be summarized as:

$$\text{Brightness}(\%) = 61.421 + 1.949P - 0.098Ak + 0.833Si - 1.376Tp - 3.578Ti + 2.601P*Ak - 1.458Ak*Ti + 1.106Si*Tp - 1.661Tp*Ti \quad (1)$$

Notice that the coefficients were scaled and centered, so the levels of factors should also be scaled and centered when using the model.

From the scaled and centered coefficients listed on Table 3 it is seen that the biggest positive effect on TMP brightness development is the interaction of hydrogen peroxide and alkali, followed by P, Si*Tp and Si. Other factors, ordered by Ti, Ti*Tp, Ak*Ti,

Table 3. Model obtained in the screening stage

Brightness	Scaled & Centered Coefficient	P
Constant	61.421	0.000
P	1.949	0.021
Ak	-0.098	0.893
Si	0.833	0.269
Tp	-1.376	0.084
Ti	-3.578	0.001
P*Ak	2.601	0.005
Ak*Ti	-1.458	0.070
Si*Tp	1.106	0.153
Tp*Ti	-1.661	0.044
R^2	0.877	
R^2_{adj}	0.754	
Q^2	0.6645	

Tp, and Ak, have negative effects on brightness development.

3. 1. 2 Effects of bleahcing factors and their interactions on the brightness development of TMP

The effect of peroxide, alkali and their interaction can be seen from Figs. 1 and 2. From Figure 1 it was seen that increase of peroxide content led to higher brightness when alkalinity is high enough. At very low alkalinity, increase of hydrogen peroxide adversely decreased the pulp brightness. Figure 2 also showed the high dependence of alkalinity on the level of hydrogen peroxide. When hydrogen peroxide content was low (1% on O. D. pulp), increase of alkalinity decreased the brightness development, while when hydrogen peroxide content was high (5% on O. D. pulp), increase the alkalinity dramatically increased the brightness development of TMP. Interestingly enough, at a medium hydrogen peroxide level of 3%, alkalinity had little influence on brightness of TMP.

The interaction between hydrogen peroxide and alkalinity can be easily explained by the following reaction:

$$H_2O_2 + HO^- \leftrightarrow HOO^- + H_2O \qquad (2)$$

The hydroperoxide anion or perhydroxyl anion, HOO^-, is the principal active specie involved in the elimination of chromophores in lignin structure. According to the above equilibrium, peroxide bleaching should be most effective at a high concentration of perhydroxyl anion, i.e., at high concentrations of both hydrogen peroxide and sodium hydroxide.

According to one paper,[5] at least three types of reactions may take place during peroxide bleaching. First there are the brightening reactions themselves, which involve reactions between perhydroxyl ions and lignin chromophores. Secondly there are peroxide decomposition reactions as shown by equation 3. This reaction involves interaction between hydrogen peroxide and its conjugate base, HOO^-, in the presence of a transition metal catalyst or enzyme.[4] Thirdly, there are alkali darkening reactions, which consume caustic, involving formation of colored groups[6,7] and catalyzed by peroxide decomposition intermediates which include radicals such as the hydroxyl radical ($HO\cdot$) and the superoxide ion ($O_2\cdot^-$).[8]

$$H_2O_2 + HOO^- \xrightarrow{\text{M or enzyme}} O_2 + OH^- + H_2O \qquad (3)$$

Thus if the hydrogen peroxide concentration is high but alkalinity is not enough, the brightening reaction is very slow.[9] The mechanism changes according to reaction 4 where the H^+ ion delignifies and produces new chromophore structures, leading to unfavorable brightness drop. And if hydrogen peroxide is insufficient and alkalinity is too high, decomposition and darkening become dominant which also leads to brightness drop.

$$H_2O_2 + H^+ \leftrightarrow HO^+ + H_2O \qquad (4)$$

Figures 3 and 4 showed that increasing either the bleaching temperature or time decreased the brightness development. By higher bleaching temperature and longer bleaching time, detrimental effects on brightness development appeared apparently. This phenomenon was also observed by J. Colodette, *et. al*,[4] where stonegroundwood pulp was bleaching by alkaline peroxide.

This is because high temperature and prolonged bleaching time favor decomposition

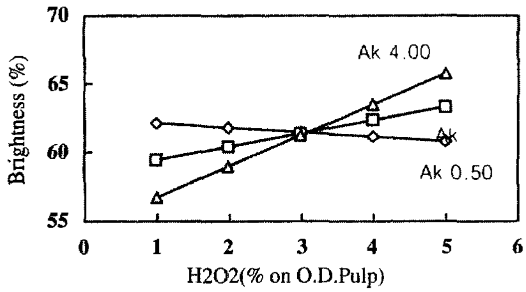

Fig. 1. Effects of H_2O_2 and its interaction with NaOH on brightness illustrated at the center point, i.e., silicate 2.25%, 72.5° C and 110 min.

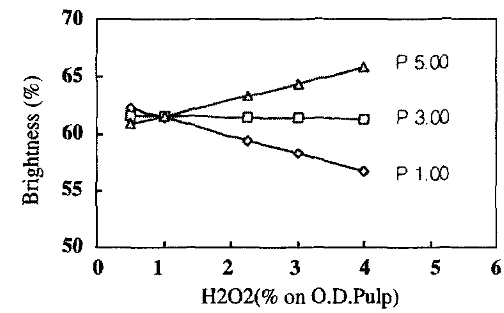

Fig. 2. Effects of NaOH and its interaction with H_2O_2 on brightness illustrated at the center point, i.e., silicate 2.25%, 72.5° C and 110 min.

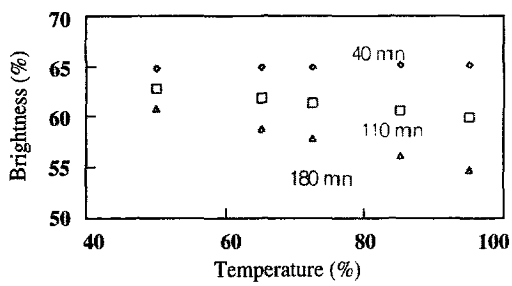

Fig. 3. Effect of temperature and its interaction with reaction time on brightness illustrated at center point, i.e., H_2O_2 3%, NaOH 2.25% and silicate 2.25%.

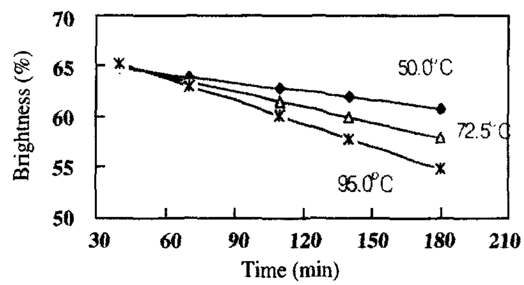

Fig. 4. Effect of reaction time and its interaction with temperature on the brightness illustrated at center point, i.e., H_2O_2 3%, NaOH 2.25% and silicate 2.25%.

of hydrogen peroxide by a free radical route (equation 3, 4 and 5), releasing oxygen other than singlet oxygen which then initiates the formation of conjugated chromophoric structures and fragmentation of lignin and cellulose.[10]

$$H_2O_2 \rightarrow HOO\cdot + H\cdot \quad (5)$$
$$HOO\cdot + OH\text{-} \; RO_2^{-}\cdot + H_2O \quad (6)$$
$$H_2O_2 \rightarrow 2HO\cdot \quad (7)$$

It was stated that under routine bleaching conditions at high consistency, though have certain limitations, time and temperature could be interchanged.[11] That is, an increase in bleaching temperature can compensate for a reduction in retention time up to a point. Conversely, if bleaching temperatures are held below 60° C, extending the reaction time often produces the same brightness response. This interchangeable property was not observed in the range investigated in this study, possibly it may be observed under the range of lower temperature and shorter bleaching time.

Table 3 showed that the interaction of alkali and bleaching time was significant at 10% level of significance. Figures 5 and 6

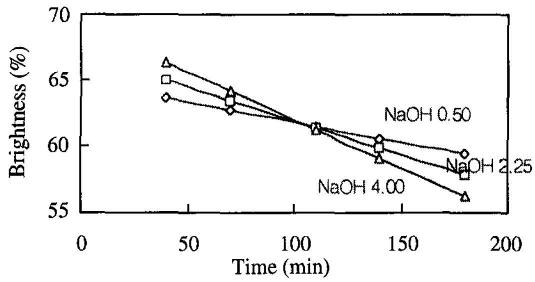

Fig. 5. Interaction of alkali and bleaching time on brightness illustrated at center point, i.e., H_2O_2 3%, silicate 2.25%, temperature 72.5° C.

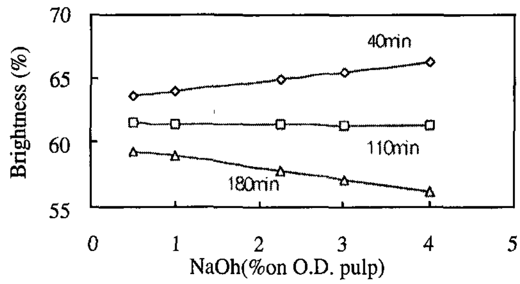

Fig. 6. Interaction of alkali and bleaching time on brightness illustrated at center point, i.e., H_2O_2 3%, silicate 2.25%, temperature 72.5° C.

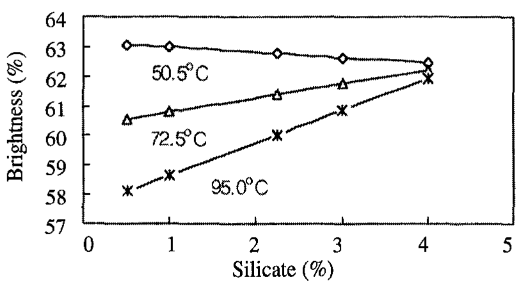

Fig. 7. Interaction of silicate and temperature on brightness illustrated at center point, i.e., H_2O_2 3%, silicate 2.25%, bleaching time 110 min.

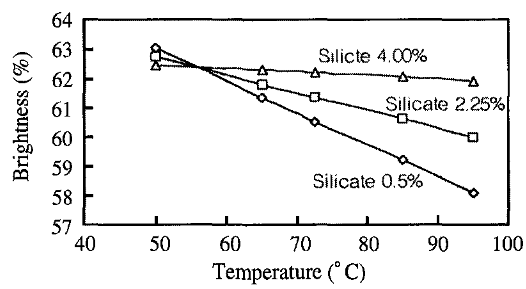

Fig. 8. Interaction of silicate and temperature on brightness illustrated at center point, i.e., H_2O_2 3%, silicate 2.25%, bleaching time 110 min.

showed when bleaching time was set at 40 min, increasing the alkali content increased the brightness while at longer reaction time, say over 110 min, a reverse result was observed. Besides, Fig. 5 showed again that increasing the reaction time decreased brightness over the whole alkali range.

Table 3 also showed that the interaction of silicate and bleaching temperature was significant at 16% level of significance. As mentioned above, although the 16% level of significance is too big, this effect was not eliminated from the model to keep the large R^2 and maximum Q^2 values.

Figures 7 and 8 showed that at high temperature, increasing the silicate content increased the brightness development, but at lower temperatures, increasing the silicate content showed little effect on brightness development. On the other hand, at low silicate content, negative effect of temperature on brightness appeared, while at high silicate content, brightness is stable over temperature variation.

It was well known that silicate is a cost-effective stabilizer for alkaline peroxide bleaching and produces two strong benefits: it significantly reduces peroxide decomposition during bleaching and it improves the internal stability of the bleach liquor itself.

Several theories about the role of silicate in the peroxide bleaching of (chemi)-mechanical pulp have been suggested. These roles include silicate acting as a peroxide stabilizer, metal ion sequestrant, buffering agent, and metal surface passivator. However, the chemical composition in silicate solution is very complicated, it was know that Na_2SiO_3, $Na_2Si_2O_5$, $Na_2Si_4O_9$ and many other polysilicates co-exit in the solution. It is still not very clear how these components contribute to the bleaching process. However, Fig. 7 and 8 indicates that temperature has some effects on the activity of silicate solution.

3. 2 Effects of bleaching factors on brightness development by response surface methodology (RSM)

The results obtained from the above screening experiments assume that it will be beneficial to keep both the temperature and reaction time at low levels. Thus in this RSM stage, temperature was set at 50° C and time for 50 minutes. The experiments carried out were shown in Table 2. The result of modeling was shown in Table 4 and the scaled on centered model was as follows:

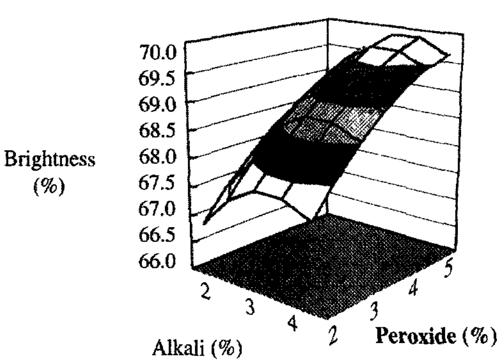

Fig. 9. Effect of peroxide and alkali on brightness.

Table 4. Model obtained in the RSM stage

	Scaled & Centered Coefficient	P
Constant	69.144	1.513e-24
P	1.048	4.870e-8
Ak	0.315	1.442e-3
Si	0.141	0.079
P*P	-0.350	0.031
Ak*Ak	-0.537	3.240e-3
R^2	0.9671	
R^2_{adj}	0.9507	
Q^2	0.9098	

$$Br. (\%) = 69.144 + 1.048P + 0.315Ak + 0.141Si - 0.350P^2 - 0.537Ak^2 \quad (8)$$

Fig. 9 was obtained based on the model and it showed that increasing the peroxide content increased the brightness development, but at the high level of peroxide addition, the ratio of brightness increase slowed down gradually. On the other hand, alkali showed maximal effects on brightness at a level around 3.5%. No interaction between hydrogen peroxide and alkali was found in the range investigated at this RSM condition.

Figure 10 showed that increasing the silicate content increased the brightness development, but this effect, with the p-value of 0.079, is not significant at 5% level of significance.

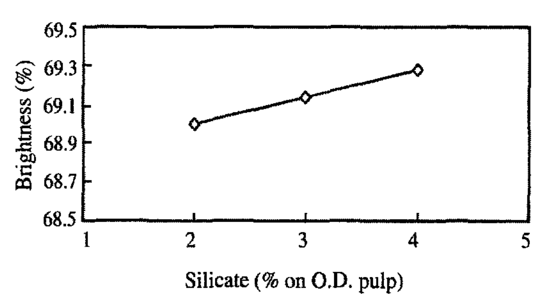

Fig. 10. Effect of silicate on brightness.

Table 5. Optimal bleaching conditions suggested by Modde and the practical predictability of the model

	P(%)	Ak(%)	Si(%)	Brightness Predicated	Brightness Practical
1	4.9997	3.2419	3.9995	70.028	70.05
2	5.0000	3.2986	3.9994	70.029	-
3	4.9984	3.2871	3.9995	70.029	-
4	5.0000	4.0000	4.0000	69.760	69.70
5	4.9999	3.4041	3.9905	70.021	70.20
6	4.9984	3.3128	3.9993	70.028	-
7	5.0000	4.0000	4.0000	69.761	-
8	5.0000	3.0000	3.0000	69.842	69.50

3. 3 Using the model for predication

In this step, brightness target was set to be maximal and Modde 4.0 predicated the conditions by which to get the target based on the above RSM model. The results were listed in Table 5.

Four of the eight experiments in Table 5 were repeated and the results also listed in Table 5. It can be seen that the predicated and practical values coincided very well, which means the model developed in the RSM step is very successful in predicating target brightness. It was also found that the under the bleaching conditions of 50°C, 50 min, hydrogen peroxide 5%, sodium hydroxide 3.2-3.4%, and silicate 4% based on oven-dried pulp, maximal brightness of 70% ISO can be achieved.

However it must be clear that conditions where maximal brightness was achieved, in most cases, are not the optimal condition of bleaching. Other pulp properties, such as strength properties and brightness stability should also be considered in determining the optimal bleaching conditions. This unresolved problem will be studied further in our later research.

4. Conclusions

This paper shows that statistical experimental design and multiple regression method are very effective in screening the complicated factors and finding their interactions that affects the brightness development in peroxide bleaching of TMP. Interactions of hydrogen peroxide with alkali, time with temperature, alkali with time and silicate with temperature were found to be significant which means that hydrogen peroxide bleaching will be favored at stable concentration of perhydroxyl ion, relatively short time and low temperature, and high level of silicate. Mathematical model which has good predictability for target brightness in one stage peroxide bleaching can also be established easily. Base on the model, maximal brightness of 70% ISO was found to at 50°C and 50 minutes by chemical additions of 5% for hydrogen peroxide, 3.2-3.4% for sodium hydroxide and 4% for silicate based on O. D. pulp. However, this result might not be suitable for situations where furnishes are different from ours, or different pretreatment is used, or bleaching carried out at different pulp consistency. In these cases it will be good to re-investigate the process by a similar methodology as was used in this study.

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