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DIMETHYLDIOXIRANE IN TCF BLEACHING SEQUENCES

by

Nayereh Mahdavi

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfilment of the
requirements for the
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Department of Paper and Printing Science and Engineering

Western Michigan University
Kalamazoo, Michigan
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I would like to dedicate my thesis to my late mother for her loving, sensitive support, and continuing involvement in my life and education.

Nayereh Madhavi

DIMETHYLDIOXIRANE IN TCF BLEACHING SEQUENCES

Nayereh Mahdavi, M.S.

Western Michigan University, 1999

The use of chlorine containing bleaching process creates various organic compounds such as chlorinated furan, dioxin, and AOX (adsorbable organic halogen). The human and aquatic life has been affected with the formation of these chlorinated organic compounds. EPA is proposing new regulations to impose discharge limits on the conventional pollutant materials of the bleaching effluents.

The objective of this research was to evaluate two TCF (Total Chlorine Free) bleaching sequences that use hydrogen peroxide and DMD on oxygen delignified hardwood kraft pulp. In one of the sequences, the DMD stage (A) was used prior to the hydrogen peroxide stage (P), and in the other, the DMD stage was used after the hydrogen peroxide. Oxygen delignified hardwood kraft pulp was chelated (Q) prior to bleaching with peroxide and DMD.

Both QQAP and QQPA bleached pulps resulted in brightness above the 80's with comparative paper properties. The QQAP bleaching sequence significantly gave a higher brightness, viscosity, burst strength, and pentosan content than QQPA. Statistical analysis shows no difference in tear and tensile in different bleaching sequences. Both QQAP and QQPA bleaching sequences were the same in alpha cellulose content. QQAP has less beta cellulose and higher gamma cellulose content than the content of QQPA bleached pulp.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
LIST OF TABLES	vi
LIST OF FIGURES	viii
CHAPTER	
I. INTRODUCTION	1
New Challenges for TCF Bleaching	1
II. LITERATURE REVIEW	4
Dimethyldioxirane as a Bleaching Agent	4
III. PROBLEM STATEMENT AND OBJECTIVE	16
IV. EXPERIMENTAL PROGRAM	17
Schematic of Experiment	17
Bleaching Stages	17
Chelation (Q) Stage	17
Hydrogen Peroxide (Q) Stage	20
DMD (A) Stage	22
Experimental Design	23
Chelation Stage	24
Application of the RSM in Peroxide Stage	24
Application of the RSM in DMD Stage	25

Table of Contents–Continued

CHAPTER

Testing Methods	26
Consumption of Hydrogen Peroxide	26
Kappa Number of the Pulp	28
Hemicellulose Content in the Pulp	28
Alpha, Beta, Gamma Cellulose Content in the Pulp	30
Paper Properties of the Bleached Pulps	30
Brightness of the Pulp	30
Viscosity of the Pulp	31
BOD, COD, and TOC of the Effluents	31
V. RESULTS AND DISCUSSION	32
Optimization of Peroxide Stage	32
Optimization of Dimethyldioxirane Bleaching	42
Final Bleaching Sequences	49
Kappa Number, Brightness, Viscosity	52
Alpha, Beta, Gamma Celluloses and Pentosans	55
Strength Properties of Handsheets	60
BOD, COD, and TOC	62
VI. CONCLUSIONS	66
VII. SUGGESTIONS FOR FUTURE STUDY	67

Table of Contents–Continued

REFERENCES	68
APPENDICES	
A. Statistical Data for Optimization of Peroxide Bleaching With the Use of RSM	70
B. Statistical Data for Optimization of DMD Bleaching With the Use of RSM	76
C. Calculations for BOD, COD, and TOC	85
BIBLIOGRAPHY	88

LIST OF TABLES

1. Variable Levels for Hydrogen Peroxide (2%) Bleaching	25
2. Variable Levels for DMD Bleaching	26
3. Testing Methods	27
4. Chemical Additions Used for Micro Kappa Number Determinations	29
5. Variable Levels for Hydrogen Peroxide (2%) Bleaching	33
6. First Order Design Runs for Optimization of Peroxide Bleaching	34
7. Hydrogen Peroxide Bleaching With and Without Sodium Silicate	35
8. The Effect of Reaction Time on Hydrogen Peroxide Bleaching With and Without Sodium Silicate	36
9. Peroxide Residuals With and Without Sodium Silicate	37
10. Comparison of Physical Properties of Bleached Pulps	38
11. Central Composite Design Runs for Peroxide Bleaching	39
12. Optimized Conditions for Hydrogen Peroxide Bleaching	43
13. Variable Levels for DMD Bleaching	43
14. First Order Design Runs for Optimization of DMD Bleaching	44
15. Central Composite Design Runs for DMD Bleaching	46
16. Final Optimization Runs for DMD Bleaching	48
17. Effluent Quality for OQAP and OQPA Bleaching	55
18. Final Testing Results for Bleached Pulps	56

List of Tables—Continued

19. ANOVA Table for Kappa Number	57
20. ANOVA Table for Brightness	57
21. ANOVA Table for Viscosity	58
22. ANOVA Table for Alpha Cellulose	58
23. ANOVA Table for Beta Cellulose	59
24. ANOVA Table for Gamma Cellulose	59
25. ANOVA Table for Pentosan	60
26. ANOVA Table for Tensile Strength	61
27. ANOVA Table for Tear Index	61
28. ANOVA Table for Burst Index	62
29. Statistically Significant Values for the Bleaching Sequences	63

LIST OF FIGURES

1. General Reaction Mechanism for Peroxymonosulfate and Ketone	5
2. A Process Diagram for In-situ Activated Oxygen Bleaching and Recovery . . .	8
3. A Process Diagram for the Regeneration of Inorganic Chemicals From the Green Liquor for Activated Oxygen Bleaching	9
4. Schematic of Bleaching Sequences	18
5. Effect of Sodium Hydroxide on Peroxide Bleaching	21
6. Effect of Sodium Silicate on Peroxide Bleaching	22
7. Effect of Alkali Concentration and Temperature on Brightness in Peroxide Bleaching	41
8. Effect of Alkali Concentration and Temperature on Viscosity in Peroxide Bleaching	42
9. Effect of Temperature and Activated Oxygen % on Brightness in DMD Bleaching	49
10. Effect of Buffer and Activated Oxygen on Brightness in DMD Bleaching . . .	50
11. Effect of Temperature and Buffer on Brightness in DMD Bleaching	51
12. Effect of Buffer and Temperature on Viscosity in DMD Bleaching	52
13. Effect of Temperature and Activated Oxygen on Viscosity in DMD Bleaching	53
14. Effect of Buffer and Activated Oxygen on Viscosity in DMD Bleaching	54
15. Tear-Tensile Curves for the Two Bleaching Sequences	63

CHAPTER I

INTRODUCTION

New Challenges for TCF Bleaching

During the bleaching process, the residual lignin in kraft pulp is removed, leading to a greater brightness of the pulp. Conventional bleaching includes the application of chlorine with a small amount of chlorine dioxide in the first stage. It can bleach pulps to high brightness without great loss of pulp strength (1). Reactions in chlorine bleaching are oxidation and substitution. Oxidation reactions create free phenolic moieties. Substitution reactions cause the aromatic ring opening which makes the fragments soluble in a dilute alkaline solution.

Chlorine dioxide reacts with the phenolic structure of lignin. Demethylation, oxidation of the C1 carbon to form 2-methoxy-p-quinone of the aromatic rings, results in ring opening, and cleavage of ether linkages. These are the principal reactions of chlorine dioxide delignification (2).

The use of chlorine containing bleaching processes creates various organic compounds such as chlorinated furan, dioxin, and AOX (adsorbable organic halogen). Human and aquatic life have been affected by the formation of these chlorinated organic compounds. EPA is promulgating new regulations to impose discharge limits on the conventional pollutant materials of the bleaching effluents (Federal Register: April 1998,

page 18653-18702).

The pulp and paper industry has implemented necessary changes in technology to reduce or eliminate the discharge of chlorinated organic materials and to comply with the various dioxin and AOX regulations. ECF (elemental chlorine free) bleaching has been the most common means to reduce chlorinated compounds. The effluents from ECF still have some potential to be harmful in the environment.

Environmental concerns have pushed the industry to completely eliminate chlorine compounds from bleaching and provide TCF (totally chlorine free) pulps. TCF pulp is produced with different combinations of ozone, oxygen, and hydrogen peroxide (2).

To eliminate chlorine in the bleaching of chemical pulps without a heavy capital investment, hydrogen peroxide can be used. Hydrogen peroxide is a nucleophilic reagent that reacts with carbonyl and conjugated carbonyl structures to remove chromophore groups without any significant delignification. Low reactivity of hydrogen peroxide with lignin is a drawback for replacing chlorine-containing compounds in the bleaching process. Oxygen delignification is another alternative to remove lignin up to 50% before a severe loss of pulp strength. Ozone is the other bleaching agent for replacing chlorine-containing compounds in the bleaching process. Ozone is an electrophilic reagent and an effective delignifying agent. Aggressive radical reactions that occur in ozone delignification cause unwanted carbohydrate degradation (2). Therefore, ozone and oxygen are not selective agents for replacing chlorine-containing compounds in the bleaching process.

There is a need for a selective and effective bleaching agent for chemical pulps. Recently, DMD (dimethyldioxirane) has been proposed as a candidate. DMD was isolated and characterized in 1985. This new, proposed bleaching agent does not have an established bleaching symbol. "A", "T", and "T" have been used for DMD bleaching. However, the most common symbol indicating an activated state is "A".

DMD is an electrophilic oxidant which reacts with C=C bonds in aliphatic side chains and the aromatic structure of lignin. Reaction of DMD with the aliphatic side chains forms epoxides; with the aromatic rings, it forms arene oxides. These epoxides are hydrolyzed to diols, which undergo ring opening with the DMD. This reaction is the same as one of the major reactions caused by chlorine dioxide. Recently, the cleavage of ether bonds by dioxiranes has been reported. Studies showed that there is not any radical involved in dioxirane oxidation (2).

In this research, the effectiveness and selectivity of DMD in optimized conditions for two TCF bleaching sequences, OQPA and OQAP (A, P, and Q are respectively DMD, hydrogen peroxide, and chelation stages) will be evaluated. Cellulose, hemicellulose, and lignin contents in both OQPA and OQAP sequences bleached pulps will be determined. In addition, their bleaching effluents will be characterized.

CHAPTER II

LITERATURE REVIEW

Dimethyldioxirane as a Bleaching Agent

Peroxymonosulfate is a known electrophilic agent and can oxidize a wide variety of compounds in the presence of a ketone.

Dimethyldioxirane can be generated by oxidizing acetone with the potassium salts of Caro's acid (peroxymonosulfuric acid). DMD reacts with electron-rich aromatic and olefinic structures of lignin, without any effect on electron poor structure of cellulose and hemicellulose. Formation of dimethyldioxirane in the presence of acetone and the reaction of dimethyldioxirane with the lignin is shown in Figure 1 (3).

As shown, the reaction transfers an extra oxygen atom into the carbonyl group of acetone which results in the formation of dimethyldioxirane. Dimethyldioxirane has a three-member ring containing two oxygen atoms and one carbon atom with two methyl substituents. This strained ring structure characterizes the DMD as a powerful and reactive oxidizing agent.

The effect of acetone, 2-butanone, 3-pentanone, and cyclopentanone on bleaching properties of peroxymonosulfate with softwood kraft pulp has been studied (3). The use of cyclopentanone retarded the bleaching properties of Caro's acid (peroxymonosulfuric acid, an oxidized form of sulfuric acid). 2-butanone, 3-pentanone and acetone enhanced

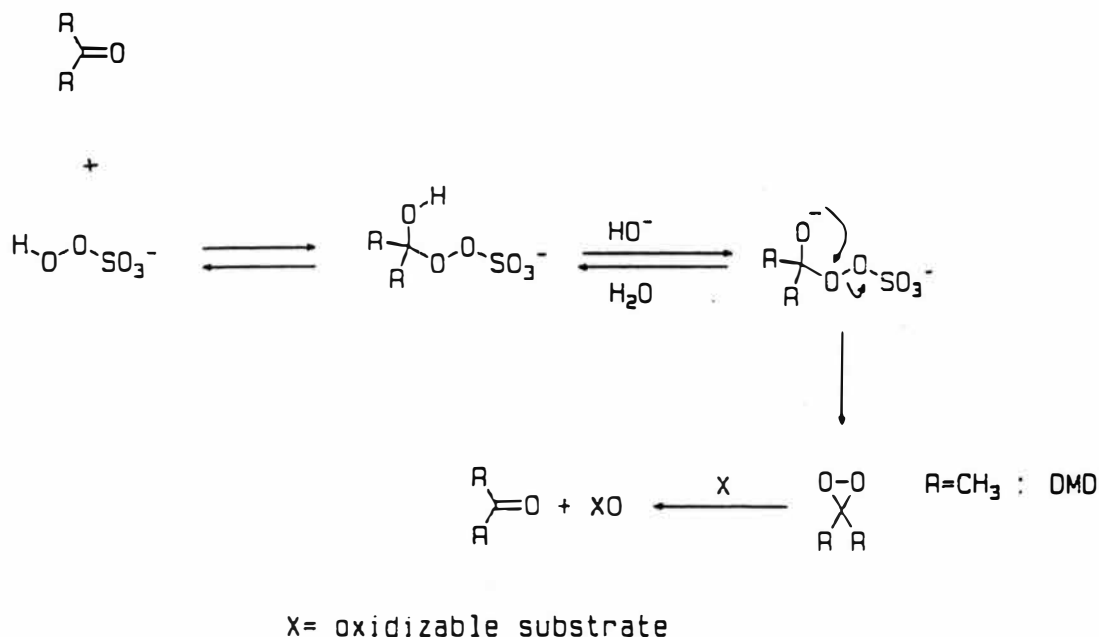


Figure 1. General Reaction Mechanism for Peroxymonosulfate and Ketone (3).

the bleaching properties of peroxymonosulfate. Acetone was suggested as the most effective catalyst for this reaction. It is believed that the water solubility of the ketone and possible differences in steric and electronic characteristics could influence the effect of ketone in bleaching properties.

Metal-induced decomposition of peroxymonosulfate has also been investigated (4). Mn, Fe, Cu, Ni, V and Co metals were added to kraft pulp bleaching with DMD. Metal-induced decomposition was investigated at pH 1.0, 2.0, 5.0, and 8.0. Cobalt was the most effective catalyst at pH 2.0 and 5.0. At pH 8.0, cobalt and copper were effective. Adding the DTPA retarded the metal-induced decomposition at pH 2.0, 5.0, and 8.0. At pH 1.0, cobalt was only weakly catalytic in the presence of DTPA.

Ragauskas (5) studied the reactivity and efficient oxidizing capabilities of

dimethyldioxirane as a bleaching agent. Initial research work was focused on determining the effectiveness of DMD bleaching. The acetone/sodium bicarbonate/oxone was applied in these experiments. A five-percent charge of DMD was applied on softwood kraft pulp with an initial 39.5 kappa number. After 1.5 hours at room temperature, the lignin drop for pulp was 66%. This high delignification indicates that DMD is an exceptionally reactive peroxide with unique bleaching properties. To develop a bleaching system with differing potential, the bleaching mixture employed varying amount of acetone-water. Results showed that the bleaching response is very sensitive to premixing conditions and the application of acetone. Optimal time for premixing appears to be five minutes. Results also showed that it is not necessary to employ acetone as a co-solvent during bleaching. Instead, with applying proper premixing conditions, less acetone can be employed for an effective bleaching response.

Recently, the effectiveness of potassium peroxymonosulfate as a bleaching agent was studied using groundwood and kraft pulps produced from both hardwoods and softwoods (6). The same pulps were bleached with equivalent amounts of alkaline hydrogen peroxide for comparison. Potassium peroxymonosulfate was as effective as alkaline hydrogen peroxide in bleaching pulps containing 1 percent lignin or less. In addition, the conditions were milder for peroxymonosulfate bleaching. The temperature was lower and the reaction time was less than that for hydrogen peroxide. The viscosities were higher (viscosity for hydrogen peroxide bleached pulps were 11 cp and for DMD bleached pulps were between 19 and 24 cp) for peroxymonosulfate bleached pulps.

Results suggested that potassium peroxymonosulfate is a stronger oxidizing agent than hydrogen peroxide. In further experiments, the pulp was treated with a chelant prior to bleaching with potassium peroxymonosulfate. Chelation improved the brightness from 65.3% to 67.4%.

Optimal conditions for pH, temperature, and time of DMD bleaching on hardwood and softwood kraft pulps were studied (7). The results showed that the DMD bleaching was sensitive to pH and temperature. In this experiment, a pH of 7 and temperature of 80°C were suggested as optimum conditions for DMD bleaching. Also, delignification reactions were found to be completed in one hour.

Lee (8) indicated that DMD reacts with residual lignin in the same way as chlorine and chlorine dioxide. A hemlock kraft pulp was bleached with 6% activated oxygen in this experiment. Following the DMD stage (A), an extraction stage (E) was applied on pulp. AE-bleached pulp had a comparable viscosity to the same pulp bleached by a (C+D)E sequence with the same degree of delignification. Strength and brightness of the AE bleached pulps followed with the DED stages was identical to the (C+D)EDED and O(C+D)DED bleached pulps. In further trials dimethyldioxirane was used prior to chlorine dioxide. The pulp bleached with AD showed a comparable zero-span tensile strength to that of the pulp bleached by the conventional bleaching stage (C+D)ED.

Lee (9) also bleached an oxygen delignified softwood kraft pulp with activated oxygen and peroxide (OQAE_{OP}P sequence) in a pilot plant and in the laboratory. In this experiment, activated oxygen was produced by reacting concentrated sulfuric acid with

hydrogen peroxide. Bleaching results after QAE_{OP} showed a negligible viscosity loss (0.4Pa.s - 1.3 mPa.s) and 77%-78% kappa reduction for the pulps from the pilot plant and the laboratory. The $OQAE_{OP}$ bleached pulps and the conventional $OC_D E_O DED$ pulps demonstrated similar pulp strengths. Also, it was found that the operating cost of the DMD bleaching sequence is competitive with the hydrogen peroxide stage.

The schematics shown in Figures 2 and 3 have been proposed to achieve both effective generation of monoperoxysulphate and a good mill chemical balance. As shown in Figure 2, monoperoxysulphuric acid is neutralized with sodium carbonate and mixed

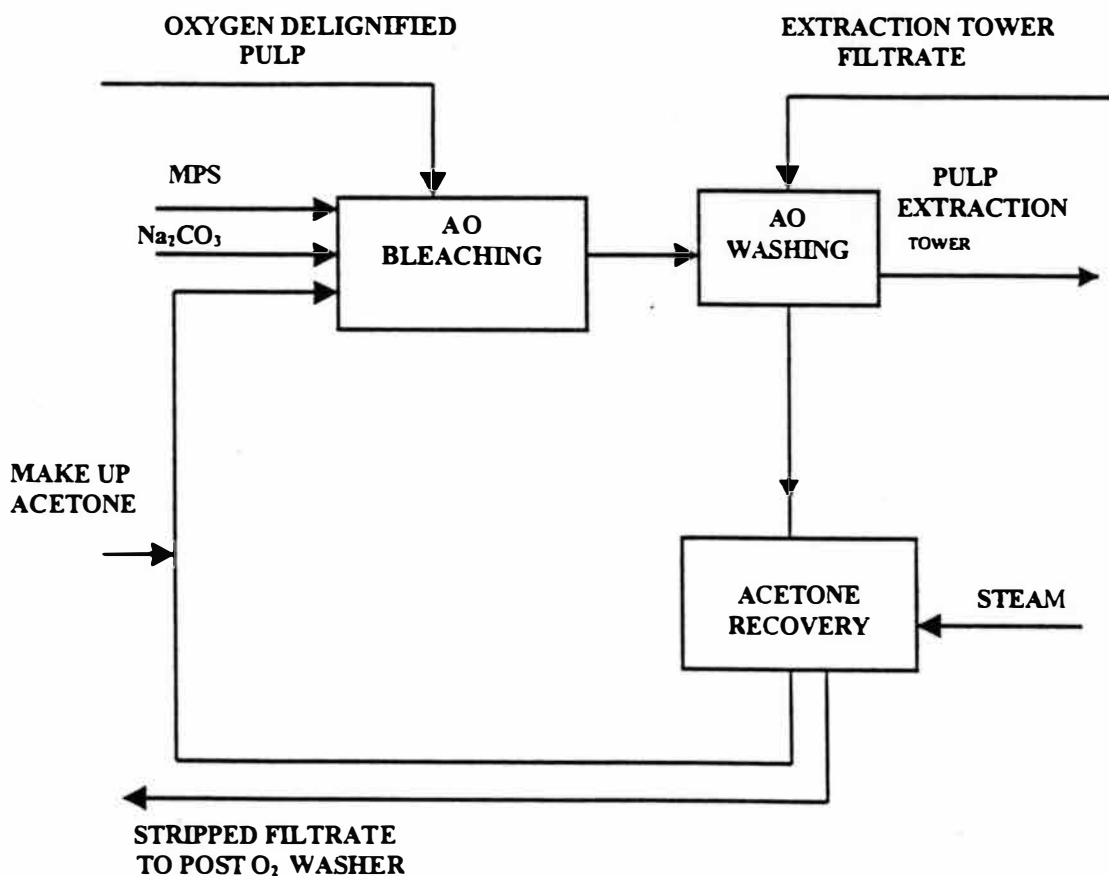


Figure 2. A Process Diagram for In-situ Activated Oxygen Bleaching and Recovery (9).

with the pulp and acetone. The acetone is washed from the pulp and sent to a distillation system. The other process (Figure 3) has been proposed to recover the sodium and sulphur as alkali and acid from the green liquor. The clarified green liquor is carbonated with carbon dioxide to generate sodium carbonate and hydrogen sulphide gas. A portion of this sodium carbonate is used for neutralization in the activated oxygen system and the excess is sent to the causticizers. The hydrogen sulphide gas is converted to concentrated sulphuric acid. Concentrated sulphuric acid is mixed with hydrogen peroxide for producing monoperoxsulfuric acid.

Thomas (10) showed that combining the DMD and peroxide has a synergistic

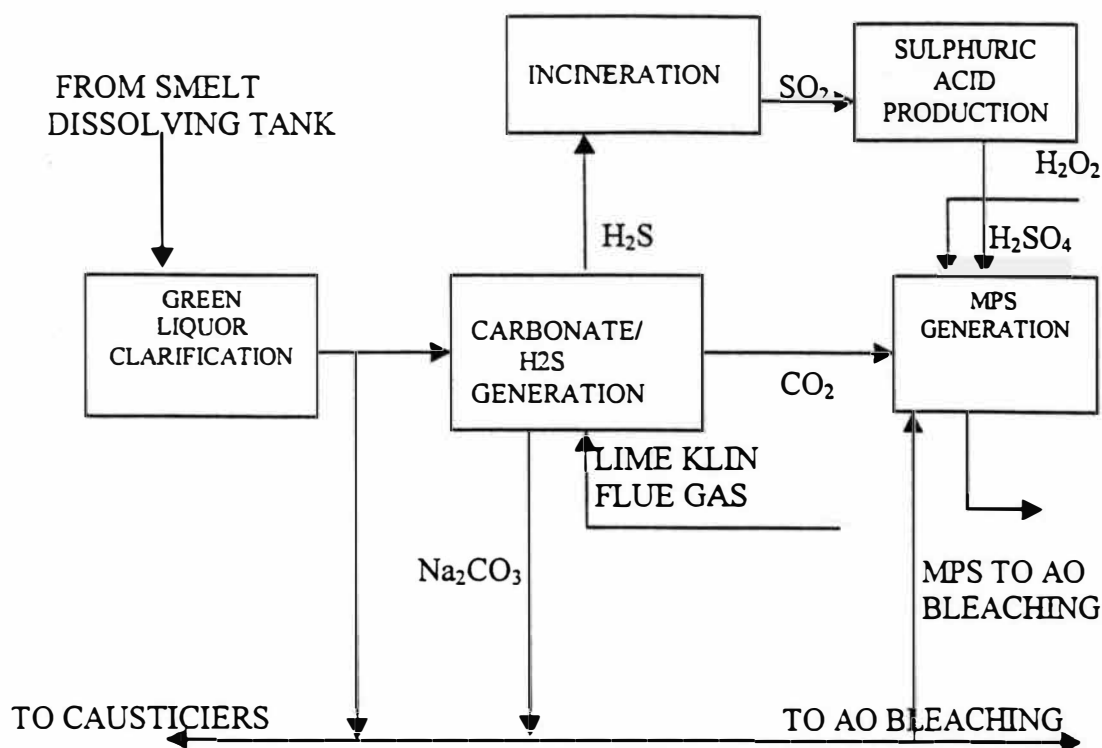


Figure 3. A Process Diagram for the Regeneration of Inorganic Chemicals From the Green Liquor for Activated Oxygen Bleaching (9).

effect on delignification. Delignifying and brightening OQPA and OQAP sequences were studied with identical chemical changes and bleaching conditions on softwood kraft pulp.

By placing the DMD at the final stage, removal of more lignin at low DMD charges resulted. Placing the DMD before hydrogen peroxide increased the percent delignification in QP sequence. The higher the DMD charges which were used, the greater was the percent delignification in QP sequence. A synergistic effect between the QP sequence and the DMD stage can explain these observations.

Placing the DMD at an earlier stage in the sequence resulted in a higher final brightness compared with using DMD in the latter stage of the sequence. Delignification and conditioning of the remaining lignin to peroxide treatment caused by DMD in the earlier stage were the reasons for brightness improvement. Also, results showed that no net brightness was gained when the DMD was used in the final stage. It is believed that DMD creates the chromophores in the low kappa number bleached pulp emerging from an OQP sequence.

The selectivity of DMD has been proven with the viscosity and zero-span tensile strength measurements. The viscosity losses were negligible up to 2% application of DMD. Application of DMD early in the sequence resulted in a lower viscosity loss compared to the application of DMD late in the sequence. Also, the OQAP sequence remained selective at a high brightness level. The zero-span tensile strength measurements showed slight loss of fiber strength (5-7%) at 1% charge of DMD. At the higher DMD charges, there is no evidence of additional strength loss in both sequences.

Dimethyldioxirane as an interstage bleaching agent was tested in an OAO sequence for bleaching softwood kraft pulp. As a comparison, bleaching via the ODO sequences (chlorine dioxide stage in this experiment was carried out at two different temperatures of 25°C and 75°C) on same pulp was tried (11). The brightness gained per kappa number reduction by dimethyldioxirane, up to 1.25% applied oxidant charge, was greater than obtained by chlorine dioxide at both temperatures. Further, dimethyldioxirane was reported to be more effective than chlorine dioxide at an applied oxidant charge of up to 1.25%. Also, results showed that intermediate treatment with dimethyldioxirane enhanced the kappa number reduction in second oxygen delignification stage just as with chlorine dioxide.

The linear regression equation, which described the relationship between viscosity and kappa number for OAO and ODO bleached pulps, was similar. The zero-span tensile strength for all bleached pulps either treated with dimethyldioxirane or chlorine dioxide was similar. Therefore, dimethyldioxirane was proposed as an effective and selective brightening agent for chemical pulps.

DMD bleaching effluent was characterized in a recent experiment (12). DMD was used in different bleaching sequences on kraft hardwood pulps. For comparison, the effluent of control bleaching sequences, which contained chlorine dioxide, was tested. Results indicated that DMD bleaching effluent contained higher levels of organic materials. The most environmentally friendly sequence was an optimized OAE sequence with the stepwise addition of DMD which resulted in a decrease in BOD and COD.

To optimize the conditions for hydrogen peroxide (P) and DMD (A) stage, a response surface methodology (RSM) is used. The initial experiments are run to find a suitable approximation for the true functional relationship between response and control variables. Experiments follow an orthogonal first order design with some center points. After performing the initial experiments and measuring the response variables, a first order is fitted to the data by using a first order regression procedure. If the first order model fitted, either the steepest ascent or descent method is used for moving sequentially along the path of steepest ascent (in case of maximizing the response) or descent (in case of minimizing the response). The path of steepest ascent is proportional to the signs and value of the regression coefficient in the fitted model. For determining the origin point of the steepest ascent the point $x_1=x_2=\dots=x_k=0$ will be assumed. The step size for one of the main control variables will be chosen and the step size for the other variable will be determined. These coded variables can be converted to the natural variables. Computing the points along this path will be continued until a decrease in observed response is noted. Then another first-order model may be fitted, and the new steepest ascent will be determined. This procedure will be continued until the vicinity of the optimum is reached. This is usually indicated by a lack of fit for a first-order model. Then, a model of degree two or higher is necessary to approximate the response in order to specify the curvature in the true response. In most cases, the second order model will be satisfactory.

Use of central composite design is helpful to fit the second order model by adding

center points and axial points to the model. Also, central composite design is helpful to locate the stationary point. Canonical analysis and contour plots are the ways to characterize the stationary points as a maximum, minimum, or saddle point. Ridge systems can be used, if the stationary point is far outside the region of exploration for the fitting the second order model (13).

For the design and analysis of final phase experiments, first, it is necessary to describe some elementary concepts. Random errors arise from variation that is uncontrolled and generally unavoidable. The presence of errors implies that the response variables are random variables. The variance to define a variance operator which, mathematically, is defined as:

$$V(y_{ij}) = E[(y_{ij} - \mu)^2] = \sigma^2$$

The mean of a probability distribution is a measure of its central tendency, and mathematically, is defined as the mean, $\mu = E(y) = \int f(y) dy$.

The methods for the design and analysis of single-factor experiments with 'a' level treatments are presented to study the effect of the two different bleaching sequences on kraft pulp.

In these experiments, there will be n observations under the two bleaching sequences, OQAP, OQPA, for comparison. The observed values from each of the treatments are random variables. The linear statistical model of observations can be presented as follows:

$$Y_{ij} = \mu + \tau_i + \epsilon_{ij} \quad \{i=1,2,\dots,a \quad j=1,2,\dots,n\}$$

Y_{ij} is the (ij) th observation, μ is the overall mean for all treatments, τ_i is the i th treatment effect, and ϵ_{ij} is the random error component. The objective is to test appropriate hypotheses about the treatment effects and to estimate them. For hypothesis testing, the model errors are assumed to be normally and independently distributed random variables with mean zero and variance σ^2 . The variance is assumed to be constant for all treatments. An appropriate means, for testing the equality of a treatment means is the analysis of variance. Analysis of variance provides two estimates of σ^2 -- one based on the inherent variability between treatments and one based on the variability between treatments. If there are no differences in the treatment means, these two estimates should be very similar, and if they are not similar, the observed differences must be caused by differences in the treatment means.

Comparing $MS_{\text{treatment}}$ and MS_{Error} , one can perform a test of the hypothesis of no difference in treatment means. Therefore, if the null hypothesis of no difference in treatment means is true, the ratio $F_0 = (SS_{\text{treatment}}/a-1)/(SS_{\text{Error}}/N-A) = MS_{\text{treatment}}/MS_{\text{Error}}$ is distributed as F with $a-1$ and $N-a$ degrees of freedom (N is the total number of observation and a is level of treatments). If the null hypothesis is false, then the expected value of $MS_{\text{treatment}}$ is greater than σ^2 .

It is unwise to rely on the ANOVA until the validity of the basic assumptions has been checked. The examination of residuals ($e_{ij} = y_{ij} - \bar{y}_i$) provides the adequacy of the model and violations of the basic assumptions. If the model is adequate, the residuals versus the fitted values should be structureless. In practice, they should be unrelated to

any other variables, including the predicted response (13).

A check of the normality assumption can be made by a graph of the cumulative distribution of the residuals on normal probability paper. Normal distribution plots as straight line (13).

CHAPTER III

PROBLEM STATEMENT AND OBJECTIVE

DMD has been proposed as a selective and effective bleaching agent. Thomas et al. (10) showed that combining the DMD and peroxide has a synergistic effect on delignification. Results showed that when DMD was applied before peroxide, the final brightness was much higher and the viscosity drop was less. Results also showed that DMD was not an active brightening agent in the final stage. However, there is no information available about how DMD changed the composition of the fiber or about the quality of TCF bleaching effluents in these sequences. It would be necessary to study the effect of DMD on the cellulose, hemicellulose, and lignin content of the bleached pulps from the different sequences (OQPA, OQAP). Also, the effluents of these TCF bleaching sequences need to be characterized.

The objective of this research is to evaluate two TCF bleaching sequences that use hydrogen peroxide and DMD on oxygen delignified hardwood kraft pulp. In one of the sequences, the DMD stage will be applied prior to the hydrogen peroxide stage, and in the other one, the DMD stage will be used after the hydrogen peroxide. The conditions will be optimized for DMD and hydrogen peroxide. For both optimized bleaching sequences, the cellulose, hemicellulose, and the lignin contents will be determined and the effluents will be characterized.

CHAPTER IV

EXPERIMENTAL PROGRAM

Schematic of Experiment

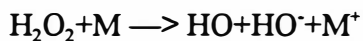
The objectives are to evaluate the effect of DMD as a bleaching agent and its effect on holocellulose and lignin in optimized TCF bleaching sequences. A schematic of the bleaching sequences is shown in Figure 4.

Bleaching Stages

The bleaching procedure includes three main stages: (1) Chelation stage, (2) Hydrogen peroxide stage, and (3) DMD stage.

Chelation (Q) Stage

Hydrogen peroxide can brighten kraft pulp under alkaline conditions. Maximizing the selectivity of hydrogen peroxide toward the lignin and minimizing peroxide consumption require the management of the profile of pulp metal ions. Ions are different in their ability to catalyze H_2O_2 decomposition. Some ions, e.g., Mg^{+2} , CA^{+2} , and SiO_3^{-2} , stabilize the peroxide and some others, e.g., manganese, iron, and copper ions catalyze the decomposition of hydrogen peroxide and radical formation:



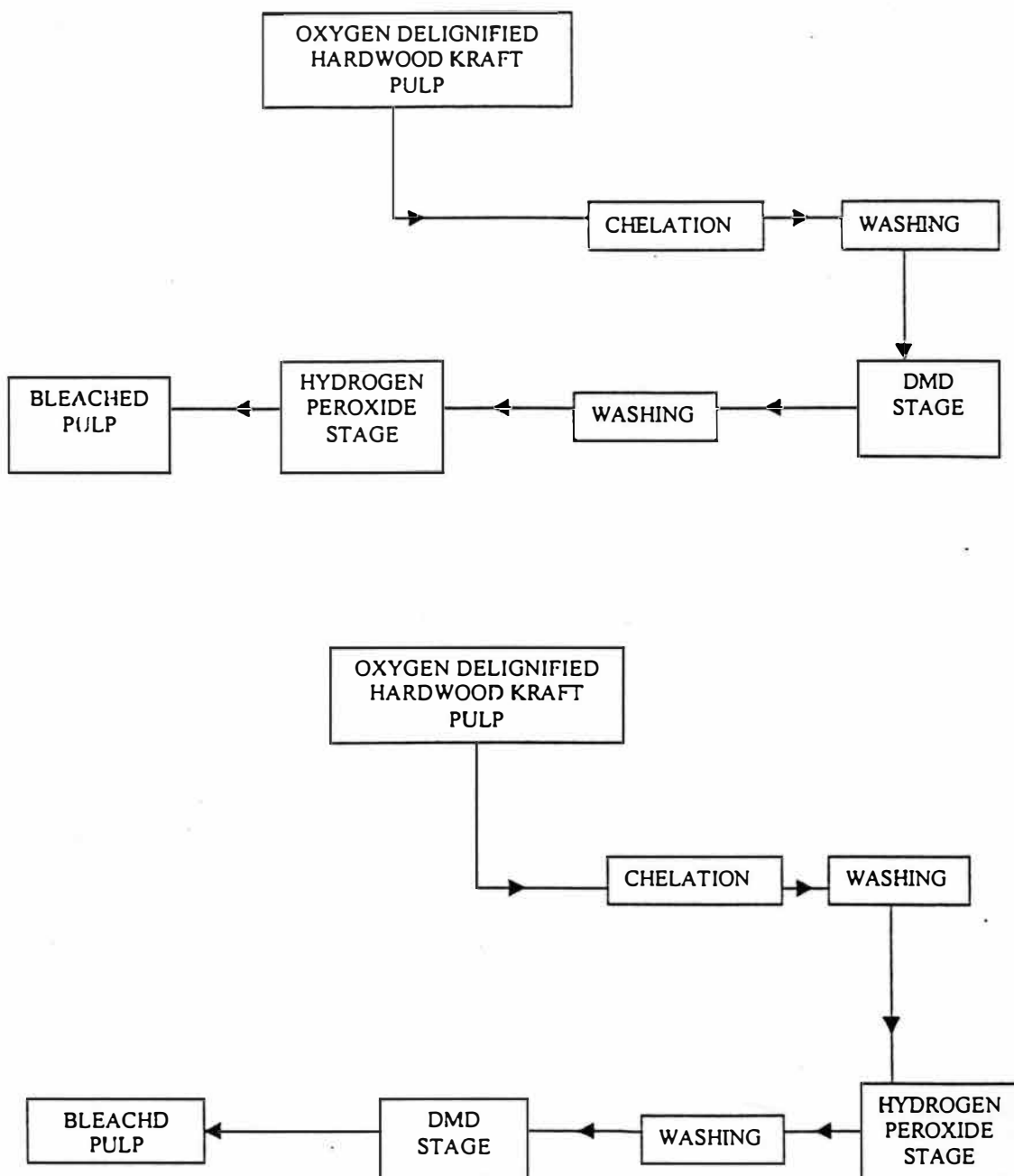
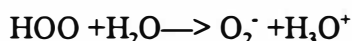
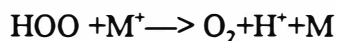
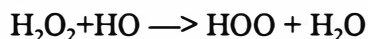
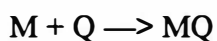


Figure 4. Schematic of Bleaching Sequences.



EDTA with six bonding sites and DTPA with eight bonding sites chelate metal ions in a 1:1 ratio which can be written:



The equilibrium, or formation, constant, K_{eq} , which represents the thermodynamic stability between the metal and the chelant, is given by:

$$K_{\text{eq}} = [\text{MQ}^{n-r}] / ([\text{M}^n][\text{Q}^r])$$

where MQ^{n-r} is the newly formed metal chelate, n is the charge of the metal, and r is the charge of the chelant. Increasing the bonds between chelant and metal increases the value of K_{eq} . For the same metal, the value of K_{eq} is higher for DTPA than that of EDTA. Metal accessibility, diffusion, and energy of diffusion are sources of the limiting factors for metals removal by the chelant (14).

The metal induced decomposition of peroxymonosulfate has been studied. Results indicated that copper and a high concentration of cobalt resulted in decomposition of peroxymonosulfate. Under alkaline conditions, the rate of decomposition of peroxymonosulfate by these metals was higher. Also, it was reported that free radicals were not responsible for this decomposition and the reaction between HSO_5^- and SO_5^{2-} were involved in a decomposition mechanism.

In this study for obtaining the optimal metal profile, chelation was performed at

60°C and pH 5.5 for 60 minutes, followed by a water wash.

Hydrogen Peroxide (P) Stage

The most known reaction of lignin during hydrogen peroxide is the destruction of the orthoquinone chromophore structure in lignin.

Hydrogen peroxide can also cause the demethylation and cleavage of side chains. The phenolic structures in lignin are not substantially attacked by alkaline hydrogen peroxide.

The active ion for bleaching in hydrogen peroxide is the perhydroxyl ion. The presence of this ion depends on the pH. pH 10.5 favors equilibrium toward the perhydroxyl ion without significant decomposition of hydrogen peroxide. Higher pH not only increases the perhydroxyl ions, but also accelerates the decomposition of hydrogen peroxide to oxygen and water (15).

Sodium silicate and sodium hydroxide are two sources of alkalinity for the preparation of the hydrogen peroxide bleaching liquor. Also, sodium silicate is used as a buffering solution. Optimization of sodium silicate and sodium hydroxide needs to be done empirically in each bleaching system.

As shown in Figure 5 (15), the residual of hydrogen peroxide drops with the increasing sodium hydroxide concentration in the peroxide bleaching. But brightness first increases with increasing sodium hydroxide concentration and then drops. Therefore, the optimization of sodium hydroxide at each peroxide application level and particular pulp

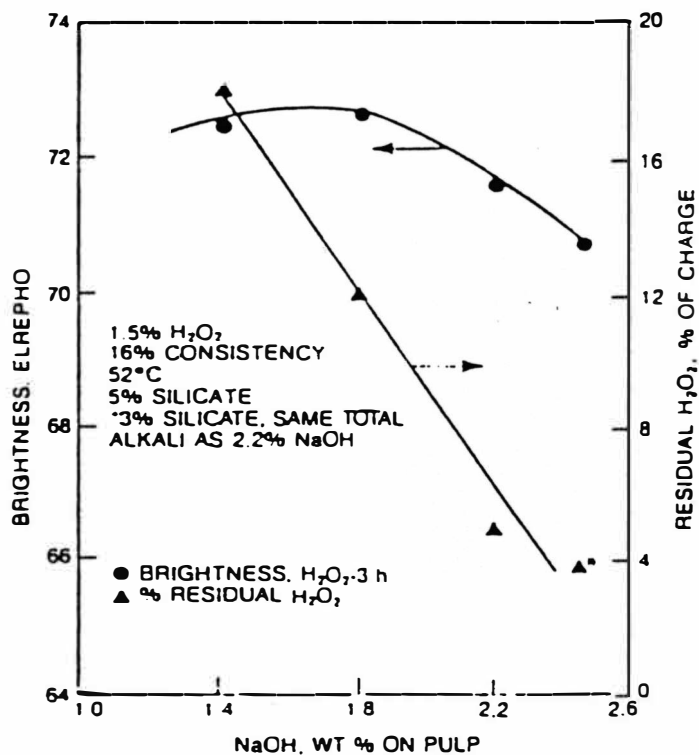


Figure 5. Effect of Sodium Hydroxide on Peroxide Bleaching(15).

should be emphasized.

As shown in Figure 6 (15), with the increase of sodium silicate from 1.0% to 5.0% on O.D. pulp, the brightness and hydrogen peroxide residual increased. The amount of sodium silicate must be optimized to prevent alkali darkening of the pulp.

Magnesium sulfate is used in preparation of hydrogen peroxide liquor. Magnesium stabilizes the bleach liquor by adsorbing unwanted heavy metal ions such as manganese, iron, or copper (15).

High consistency pulp increases the efficiency of hydrogen peroxide bleaching. It reduces the aqueous volume for bleaching chemicals and increases the possibility of

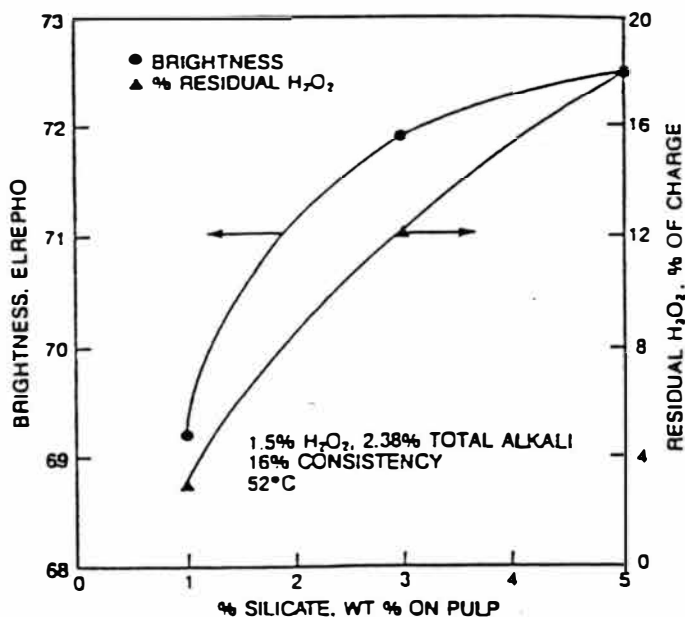


Figure 6. Effect of Sodium Silicate on Peroxide Bleaching (15).

hydrogen peroxide consumption.

High temperatures increase the rate of chemical reaction, but temperatures above 80°C accelerate the decomposition rate of hydrogen peroxide. The optimization of temperature is required. A time period of two hours is recommended for complete hydrogen peroxide bleaching reactions (15).

DMD (A) Stage

Adding potassium peroxymonosulfate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), oxone, to an acetone solution generates DMD (dimethyldioxirane).

The acetone/water/sodium bicarbonate/oxone mixture will be applied in this stage. The bleaching response with DMD is very sensitive to premixing conditions of acetone-

water and the application of acetone. Five minutes is suggested as the optimal time for premixing acetone-water. The volume ratio of 3.0/1.0 is suggested for the acetone/water premixture.

DMD bleaching is sensitive to pH. The amount of sodium bicarbonate has to be optimized for obtaining a pH of 7.

Most research on DMD bleaching has been done at room temperature. An optimization of temperature needs to be done for DMD bleaching.

Ninety-five percent of the reactions between DMD and lignin is completed in the first five minutes. A time period of one hour is needed to complete the reactions.

The concentration of activated oxygen will be optimized for this experiment.

Experimental Design

The objectives are to optimize the conditions for OQPA and OQAP bleaching sequences with respect to brightness and viscosity and to compare pulp properties, fiber composition, and effluent characteristics between the two optimized TCF bleaching sequences. This experiment will be divided into two main stages: (1) optimization of bleaching stages with respect to brightness and viscosity, and (2) study of the cellulose, hemicellulose, and lignin content, physical and optical properties of bleached pulps, and the effluent characteristics (in optimized OQPA and OQAP bleaching sequences).

Optimization experiments were done employing response surface methodology, and the final phase was carried out by using single factor experiments at different levels

with replications.

Chelation Stage

Chelation was done on oxygen delignified hardwood kraft pulp (with a kappa number of 8.9, viscosity of 18.46, brightness of 45.28; northern soft maple: 99% birch, 1% aspen) with 0.5% EDTA for one hour at room temperature and pH 5.5 prior to the peroxide and DMD bleaching. First, pulp was diluted to 2% consistency and pH of 5.5 was maintained for the pulp; then EDTA was added to the pulp. The pulp was mixed frequently. After one hour, the pulp was washed with distilled water adequately.

Application of the RSM in Peroxide Stage

The objective of this part of the research is to optimize the process conditions for hydrogen peroxide bleaching.

In peroxide bleaching, first a solution of sodium hydroxide, sodium silicate, and magnesium sulfate, and then hydrogen peroxide were added to the chelated pulp. Every 15 minutes, the pulp was kneaded for one minute. Experiments were conducted at 5% consistency, pH 10.5 and above, and a reaction time of two hours.

The initial experiments for optimization of peroxide bleaching were conducted to find a suitable relationship between response and control variables. Optimization of process variables has been done with respect to brightness and viscosity. Levels of control variables for the initial experiments are presented in Table 1.

Table 1
Variable Levels for Hydrogen Peroxide (2%) Bleaching

Variables	Factor	
	High Level	Low Level
Temperature, °C	75	55
NaOH, %	1.5	1.0
Na ₂ SiO ₃ , %	2.0	1.5

Application of the RSM in DMD Stage

For the DMD bleaching stage, first a buffer solution, then a premixed solution of water and acetone, and lastly oxone were added to the chelated pulp. Every 15 minutes the pulp was kneaded for one minute. Experiments were conducted at 5% consistency, pH 7.0-7.8, for one hour reaction time.

The initial experiments for optimization for DMD bleaching were run to find a suitable relationship between response and control variables. Optimization of process variables was done with respect to brightness and viscosity. Levels of control variables for the initial experiments are presented in Table 2.

Table 2
Variable Levels for DMD Bleaching

Variables	Factor Level	
	High Level	Low Level
Temperature, °C	45	25
Activated oxygen, %	5	1
Buffer/Activated oxygen, mol	9	7

Testing Methods

Oxygen kraft pulp was chelated before bleaching stages. Chelated pulp was used to optimize the process conditions for peroxide and DMD. Two bleaching sequences, OQPA and OQAP, were used to bleach the oxygen pulp in optimized conditions. At the end of the sequences, bleached pulps were tested for brightness, viscosity, tensile, tear, burst, alpha/beta/gamma cellulose, lignin, and pentosan. The effluents were tested for BOD, COD, and TOC. The TAPPI standards used to perform the above tests are listed in Table 3.

Consumption of Hydrogen Peroxide

The bleached pulp was placed in a clean Buchner funnel and pressed to collect

Table 3
Testing Methods

No.	Test Particulars	TAPPI Methods
1	Brightness Pads	T-218 om-91
2	Brightness	T-524 om-86
3	Kappa Number	T-236 cm-85 & UM 246
4	Viscosity	T-230 os-76
5	Burst Index	T-403 om-91
6	Tear Index	T-414 om-88
8	Tensile Index	T-494 om-88
10	Pentosan	T-223 cm-84

100 mL of filtrate. Twenty-five mL of the filtrate solution was pipetted into a 250 mL Erlenmeyer flask. Then 10-15 mL of 25% H₂SO₄, 5 ml of KI solution, and 3 drops of indicators were used to determine the hydrogen peroxide consumption (17):

$$\text{H}_2\text{O}_2\% \text{ on pulp} = (0.1 \text{ N THIO.} * 17/25 \text{ mL}) * (100-D)/D * (1/10) * \text{mL thio.}$$

$$D = \% \text{ consistency on OD basis}$$

$$\text{Residual, as \% of applied} = (\% \text{RESIDUAL ON PULP} / \% \text{H}_2\text{O}_2 \text{ APPLIED}) * 100$$

$$\text{Chemical consumed as \% of applied} = [(\% \text{H}_2\text{O}_2 \text{ applied} - \% \text{residual on pulp}) / (\% \text{H}_2\text{O}_2 \text{ applied})] * 100$$

Kappa Number of the Pulp

Both bleached pulps and unbleached pulps were tested for lignin content. TAPPI T236 cm-85 method was used for determination of lignin content. Kappa numbers for bleached pulps were too low to be determined. The standard procedure UM 246 Micro kappa number was used to determine the residual lignin of the pulp. Tests were done in triplicate for each pulp. The chemical additions, used in the micro kappa number procedure for kappa number determination, are presented in Table 4. Used in the procedure was 0.2 normal of thiosulfate solution.

Hemicellulose Content in the Pulp

Hemicelluloses are the noncellulosic carbohydrate part of wood. Hardwood hemicelluloses mainly consist of pentosans (19-25%). Therefore, the pentosan part of hemicellulose was determined for bleached pulps and the test for each bleached pulp was duplicated. High pentosan content contributes to the strength of paper. The pentosan content was determined according to TAPPI T223-cm 84.

For bleached samples, 2 grams of pulp samples were used. To prepare a calibration graph, 20, 40, 60, 80, and 100 mg of pure d-xylose (d-xylose were dried in the oven for 5 hours, prior to the experiment) were used. The test specimen was placed in a boiling flask and NaCL and 3.85N HCL were added based on suggested T223-cm84; the flask connected to the distillation apparatus and the acid level in the flask was marked. Heat was applied. During distillation, the acid was added to the flask from the separatory

Table 4

Chemical Additions Used for Micro Kappa Number Determinations

Volumes and Weights	
0.1 N KMNO_4 solution, (ml)	100
Volume of 4N H_2SO_4 , (ml)	100
Volume of Water, (ml)	800
Total Volume, (ml)	1000
Weight of a Specimen, (g)	10
Volume of 1 N KI solution, (ml)	20

funnel at a uniform rate to maintain a constant volume. After 90 minutes the distillate was collected and the temperature of the distillate was brought down to about room temperature and 3.85 N HCL was added to each distillate to maintain a constant volume. Orcinol reagent and then ethanol were added up to 5 mL of distillate and kept in a water bath of 25°C for about 60 minutes after the addition of each chemical. The absorbency of the solution was then measured at 630 nm with the use of 8451A DIODE ARRAY spectrophotometer. For pulps, 2 mL of hydrolysate samples were diluted to 10 mL with 13.5% HCL prior to absorbency measurements. Then 2 mL of the hydrolysate was used for absorbency measurements at 630 nm. The number of equivalent milligrams of xylose in the test specimen was read from the prepared calibration graph.

Alpha, Beta, Gamma Cellulose Content in the Pulp

Alpha cellulose is the pulp fraction resistant to 17.5% sodium hydroxide under test conditions described in T-203 om-88. In general, the alpha-cellulose indicates the undegraded cellulose content in pulp. Beta cellulose is the soluble fraction, which is reciprocated on acidification of the solution (T-203 om-88), and indicates the amount of degraded cellulose. Gamma cellulose is that fraction remaining in solution after acidification and consists mainly of hemicellulose in the T-203 om-88 method. The tests for each bleached pulp were done in triplicate.

Paper Properties of the Bleached Pulps

Twenty-eight g O.D. of bleached pulps at 10% consistency were beaten in a PFI mill, 5000 revolutions, according to TAPPI 248 cm-85. TAPPI method 205 om-88 was followed to make hand sheets from beaten pulps. Freeness was measured with the use of T277 om-94 before making hand sheets for each bleached pulp. Hand sheets were stored in conditioned rooms for 36 hours before they were tested for tear, tensile, and burst strengths. T494 om-88, T414 om-88, and T403 om-91 methods were used to determine tensile index, tear index, and burst index, respectively.

Brightness of the Pulp

T218 om-91 was used to form hand sheets for reflectance testing of pulp. Hand sheets were stored in conditioned rooms for 48 hours. Brightness values were measured

with a BRIGHTMETER MICRO S4-M.

Viscosity of the Pulp

Also prepared were 0.5% solutions of pulp CED and the viscosities were determined with a Fisher (size 200), M151 (size 200), and W861 (size 200) capillary viscometers. The viscometers were calibrated with a standard oil. TAPPI 230 OS-76 method was used to determine the viscosity of the pulps. Viscosity tests were duplicated for each bleached pulp.

BOD, COD, and TOC of the Effluents

BOD and COD tests were used to measure the organic content in bleaching effluents which can be oxidized by microorganisms and chemical means, respectively. Standard Methods of BOD, COD, and TOC for wastewater were used to evaluate effluents in this research (16). The calculations for BOD, COD, and TOC are shown in Appendix C.

CHAPTER V

RESULTS AND DISCUSSION

Optimization of Peroxide Stage

The objective of this part of the research was to optimize the process conditions for hydrogen peroxide bleaching.

Chelation was done on pulp before the bleaching stage to remove metal ions. Added to the pulp prior to the peroxide stage bleaching was 0.5% EDTA for one hour at room temperature and pH 5.5. The pulp after chelation was washed appropriately.

The initial experiments for optimization of peroxide bleaching were conducted to find a suitable relationship between response and control variables. Optimization of process variables has been done with respect to brightness and viscosity. Levels of control variables for the initial experiments are presented in Table 5.

The total number of initial experiments was 11, which included 3 replicates at the center point. All the experiments were conducted at 5% consistency, pH 10.5 and above, and a reaction time of two hours. Every 15 minutes the pulps were kneaded for one minute. The results and the run details are presented in Table 6.

Analysis of Variance (Appendix A, Tables 1 & 2) revealed that the curvature effects were significant with respect to both brightness and viscosity.

The regression equations for the first order model are shown below:

Table 5
Variable Levels for Hydrogen Peroxide (2%) Bleaching

Variables	Factor Level	
	High Level	Low Level
Temperature, °C	75	55
NaOH, %	1.5	1.0
Na ₂ SiO ₃ , %	2.0	1.5

Brightness, % = $36.6 - 0.18a + 1.62b + 0.307T$ ($R^2 = 91.1\%$, $R^2(\text{adj}) = 88.4\%$)

Viscosity, cp = $13.5 + 0.66a + 0.88b + 0.0032T$ ($R^2 = 5.8\%$, $R^2(\text{adj}) = 0$)

The regression equation for brightness shows that brightness increases with temperature (T) and sodium hydroxide (b) concentration, but decreases with the sodium silicate concentration (a).

The effect of sodium silicate in decreasing the brightness is contrary to the results reported in earlier literature (17). However, repeated trials with and without silicate in this research confirmed that brightness decreases in the presence of sodium silicate (Table 7). The type of pulp can be an answer to this issue because, in peroxide brightening of chemical pulps, the stabilizing effect of MgSO₄ is generally sufficient. Sodium silicate is not always needed.

The effect of sodium silicate in providing brightness (compared to no sodium

Table 6

First Order Design Runs for Optimization of Peroxide Bleaching

Run #	Na ₂ SiO ₃ , %(a)	NaOH, %(b)	Temp, °C	Response Values	
				Brightness, %	Viscosity, cp
1	1.5	1.0	55	54.7	15.50
2	2.0	1.0	55	54.1	17.04
3	1.5	1.5	55	54.7	16.16
4	2.0	1.5	55	55.2	16.88
5	1.5	1.0	75	60.4	15.82
6	2.0	1.0	75	60.3	16.47
7	1.5	1.5	75	61.5	17.57
8	2.0	1.5	75	61.3	15.98
9	1.75	1.25	65	59.5	13.93
10	1.75	1.25	65	59.1	15.28
11	1.75	1.25	65	59.8	15.00

silicate) was not enhanced by an increase in the reaction time (Table 8). With a reaction time of 3 hours, pulp bleached in the presence of silicate developed a brightness of 57.2, while in the absence of silicate, the brightness developed was 60.8.

Residuals of hydrogen peroxide were higher when sodium silicate was used in

Table 7

Hydrogen Peroxide Bleaching With and Without Sodium Silicate

Run #	NaOH,%	Temp, °C	MgSO ₄ ,%	Na ₂ SiO ₃ ,%	Response Values	
					Brightness,%	Viscosity,cp
1	1.0	55	0.05	-	59.8	15.28
2	1.0	55	0.05	2	55.5	17.04
3	1.5	55	0.05	-	60.8	14.69
4	1.5	55	0.05	1.5	54.8	16.16
5	1.0	75	0.05	-	63.4	15.04
6	1.0	75	0.05	2	60.3	16.47
7	1.5	75	0.05	-	65.6	14.06
8	1.5	75	0.05	1.5	61.5	17.52

peroxide bleaching (Table 9). The above experiments confirm that the presence of sodium silicate decreases the decomposition rate of hydrogen peroxide. That can be an answer for having a higher viscosity in the presence of sodium silicate in peroxide bleaching, which is presented in Table 7.

More studies need to be done in this area to define the behavior of sodium silicate in hydrogen peroxide bleaching. The viscosity variations in different pulps did not have a significant effect on paper properties (Table 10). Then, in the second order

Table 8

The Effect of Reaction Time on Hydrogen Peroxide Bleaching
With and Without Sodium Silicate

Bleaching Conditions						
Run #	Reaction Time,hr	Na ₂ SiO ₃ ,%	NaOH,%	MgSO ₄ ,%	Temp, °C	Brightness, %
1	4.0	-	1.5	0.05	55	62.0
2	4.0	2	1.5	0.05	55	58.4
3	3.5	-	1.5	0.05	55	61.0
4	3.5	2	1.5	0.05	55	58.2
5	3.0	-	1.5	0.05	55	60.8
6	3.0	2	1.5	0.05	55	57.2
7	2.5	-	1.5	0.05	55	60.1
8	2.5	2	1.5	0.05	55	57.3

experiments, silicate was not used. Since the first order fit was not sufficient, both temperature and sodium hydroxide concentration had an effect on brightness; the second order design was implemented with a center point of 1.5% for sodium hydroxide and a temperature of 65 °C. A higher temperature would have proved beneficial, but it was not possible to maintain it. ANOVA tables for brightness and viscosity for the second-order model are shown in Appendix A (Tables 3 and 4). The ANOVA table (Table 3) for brightness shows a significant curvature to confirm the second order model for

Table 9
Peroxide Residuals With and Without Sodium Silicate

Conditions for Bleaching					
Run #	Na ₂ SiO ₃ , %	NaOH, %	MgSO ₄ , %	Temperature, °C	H ₂ O ₂ Residuals as % of applied
1	2.0	1.5	0.05	55	0.860
2	-	1.5	0.05	55	0.452

brightness. The ANOVA table (Table 4) for viscosity shows that curvature and main effects are not significant in the second order model for viscosity.

Therefore, the central composite design procedure was applied to fit the second order model with the use of additional axial points to the model. Also, this design was used to locate the stationary point. Central composite runs (12-25) are presented in Table 11.

Estimated regression coefficients for brightness and viscosity in the central composite design showed that the blocking and temperature are significant (Tables 5 and 7; Appendix A). Blocking has been done based on lengthy time requirements for running experiments. Also, the interaction between temperature and sodium hydroxide concentration is a significant factor with respect to viscosity.

R^2 is loosely interpreted as the proportion of the variability in the data explained

Table 10

Comparison of Physical Properties of Bleached Pulps

Effects of Viscosity Change on Physical Properties					
Bleaching	Hydrogen peroxide	Hydrogen peroxide	Hydrogen peroxide	DMD	DMD
Experimental Condition	1.75% NaOH 70°C	1.75% NaOH 55°C	1.75% NaOH 55°C	5% AO 55°C Buffer/AO 9 mol	7% AO 55°C Buffer/AO 10 mol
Viscosity, cp	13.51	14.91	15.89	9.67	6.43
Tensile Index, N.m/g	24.2	27.1	27.7	31.6	25.3
Tear Index, mN.m ₂ /g	8.6	8.0	8.2	8.7	8.6
Burst Index, Kpa.m ₂ /g	4.1	3.2	3.8	4.4	4.5
Brightness	62.9	58.7	59.3	72.8	71.9

Table 11
Central Composite Design Runs for Peroxide Bleaching

Experimental Variables			Response Variables	
12	1.25	55	59.5	14.16
13	1.75	55	58.6	15.82
14	1.25	75	61.9	14.89
15	1.75	75	63.0	13.87
16	1.50	65	62.2	15.26
17	1.50	65	62.0	13.84
18	1.50	65	62.3	14.97
19	1.46	65	60.7	14.47
20	1.53	65	60.9	13.69
21	1.5	50.9	57.6	14.6
22	1.5	79.1	63.4	12.61
23	1.5	65	60.5	14.38
24	1.5	65	60.3	14.56
25	1.5	65	60.5	13.56

by the analysis of variance model ($R^2 = SS_{\text{Model}} / SS_{\text{Total}}$). Therefore, R^2 values of 70.5% for viscosity (Appendix A, Table 7) and 92.5% for brightness (Appendix A, Table 5) confirm that a second order model is adequate. A fitted model can be used to find the optimum set of operating conditions and to characterize the nature of the response surface. To determine the optimum set of operating conditions, the contour plots for brightness and viscosity were used. To characterize the stationary point as a maximum, minimum response, or a saddle point, the relative sensitivity of the responses to the variables, the canonical form of the model was used. The canonical transformation of the model is done by transforming the original model into a new coordinate system, with the origin at the stationary point, and then rotating the axes of this system until they are parallel to the principal axes of the fitted response surface. W_1 and w_2 are transformed independent variables. The coefficients of transformed variables are the eigenvalues. Magnitudes of eigenvalues identify directions in which the estimated mean response is more sensitive. The transformed response equation for brightness is shown below:

$$\text{Brightness, \%} = 68.99 - 0.5738w_1^2 - 0.03617w_2^2$$

Since the eigenvalues (-0.5738, -0.03617) are the negative terms, the response shape shows a maximum point of brightness. The magnitude of the eigenvalues shows that the sensitivity of the brightness to alkalinity is higher than temperature in peroxide bleaching. Since the coefficients of the transformed variables (-0.4377, 0.273) have different signs, the shape of the response shows a saddle point for viscosity, and the viscosity value is more sensitive to the temperature in peroxide bleaching than sodium hydroxide

concentration.

Contour plots for brightness and viscosity (Figures 7 and 8) were used to determine the stationary point. High temperatures showed the drop in viscosity and high sodium hydroxide concentration effected on the brightness drop. Both low temperatures and sodium hydroxide concentration effected the brightness drop. To maintain the best possible viscosity and brightness, optimized conditions for hydrogen peroxide were set

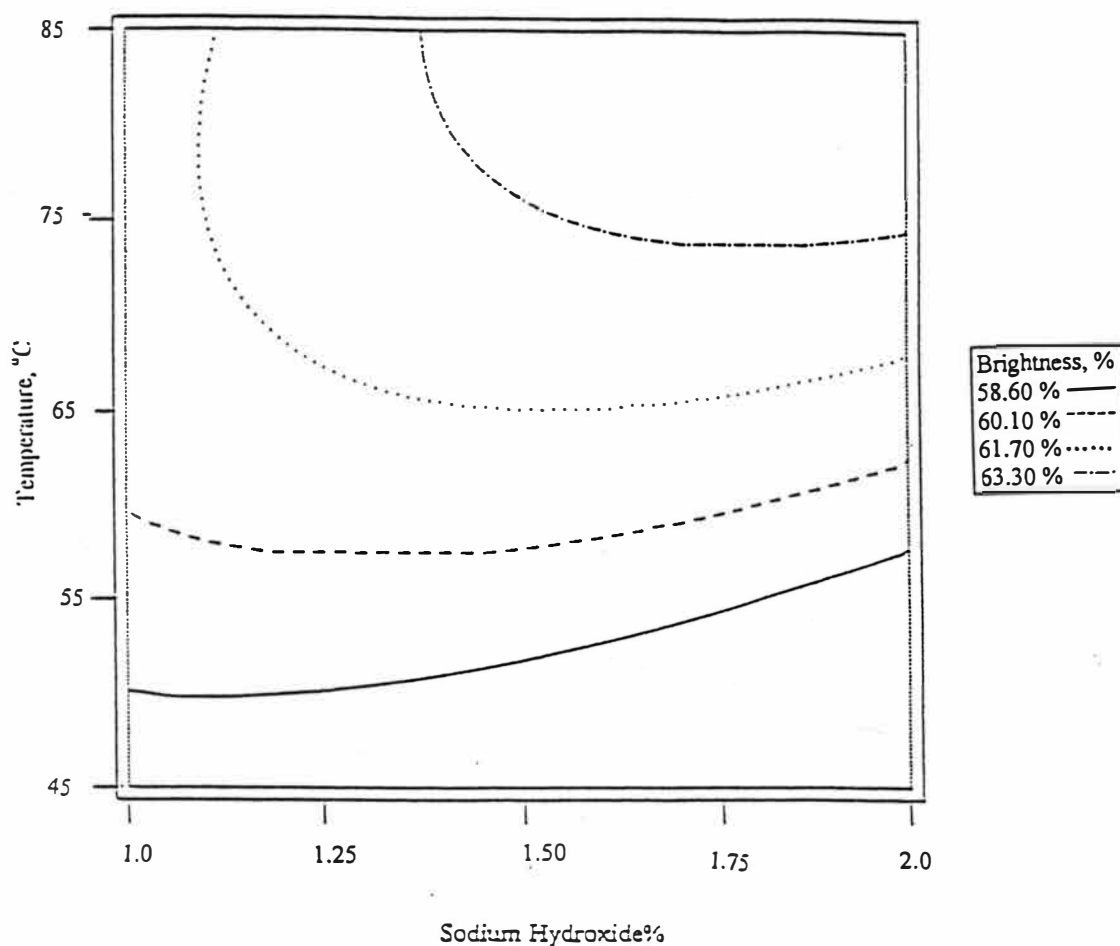


Figure 7. Effect of Alkali Concentration and Temperature on Brightness in Peroxide Bleaching.

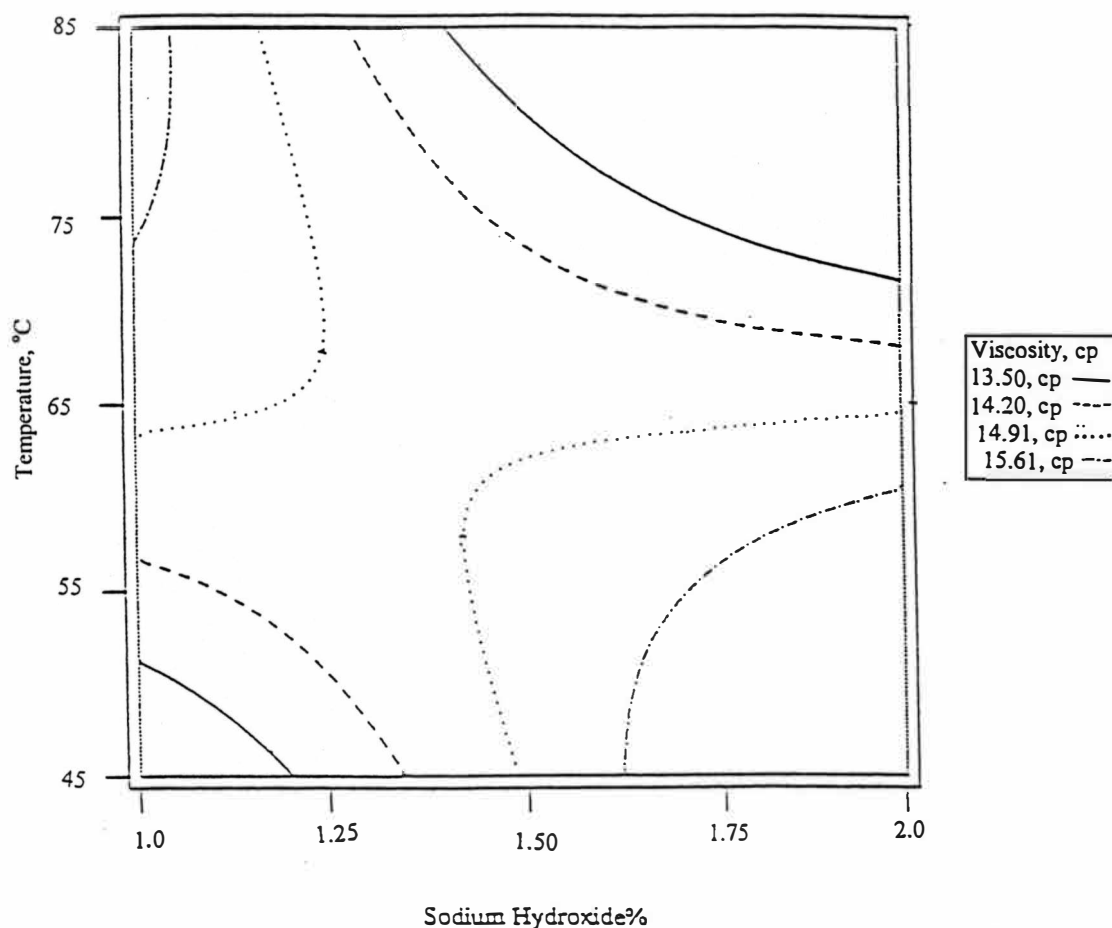


Figure 8. Effect of Alkali Concentration and Temperature on Viscosity in Peroxide Bleaching.

as shown in Table 12.

Optimization of Dimethyldioxirane Bleaching

The oxygen delignified hardwood kraft pulp (with a kappa number of 8.8, viscosity of 18.5, and brightness of 45.3) was chelated with 0.5% EDTA at pH 5.5 prior to the DMD bleaching stage for one hour at room temperature.

Table 12
Optimized Conditions for Hydrogen Peroxide Bleaching

NaOH, %	Na ₂ SiO ₃ , %	MgSO ₄ , %	Temperature, °C
1.5	0	0.05	65

The initial experiments for optimization of DMD bleaching were run to find a suitable relationship between response and control variables.

Optimization of process variables was done with respect to brightness and viscosity. Levels of control variables for the initial experiments are presented in Table 13.

The initial experiments with three replicates at the center point were conducted at 5% consistency, pH 7.0-7.8, for one hour reaction time. These runs are presented in Table 14.

Table 13
Variable Levels for DMD Bleaching

Control Levels		
Variables	High Levels	Low Levels
Temperature, °C	45	25
Activated oxygen, %	5	1
Buffer/Activated oxygen, mol	9	7

Table 14

First Order Design Runs for Optimization of DMD Bleaching

Run #	AO, % (A)	Buffer/AO, Mol, (B)	Temperature, °C (T)	Response Values	
				Brightness, %	Viscosity, cp
1	1	7	25	59.29	16.64
2	5	7	25	72.32	13.29
3	1	9	25	60.11	15.38
4	5	9	25	72.78	12.90
5	1	7	45	63.50	15.15
6	5	7	45	74.51	11.94
7	1	9	45	73.26	10.32
8	5	9	45	73.26	10.32
9	3	8	35	70.44	12.08
10	3	8	35	72.97	12.50
11	3	8	35	72.36	12.30

Analysis of variance (Appendix B, Tables 2 and 4) revealed that the curvature and the main effect were significant with respect to both brightness and viscosity. The regression equations for the first order model are shown below:

$$\text{Brightness, \%} = 51.5 + 2.0 A - 0.03B + 0.1T + 0.27AB + 0.062AT + 0.019BT - 0.0124ABT$$

$$(R^2 = 86.1\%, R^2 (\text{adj.}) = 53.6\%)$$

$$\text{Viscosity} = 16.9 - 1.24A + 0.32B + 0.223T + 0.05AB - 0.015AT + 0.0429BT + 0.0024ABT$$

$$(R^2 = 90.6\%, R^2 (\text{adj.}) = 68.6\%)$$

The first order regression model for brightness shows that the effects of activated oxygen (A) and temperature (T) are more significant than buffer concentration and the above regression model for viscosity is more sensitive to the activated oxygen (A) and buffer (B) concentration than temperature.

The ANOVA of the first order model for brightness and viscosity (Appendix B, Tables 2 and 4) shows a significant curvature for them. The new center point was chosen (5% AO, 9 mole ratio of buffer to activated oxygen, and 45°C) to prove the second order model. ANOVA for brightness and viscosity is shown in Appendix B (Tables 5 and 6) for the second order model. Three-way interactions, main effects, and curvature are significant for viscosity in the second order model. Curvature value for brightness identifies that the brightness is a saddle point.

Central composite design was applied to fit the second order by adding axial points and center points to the model. Also, this design was used to locate the stationary point. Central composite design runs (12-29) are presented in Table 15.

The ANOVA tables for brightness and viscosity in central composite design are shown in Appendix B (Tables 7 and 8). Lack of fit values confirm that the second order model fits well for both brightness and viscosity. Also, the R^2 values of 83.3% for

Table 15

Central Composite Design Runs for DMD Bleaching

Run #	AO, % (A)	Buffer/AO, Mol, (B)	Temperature, °C (T)	Response Values	
				Brightness, %	Viscosity, cp
12	5	9	45	72.9	11.00
13	5	9	45	72.3	11.23
14	5	9	45	72.8	11.90
15	5	9	45	73.0	11.47
16	3	8	35	72.2	12.57
17	7	8	35	73.6	13.67
18	3	10	35	72.9	14.07
19	7	10	35	72.5	10.49
20	3	8	55	73.0	12.98
21	7	8	55	72.1	10.53
22	3	10	55	72.4	12.51
23	7	10	55	72.5	10.69
24	8.36	9	45	72.4	11.51
25	1.63	9	45	71.0	15.02
26	5	10.44	45	71.9	13.64

Table 15–Continued

Run #	AO, % (A)	Buffer/AO, Mol, (B)	Temperature, °C (T)	Response Values	
				Brightness, %	Viscosity, cp
27	5	7.56	45	73.0	12.57
28	5	9	59.4	72.4	9.58
29	5	9	30.6	72.2	14.25
30	5	9	45	73.0	15.10
31	5	9	45	73.0	14.45

viscosity and 80.1% for brightness confirmed the adequacy of regression models (Appendix B, Tables 9 and 10). Estimated regression coefficients for viscosity and brightness in central composite design show that the activated oxygen and temperature are significant in first (A, T) and second order (A^2 , T^2), respectively.

Since the eigenvalues (0.0131, 0.233, 0.772) for viscosity have positive signs, the response -shape is a minimum for viscosity. The signs of the eigenvalues (-0.332, -0.050, 0.610) for brightness are different; thus, the response shape is a saddle point for brightness.

Canonical analysis with respect to brightness determined the values for the stationary points at 4.89% AO, 9.19 mole ratio for buffer/AO, and 55°C. With respect

to viscosity, the stationary points are at 5.356% AO, 8.09 mole ratio for buffer/AO, and 50°C.

To pinpoint the optimum conditions, runs 32-38 were performed around the optimum conditions (Table 16). Brightness values did not change significantly, but a severe viscosity drop is indicated at runs 32, 33, and 34. This can be due to higher temperatures.

Referred to contour plots (Figures 9-14) for viscosity and brightness, optimum conditions were determined as 4.78 AO% mole ratio for buffer/AO, and 30°C. These conditions resulted in a viscosity of 12.60 cp and brightness of 74.50%.

Table 16
Final Optimization Runs for DMD Bleaching

Run #	AO, % (A)	Buffer/AO, Mol, (B)	Temperature, °C (T)	Brightness, %	Viscosity, cp
32	4.89	9.19	55	72.1	6.09
33	4.89	9.19	55	72.1	6.70
34	5.32	8.09	60	72.3	5.02
35	4.72	9.03	43	71.7	12.87
36	6.5	10	53	72.5	13.68
37	8.0	10.5	63	71.2	7.87

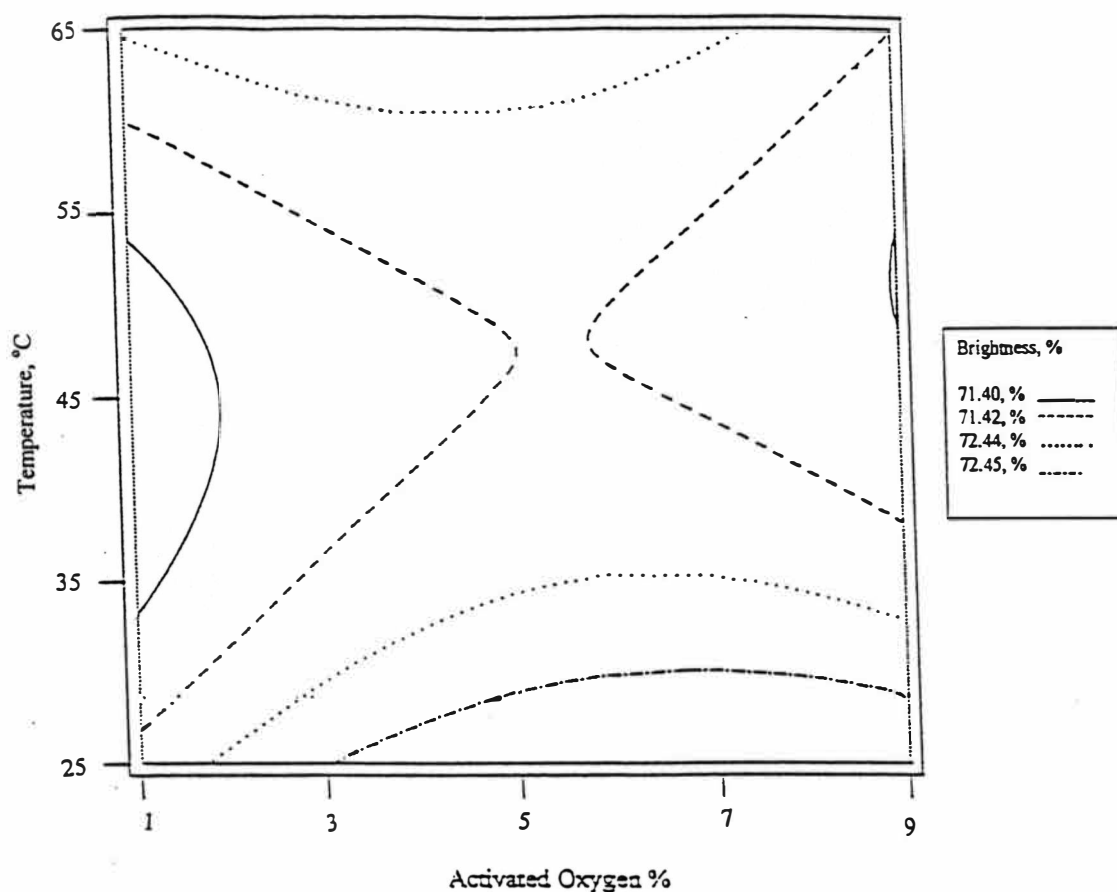


Figure 9. Effect of Temperature and Activated Oxygen % on Brightness in DMD Bleaching.

Final Bleaching Sequences

Pulps were bleached with two bleaching sequences OQAP and OQPA. The optimized conditions of 1.5% NaOH and 65°C were used for the peroxide bleaching stage and 4.78% AO, 8.89% mole ratio for buffer/AO, and 30°C for DMD bleaching stage. The pulps were tested for different paper properties (tensile, tear, burst) and fiber composition (lignin, pentosan; α , β , γ cellulose). The bleaching effluents were tested for

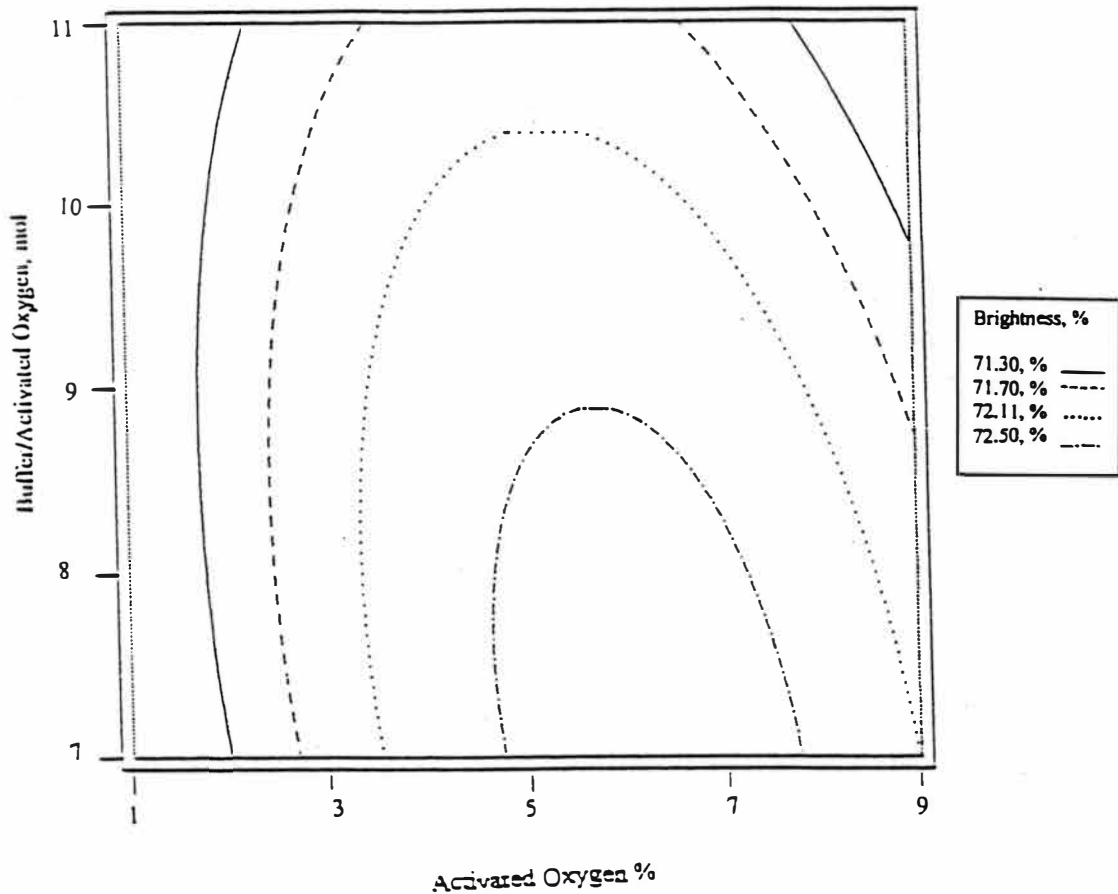


Figure 10. Effect of Buffer and Activated Oxygen on Brightness in DMD Bleaching.

COD, BOD, and TOC. The corresponding results are presented as shown in Tables 17 and 18.

ANOVA was used to compare the effect of the two bleaching sequences (OQAP and OQPA). Comparing $MS_{\text{treatment}}$ and MS_{Error} , one can perform a test of the hypothesis of no difference in treatment means. Therefore, if the null hypothesis of no difference in treatment means is true, the ratio $F_0 = (SS_{\text{treatment}}/a-1)/(SS_{\text{Error}}/N-a) = MS_{\text{treatment}}/MS_{\text{Error}}$ is distributed as F with $a-1$ and $N-a$ degrees of freedom. If the null hypothesis is false, then

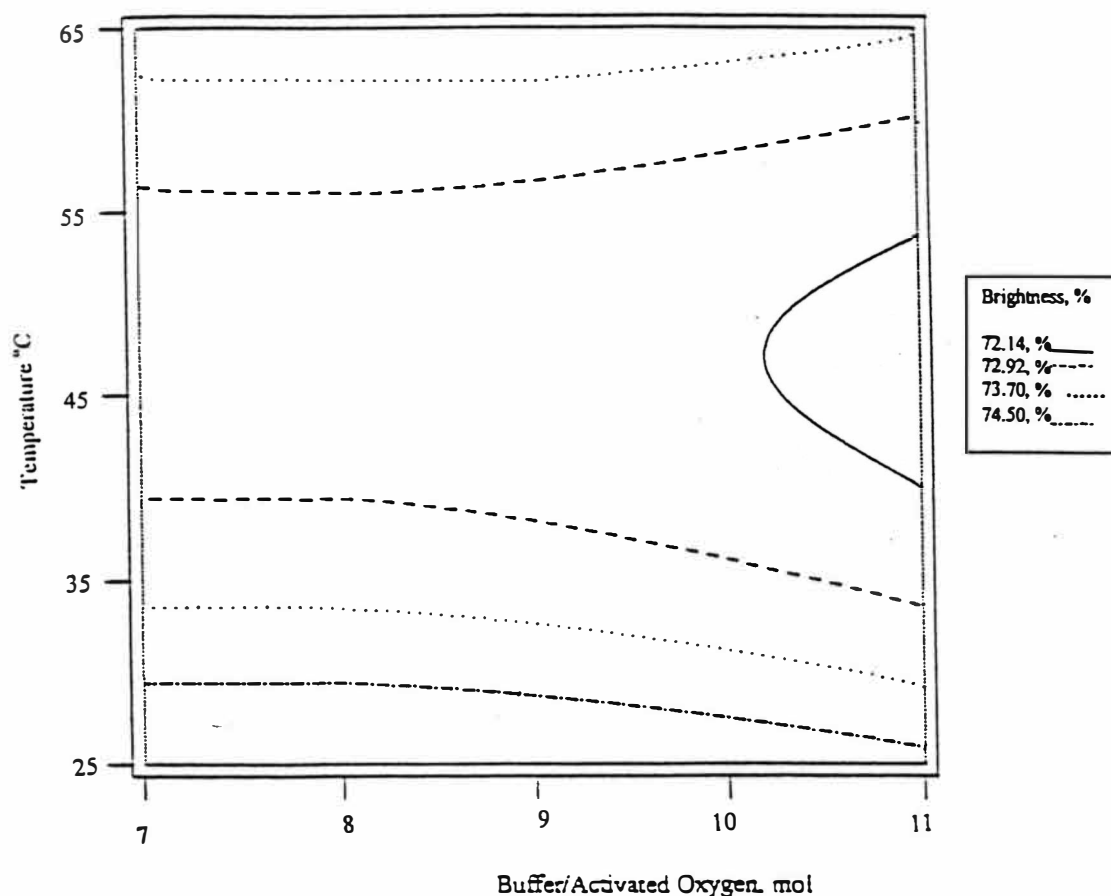


Figure 11. Effect of Temperature and Buffer on Brightness in DMD Bleaching.

the expected value of $MS_{\text{treatment}}$ is greater than σ^2 . Then, the null hypothesis will be rejected, and it can be concluded that the treatment means are different. The fiber composition variables are alpha, beta, and gamma celluloses; pentosan; and lignin. Paper properties are tensile, tear, and burst indices. Effluent characteristics are BOD, COD, and TOC. The ANOVA tables for the evaluation of two bleaching sequences for the above properties of OQAP and OQPA are used.

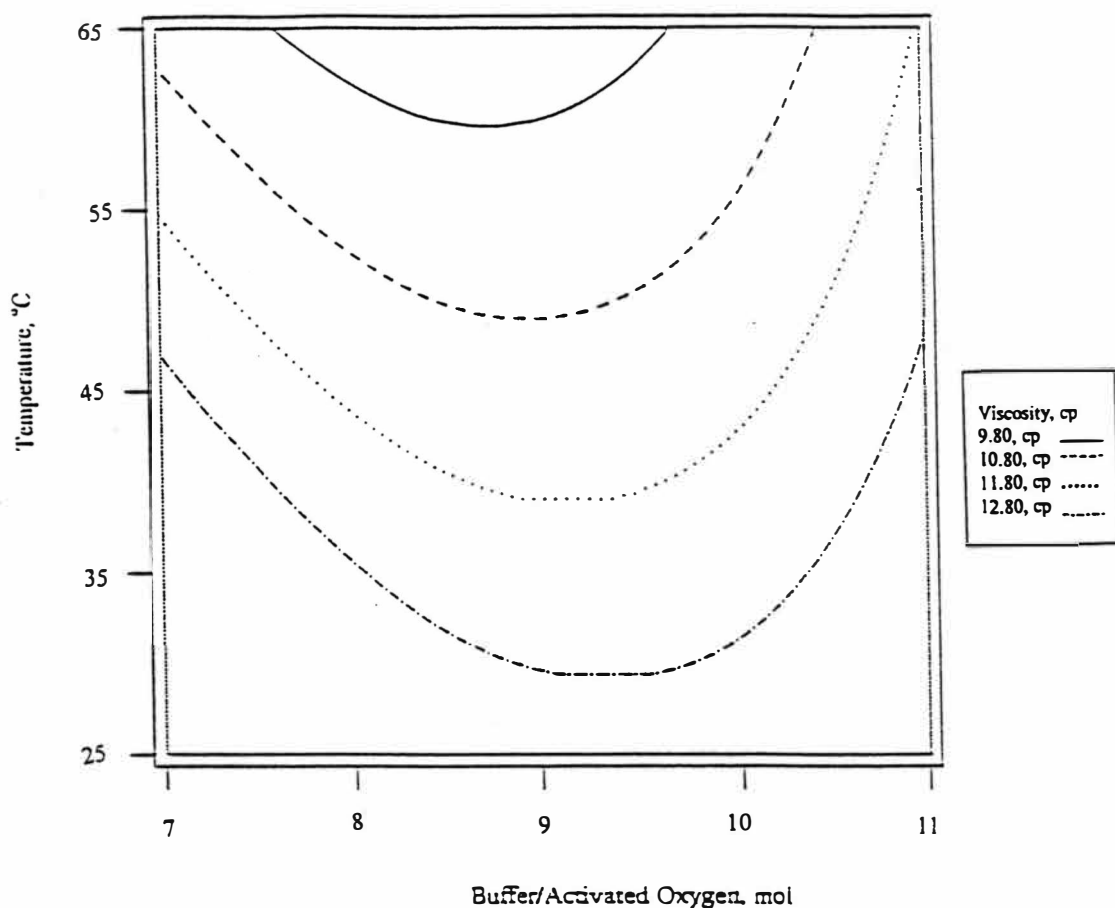


Figure 12. Effect of Buffer and Temperature on Viscosity in DMD Bleaching.

Kappa Number, Brightness, Viscosity

The results of kappa number, brightness, and viscosity were statistically evaluated. The ANOVA tables are presented in Tables 19-21.

As seen from Table 19, there is no difference in kappa numbers in bleached pulps with OQAP and OQPA sequences. Placing the DMD before or after peroxide did not show any difference in lignin removal in these experiments.

ANOVA for brightness of bleached pulp (Table 20) shows that the higher

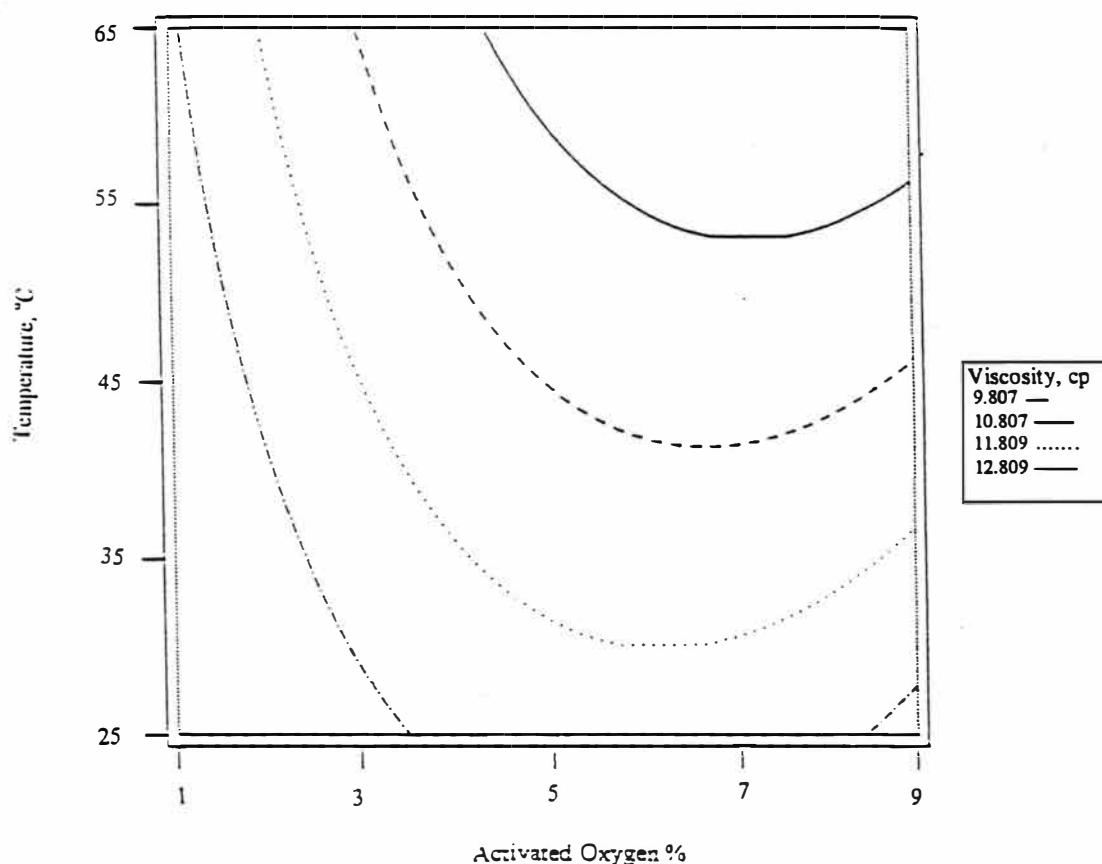


Figure 13. Effect of Temperature and Activated Oxygen on Viscosity in DMD Bleaching.

brightness value for OQAP bleached pulp is significant when compared to that of OQPA bleached pulp. Placing the DMD before peroxide is more effective on final brightness due to delignification and conditioning of the remaining lignin which makes it more responsive to hydrogen peroxide. In addition, chromophores introduced during the DMD treatment are susceptible to removal or modification by hydrogen peroxide. A large F value and low P value (0.027) for treatment is indicative of this difference in brightness.

ANOVA for viscosity (Table 21) confirmed that the bleached pulp with OQAP

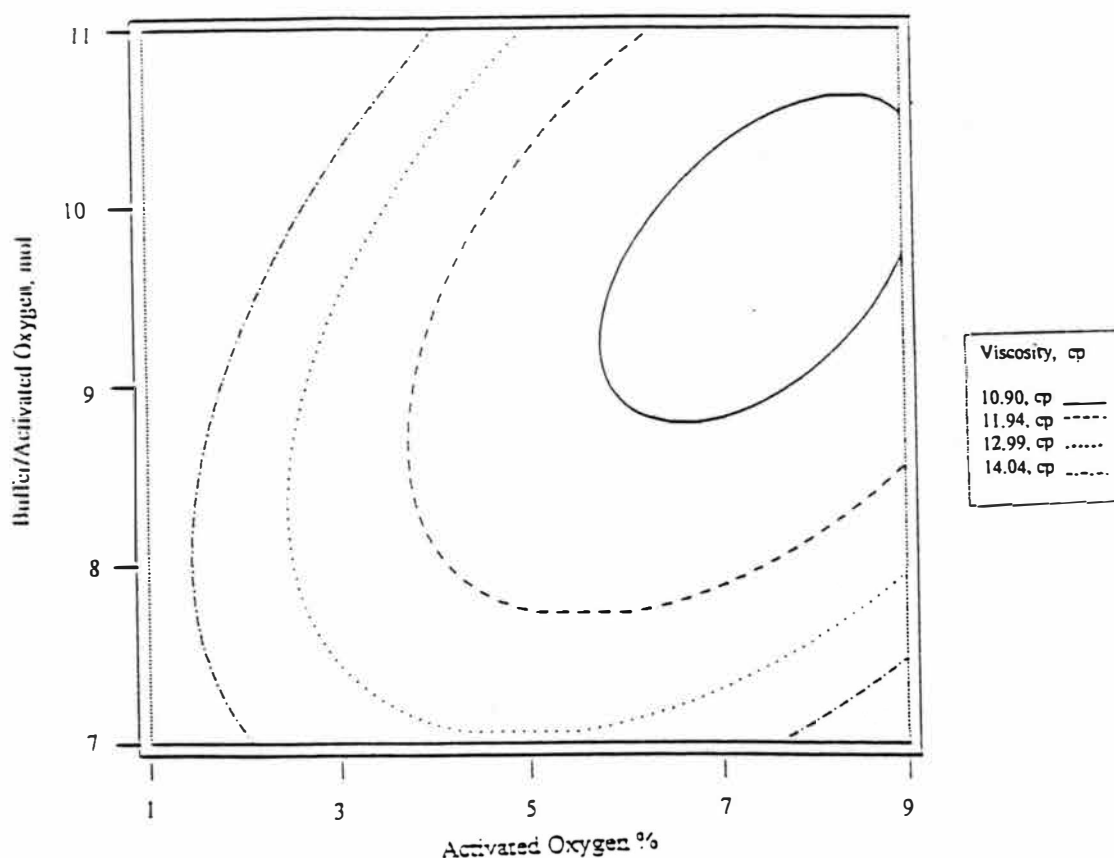


Figure 14. Effect of Buffer and Activated Oxygen on Viscosity in DMD Bleaching.

brightness value for OQAP bleached pulp is significant when compared to that of OQPA bleached pulp. Placing the DMD before peroxide is more effective on final brightness due to delignification and conditioning of the remaining lignin which makes it more responsive to hydrogen peroxide. In addition, chromophores introduced during the DMD treatment are susceptible to removal or modification by hydrogen peroxide. A large F value and low P value (0.027) for treatment is indicative of this difference in brightness.

ANOVA for viscosity (Table 21) confirmed that the bleached pulp with OQAP has slightly higher viscosity compared to the bleached pulp with OQPA. Placing the

Table 17

Effluent Quality for OQAP and OQPA Bleaching

Bleaching Sequences	OQAP Sequence			OQPA Sequence		
Effluent Characteristics	A Stage	P Stage	Total	P Stage	A Stage	Total
COD (Kg/ton)	43.2	12	55.2	8.6	54.1	62.7
BOD (Kg/ton)	3.4	5.17	8.31	2.1	2.2	4.3
TOC (Kg/ton)	3.46	1.53	4.99	2.40	3.15	5.55

DMD stage before the hydrogen peroxide is found to be more useful. The result is significant at the 5% level.

Alpha, Beta, Gamma Celluloses and Pentosans

ANOVA for cellulose and hemicellulose content of the bleached pulps with OQAP and OQPA are presented in the following tables.

ANOVA for alpha cellulose (Table 22) confirmed that both the bleaching sequences led to the same alpha cellulose content. The ANOVA (Tables 23 and 24) shows that the F value is high for both beta and gamma cellulose. They are not statistically at a high level (P values of 0.19 and 0.15). OQAP has lower beta cellulose and higher gamma cellulose than OQAP bleached pulp, with the OQAP sequence containing higher gamma cellulose (Table 24) than OQPA bleached pulp. Beta cellulose

Table 18
Final Testing Results for Bleached Pulps

Bleaching Sequences		
Properties	OQPA Sequence	OQAP Sequence
Kappa number	1.65 ± 0.52*	1.59 ± 0.24
Brightness, %	80 ± 0.056	83.8 ± 0.40
Viscosity, cp	8.48 ± 0.34	9.59 ± 0.58
Alpha Cellulose, %	94.03 ± 0.67	93.97 ± 1.02
Beta Cellulose, %	5.42 ± 0.61	5.01 ± 1.47
Gamma Cellulose, %	0.55 ± 0.22	1.03 ± 0.68
Pentosan, %	2.32 ± 0.25	2.6 ± 0.2
Tensile Index (N.m/g)	25.2 ± 0.78	23.2 ± 1.2
Tear Index (mN.m ² /g)	9.50 ± 0.37	8.2 ± 0.42
Burst Index kpa.m ² /g)	3.0 ± 0.38	3.72 ± 0.17

*2σ limits for mean ($2\sigma/\sqrt{n}$) where n is sample size

indicates a degraded cellulose. Gamma cellulose indicates the amount of hemicellulose.

The effects of the bleaching sequences is not the same on pentosan content of the bleached pulps (Table 25). The F value for treatment is significant. Hardwood hemicellulose consists mainly of pentosans (19-25%). The two bleaching sequences had

Table 19
ANOVA Table for Kappa Number

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatments	1	0.022	0.022	0.076	0.83
Batch	1	0.053	0.053	0.18	0.75
Error	1	0.288	0.288		
Total	3	0.362			

Table 20
ANOVA Table for Brightness

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	15.1321	15.1321	523.53	0.027
Batch	1	0.0484	0.0484	1.67	0.42
Error	1	0.0289	0.0289		
Total	3	15.2094			

Table 21
ANOVA Table for Viscosity

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	1.2321	1.2321	85.56	0.068
Batch	1	0.2116	0.2116	14.69	0.16
Error	1	0.0144	0.0144		
Total	3	1.4581			

Table 22
ANOVA Table for Alpha Cellulose

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	0.005	0.005	0.022	0.90
Batch	1	0.09	0.09	0.4	0.64
Error	1	0.221	0.221		
Total	3	0.316			

Table 23
ANOVA Table for Beta Cellulose

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	0.7569	0.7569	10.38	0.19
Batch	1	0.0441	0.0441	0.6	0.58
Error	1	0.0729	0.0729		
Total	3	0.8739			

Table 24
ANOVA Table for Gamma Cellulose

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	0.6642	0.6642	17.47	0.15
Batch	1	0.2550	0.2550	6.71	0.23
Error	1	0.038	0.038		
Total	3	0.9573			

Table 25
ANOVA Table for Pentosan

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	0.0756	0.0756	126	0.057
Batch	1	0.0506	0.0506	84.3	0.07
Error	1	0.0006	0.0006		
Total	3	0.1268			

different effects on pentosan content of the pulp, with OQAP giving a higher pentosan content.

Strength Properties of Handsheets

The following ANOVA tables are provided for the paper properties of the bleached pulps.

The ANOVA (Tables 26 and 27) for tensile and tear index shows the two bleaching sequences had the same effect on tensile and tear strength of the paper. ANOVA (Table 28) confirmed that there is significant effect on burst strength under different bleaching sequences in this experiment.

Although the statistical analysis shows no difference in tear and tensile from

Table 26
ANOVA Table for Tensile Strength

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	1.6	1.6	10.2	0.194
Batch	1	0.001	0.001	0.0064	0.95
Error	1	0.159	0.156		
Total	3	1.757			

Table 27
ANOVA Table for Tear Index

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	3.98	3.98	2.04	0.39
Batch	1	0.02	0.02	0.012	0.93
Error	1	1.95	1.95		
Total	3	5.95			

Table 28
ANOVA Table for Burst Index

Analysis of Variances					
Sources	DF	SS	MS	F	P
Treatment	1	0.4692	0.4692	42.6	0.10
Batch	1	0.0756	0.0756	6.87	0.23
Error	1	0.0110	0.0110		
Total	3	0.5559			

different bleaching sequences, Figure 15 shows that the OQPA bleached pulp shows higher tensile and tear values compared to OQAP bleaching sequences. More experiments need to be done to prove the effect of the two bleaching sequences on tear and tensile.

As a result of the above analysis, the properties that are statistically significant are shown in Table 29.

Referring to this table, the OQAP bleaching sequence is significantly better in producing higher brightness, viscosity, burst strength, and pentosan content.

BOD, COD, and TOC

Effluents were tested for BOD, COD, and TOC for each stage of both bleaching

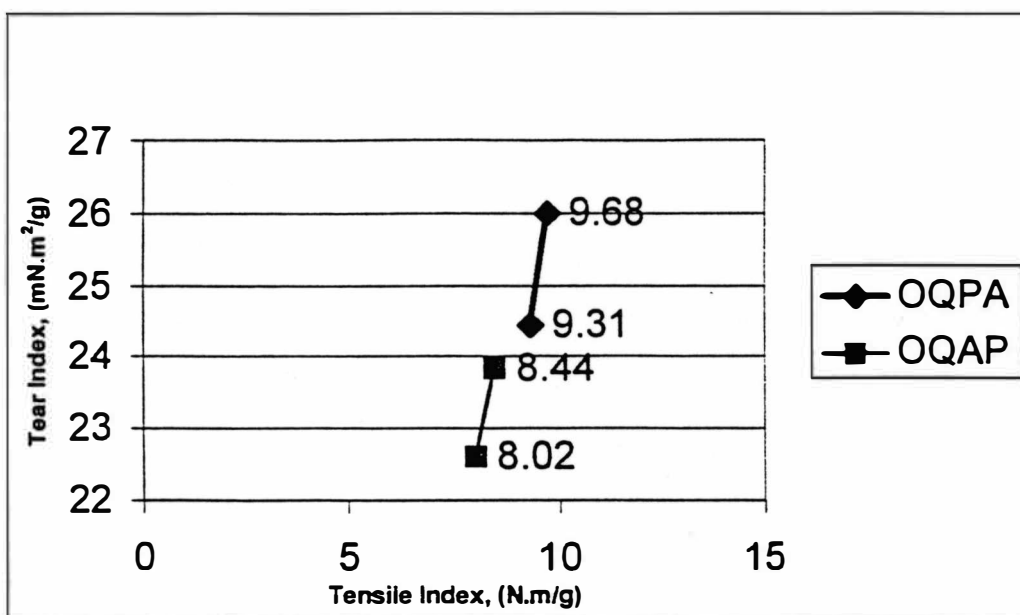


Figure 15. Tear-Tensile Curves for the Two Bleaching Sequences.

Table 29

Statistically Significant Values for the Bleaching Sequences

Property	OQPA	OQAP	Significant Value (P Value)
Brightness, %	80 ± 0.056	$83.8 \pm 0.40^*$	0.27
Viscosity, cp	8.48 ± 0.34	$9.59 \pm 0.58^*$	0.068
Burst Index, Kpa.m ² /g	3.0 ± 0.38	$3.72 \pm 0.17^*$	0.10
Pentosan, %	2.32 ± 0.25	$2.6 \pm 0.2^*$	0.057

sequences (Table 17). The OQPA bleaching sequence resulted in higher COD, but lower BOD, than OQAP.

However, the BOD values are always smaller than the COD values, because more compounds can be chemically oxidized than biologically oxidized.

TOC is another measure of organic matter present in water. The organic carbon in the presence of high temperature and catalyst oxidizes to carbon dioxide. Acidification of the sample prior to analysis eliminates errors due to the presence of inorganic carbon. Certain resistant organic compounds may not be oxidized, however. Hence, the measured TOC is slightly less than the actual amount.

Higher amounts of hydrocarbons in the bleaching effluents increase COD and BOD. Increasing the lignin content of the bleaching effluents can increase COD. Since the lignin removal of the bleached pulp was the same in both bleaching sequences, the hydrocarbons content of the bleaching effluents are contributing to the differences in BOD and COD between OQAP and OQPA effluents.

The wastewater treatment process depends on the following factors: characteristics of the wastewater, percentage of suspended solids, pH, presence of toxicity, required effluent quality, cost, and variability of land. The types of primary treatments for wastewater are screening, sedimentation, flotation, and neutralization. Effluents after primary treatment are discharged into either a receiving body of water or a secondary treatment facility. Secondary treatment includes all biological treatment processes of wastewater, both aerobic and anaerobic. Before the final stage of disposal,

the sludge needs to be thickened and dewatered. Two methods of disposal are employed for the sludge. One is land disposal and the other is incineration, which is the more frequently employed method of disposal (17).

The approach for TCF bleaching in the future depends on finding the most economical way of recycling organic discharges and how restrictive the regulations will become on chloro-organic discharges. Therefore, the treatment cost for organic discharges of OQPA and OQAP effluents should be considered for evaluating these two bleaching sequences.

CHAPTER VI

CONCLUSIONS

TCF bleaching sequences, OQAP and OQPA, were studied for different properties. In this study, both bleaching sequences resulted in a brightness above 80 with comparable paper properties. But the brightness for these TCF bleaching sequences is lower when compared to conventional bleaching.

Statistical analysis shows that the OQAP bleaching sequence gives significantly higher brightness, viscosity, burst strength, and pentosan content than OQPA. But there is no difference in tear and tensile for these bleaching sequences.

Comparison of fiber composition, for OQAP and OQPA bleached pulps, led to the same alpha cellulose content, less beta cellulose content, and higher gamma cellulose content for OQAP as compared to OQPA.

Examination of the bleaching effluents shows that the OQPA bleaching sequence resulted in a higher COD than OQAP. But the OQAP bleaching sequence has a higher BOD than the OQPA sequence.

It can be concluded that placing the DMD before (OQAP) or after peroxide (OQPA) does not show any difference in lignin removal. But it was more effective on final brightness and viscosity when DMD was placed before peroxide (OQAP).

CHAPTER VII

SUGGESTIONS FOR FUTURE STUDY

It is suggested that further study be directed to evaluating the OQAP and OQPA bleaching sequences, with the same conditions as in this study, in regards to the possibility of the recovery of the chemicals and the cost of effluent treatments. It is also suggested that the results of these TCF bleachings be compared to conventional bleaching sequences.

Although ANOVA shows the same tear and tensile indices for OQAP and OQPA bleached pulps, but the correlation of tensile-tear on the graph for those bleached pulps do not follow the same conclusion. More studies need to be done comparing tear and tensile indices for those bleached pulps. The experiments can be repeated with the same conditions used in this study.

The effect of sodium silicate in providing a higher brightness was claimed in previous studies. In this research the effect of sodium silicate was contrary to the results reported in earlier literature. The effect of sodium silicate on brightness might change with the type of the pulp. It is suggested that more studies be done in this area to define the behavior of sodium silicate in hydrogen peroxide with the use of different chemical and mechanical hardwood pulps. The experiments can be designed for three peroxide levels (1%, 2%, 4% on O.D. pulps.), six silicate levels (1%, 2%, 4%, 8%, and 16%) and two Epson salts (0% and 0.05%).

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Appendix A

Statistical Data for Optimization of Peroxide Bleaching With the Use of RSM

Table 1
Analysis of Variance in First-order Model for Brightness

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	76.9209	76.9209	25.6403	12.12	0.035
2-way	3	0.2796	0.2796	0.0932	0.04	0.985
Interaction						
3-way	1	0.1891	0.1891	0.1891	0.09	0.784
Interaction						
Residual Error	3	6.3452	6.3452	2.1151		
Curvature	1	6.0697	6.0697	6.0697	44.07	
Pure Error	2	0.2755	0.2755	0.1377		
Total	10	83.7348				

Table 2
Analysis of Variance for Viscosity in First-order model

Source	DF	Seq SS	AdjSS	AdjMS	F	P
Main Effects	3	0.6134	0.6134	0.2045	0.08	0.964
2-Way Interactions	3	2.5227	2.5227	0.8409	0.35	0.796

Table 2- Continued

Source	DF	Seq SS	AdjSS	AdjMS	F	P
<u>3</u> -Way Interactions	1	0.2520	0.2520	0.2520	0.10	0.768
Residuals Error	3	7.2529	7.2529	2.4176		
Curvature	1	6.2376	6.2376	6.2376	12.29	0.073
Pure Error	2	1.0153	1.0153	0.5076		
Total	10	10.6411				

Table 3

Analysis of Variance for Brightness in Second-order model

Source	DF	Seq SS	AdjSS	AdjMS	F	P
Main Effects	2	11.396	11.40	5.70	4.77	0.12
2-Way Interactions	1	1.05	1.05	1.05	0.88	0.41
Residuals Error	3	3.60	3.60	1.20		
Curvature	1	3.50	3.50	3.50	95.8	0.01
Pure Error	2	0.07	0.07	0.036		
Total	6	16.03				

Table 4

Analysis of Variance for Viscosity in Second-order model

Source	DF	Seq SS	AdjSS	AdjMS	F	P
Main Effects	2	0.47450	0.47450	0.23725	0.63	0.590
2-Way Interactions	1	1.79560	1.79560	1.79560	4.78	0.117
Residual Error	3	1.12584	1.12584	0.37528		
Curvature	1	0.00004	0.0004	0.0004	0.0	0.994
Pure Error	2	1.12580	1.12580	0.56290		
Total	6	3.39594				

Table 5

Estimated Regression Coefficient for Brightness in Central Composite Design

Term	Coef.	Stdev	T-ratio	P
Constant	61.3100	0.2522	243.098	0.00
Block	0.4143	0.1651	2.509	0.04
S	0.0541	0.2184	0.248	0.811
T	1.8708	0.2184	8.565	0.00
S*S	-0.2237	0.2237	-0.984	0.358
T*T	-0.3862	0.2273	-1.699	0.133
S*T	0.5125	0.3089	1.659	0.141
S=0.6178 R-sq=92.5% R-sq(adj)=86.0%				

Table 6

Analysis of Variance for Brightness in Central Composite Design

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Blocks	1	2.409	2.409	2.409	6.3	0.04
Linear	2	28.0233	28.0233	14.011	36.71	0.0
Square	2	1.3814	1.3814	0.6907	1.81	0.23
Interaction	1	1.0506	1.0506	1.0506	2.75	0.14
Residual Error	7	2.6715	2.6715	0.3816		
Lack of Fit	3	2.5811	2.581	0.8604	38.10	0.002
Pure Error	4	0.0903	0.0903	0.0226		
Total	13	35.5296				

Table 7

Estimated Regression Coefficient for Viscosity in Central Composite Design

Term	Coef	Stdev	t-ratio	P
Constant	14.435	0.2429	59.39	0.00
Block	0.3529	0.1590	2.219	0.062
S	-0.0579	0.2104	-0.275	0.791
T	0.0365	0.2190	-2.397	0.048

Table 7-Continued

Term	Coef	Stdev	t-ratio	P
S*S	0.0365	0.2190	0.166	0.872
T*T	-0.2010	0.2190	-0.918	0.389
S*T	-0.6700	0.2975	-2.252	0.059
R²=0.5951		R-sq=70.5%		R-sq(adj)=45.0%

Table 8

Analysis of Variance for Viscosity In Central Composite Design

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Blocks	1	1.7431	1.7431	1.7431	4.92	0.062
Linear	2	2.0612	2.0612	1.0306	2.91	0.120
Square	2	0.3185	0.3185	0.1592	0.45	0.655
Interaction	1	1.7956	1.7956	1.7956	5.07	0.059
Residual Error	7	2.4789	2.4789	0.3541		
Lack of Fit	3	0.7848	0.7848	0.2616	0.62	0.639
Pure Error	4	1.6941	1.6941	0.4235		
Total	13	8.3973				

Appendix B

Statistical Data for Optimization of DMD Bleaching With the Use of RSM

Table 1

Estimated Effects and Coefficients for Brightness in First-order Model

Term	Effect	Coef.	Std. Coef	t-value	P
Constant	68.7400	1.171	58.68		0.000
A	11.3425	5.6713	1.374	4.13	0.026
B	0.2825	0.1412	1.374	0.10	0.925
T	2.8425	1.4213	1.374	1.03	0.377
A*B	-0.6775	-0.3387	1.374	-0.25	0.821
A*T	-1.5075	-0.7537	1.374	-0.55	0.621
B*T	-0.3575	-0.1788	1.374	-0.13	0.905
A*B*T	-0.4975	-0.2487	1.374	-0.18	0.868

Table 2

Analysis of Variance for Brightness in First-order Model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	273.624	273.624	91.2080	6.04	0.087
2-way interactions	3	5.719	5.719	1.9062	0.13	0.93
3-way interactions	1	0.495	0.495	0.4950	0.03	0.86
Residual Error	3	45.288	45.288	15.0959		
Curvature		41.801	41.801	41.806	23.98	0.039

Table 2-Continued

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Pure Error	2	3.486	3.486	1.7432		
Total	10	325.125				

Table 3

Estimated Effects and Coefficients for Viscosity in First-order Model

Term	Effect	Coef	Std Coef	t-value	P
Constant	13.159	0.3104	42.39	0.00	
A	-2.743	-1.371	0.3640	-3.77	0.033
B	-1.542	-0.771	0.3640	-2.12	0.124
T	-2.138	-1.069	0.3640	-2.94	0.061
A*B	0.537	0.269	0.3640	0.74	0.514
A*T	0.172	0.086	0.3640	0.24	0.828
B*T	-0.717	-0.359	0.3640	-0.99	0.397
A*B*T	0.103	0.051	0.3640	0.14	0.897

Table 4

Analysis of Variance for Viscosity in First-order Model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	28.9390	28.9390	9.64635	9.10	0.051
2-way Interactions	3	1.6669	1.6669	0.55565	0.52	0.695
3-way Interactions	1	0.0210	0.0210	0.02101	0.02	0.897
Residual Error	3	3.1801	3.1801	1.06003		
Curvature	1	3.0918	3.0918	3.09184	70.06	0.014
Pure Error	2	0.0883	0.0883	0.04413		
Total	10	33.807				

Table 5

Analysis of Variance for Brightness in Second-order Model

Source	DF	Seq SS	AdjSS	AdjMS	F	P
Main Effects	3	0.1983	0.1983	0.0661	0.68	0.611
2-way Interactions	3	0.5437	0.5437	0.1812	1.85	0.2763
3-way Interactions	1	0.9870	0.9870	0.9870	10.09	0.034

Table 5-Continued

Source	DF	Seq SS	AdjSS	AdjMS	F	P
Residual Error	4	0.3911	0.09778	0.09718		
Curvature	1	0.1053	0.1053	0.1053	1.11	0.370
Pure Error	3	0.2858	0.2858	0.09572		
Total	11	2.1202				

Table 6

Analysis of Variances for Viscosity in Second-order Model

Source	DF	Seq SS	AdjSS	AdjMS	F	P
Main Effects	3	8.3165	8.3165	2.7722	5.31	0.07
2-way interactions	3	2.7130	2.7130	0.9043	1.73	0.298
3-way interactions	1	3.5644	3.5644	3.5644	6.83	0.059
Residual Error	4	2.0871	2.0871	0.5218		
Curvature	1	1.6433	1.6433	1.6433	11.11	0.045
Pure Error	3	0.4438	0.4438	0.1479		
Total	11	16.6811				

Table 7

Analysis of Variances for Brightness in Central Composite Design

Source	DF	SeqSS	AdjSS	AdjMS	F	P
Blocks	2	0.3576	0.1389	0.06946	0.23	0.799
Linear	3	1.6278	1.6278	0.54260	1.80	0.224
Square	3	7.1578	7.1578	2.38592	7.93	0.009
Interaction	3	0.5437	0.5437	0.18125	0.60	0.631
Residual Error	8	2.4056	2.4056	0.30070		
Lack of Fit	5	2.0241	2.0241	0.40483	3.18	
Pure Error	3	0.3814	0.3814	0.12715		
Total	19	12.0925				

Table 8

Analysis of Variance for Viscosity in Central Composite Design

Source	DF	SeqSS	AdjSS	AdjMS	F	P
Blocks	2	1.8532	2.2314	1.1157	1.50	0.280
Linear	3	19.9632	19.9632	6.6544	8.93	0.006
Square	3	6.3287	6.3287	2.1094	2.83	0.106
Interaction	3	2.7130	2.7130	0.9043	1.21	0.366
Residual Error	8	5.9627	5.9627	0.7453		
Lack of Fit	5	5.3636	5.3636	1.0727	5.37	0.099
Pure Error	3	0.5991	0.5991	0.1997		
Total	19	36.8209				

Table 9

Estimated Regression Coefficient for Viscosity in Central Composite Design

Term	Coef	Stdev	t-ratio	P
Constant	11.3930	0.3524	32.334	0.00
Block 1	-0.5665	0.3452	-1.641	0.139
Block 2	0.2687	0.3452	0.778	0.459
A2	-0.9287	0.2336	-3.975	0.004
B2	-0.0161	0.2336	-0.069	0.947
T2	-0.9914	0.2992	-3.313	0.011
A2*A2	0.5176	0.2275	2.274	0.052
B2*B2	0.4610	0.2275	2.026	0.077
T2*T2	0.0403	0.2275	0.177	0.864
A2*B2	-0.5100	0.3052	-1.671	0.133
A2*T2	-0.2200	0.3052	-0.721	0.492
B2*T2	0.1750	0.3052	0.573	0.582
S=0.8633 R²=83.8% R²(adj)=61.5%				

Table 10

Estimated Regression Coefficients for Brightness in Central Composite
Design

Term	Coef	Stdev	t-ratio	P
Constant	72.5226	0.2238	324.041	0.00
Block	-0.1076	0.2193	-0.491	0.637
Block 2	0.0037	0.2193	0.017	0.987
A2	0.2013	0.1484	1.356	0.212
B2	-0.1659	0.1484	-1.118	0.296
T2	-0.2898	0.1901	-1.524	0.166
A2*A2	-0.3094	0.1445	-2.141	0.065
B2*B2	-0.0566	0.1445	-0.392	0.706
T2*T2	0.5939	0.1445	4.110	0.003
A2*B2	-0.0938	0.1939	-0.484	0.642
A2*T2	-0.2413	0.1939	-1.244	0.249
B2*T2	0.876	0.0312	0.1939	0.161
S=0.5484	R ² =80.1%	R ² (adj)=52.80%		

Appendix C
Calculations for BOD, COD, and TOC

Calculation for BOD:

$$\text{BOD}(\text{mg / L}) = \frac{(D_1 - D_2) - (B_1 - B_2) f}{P}$$

$$\text{BOD}(\text{kg/ton}) = \frac{\text{BOD}(\text{mg / L}) * \text{Effluent (ml)}}{\text{O.D. pulp (gr)}}$$

D1 = DO (dissolved oxygen) of diluted sample initially

D2 = DO of diluted sample after incubation (5 days)

P = decimal volumetric fraction of sample used (ml sample added to cylinder divided by 1000 ml)

B1 = DO of seed control blank initially

B2 = DO of seed control blank after incubation period (5 days)

f = (1000 ml – ml sample added to cylinder) / 1000 ml

Calculation for COD:

$$\text{COD}(\text{mg O}_2 / \text{L}) = \frac{(A-B)*M*8000}{\text{ml sample}}$$

$$\text{COD}(\text{Kg /ton}) = \frac{\text{COD}(\text{mg O}_2/\text{L}) * \text{Effluent(L)}}{\text{O.D pulp (gr)}}$$

A= ml FAS (Ferrous Ammonium Sulfate) used for blank, average of replicates

B= ml FAS used for sample, average of replicates

M= molarity of FAS

Calculation for TOC:

$$\text{TOC (}\mu\text{g C / ml)} = \frac{\text{Average of readings for sample – acid sample}}{\text{Sample Size}}$$

$$\text{TOC (Kg /ton)} = \frac{[\text{TOC (}\mu\text{g C / ml)} * \text{effluent (ml)} * 1000]}{\text{O.D pulp (gr)}}$$

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