Modeling Hydrogen Peroxide Bleaching Process to Predict Optical Properties of a Bleached CMP Pulp

ABOUZAR HATAM *, KAMBIZ POURTAHMASI +, HOSSEIN RESALATI ++, A. HOSSEIN LOHRASEBI +++

* MSc in wood and paper sciences and industries, department of wood and paper sciences, college of natural resources, university of Tehran, P.O.BOX 3585-3114,Karaj, Iran

+ Assistant professor, department of wood and paper sciences, college of natural resources, university of Tehran, P.O.BOX 3585- 3114,Karaj, Iran

++ Assistant professor, college of wood and paper technology, university of Gorgan , Gorgan, Iran

+++ Assistant professor, department of wood science, faculty of forestry, university of British Columbia, 4041-2424 Main Mall, Vancouver, B.C, V6TIZ4, Canada

E-mail: abhatam@yahoo.com

ABSTRACT

In this paper, the possibility of statistical modeling from the pulp and peroxide bleaching condition variables to predict optical properties of a bleached chemimechanical pulp used in a newsprint paper machine at Mazandaran Wood and Paper Industries Company (MWPI) was studied. Due to the variations in the opacity and the brightness of the bleached pulp at MWPI and to tackle this problem, it was decided to study the possibility of modeling the bleaching process. To achieve this purpose, Multi-variate Regression Analysis was used for model building and it was found that there is a relationship between independent variables and pulp brightness as well as pulp opacity, consequently, two models were constructed.

Then, model validation was carried out using new data set in the bleaching plant at MWPI to test model predictive ability and its performance.

Keywords: chemimechanical pulp, hydrogen peroxide bleaching, statistical modeling, opacity, brightness.

INTRODUCTION

Pulp darkness is due to lignin and lignin degradation products during pulping and the specific compounds which cause light absorption (and therefore a coloured pulp) are termed chromophores. The goal in the bleaching of high yield chemimechanical pulp is to selectively remove the colour-contributing groups while simultaneously preserving a high pulp yield. This involves mainly the use of bleaching agents such as hydrogen peroxide. Hydrogen peroxide is the most widely used oxidative bleaching agent in high yield pulp bleaching, particularly where high pulp brightness is desired [1].

The primary objectives of a bleach plant are high pulp brightness, high production rate, low operating costs and particularly low environmental impact. The large number of variables and high costs of mill trials are a few of the problems encountered when optimizing the operation of bleaching processes [2].

To meet these purposes, controlling of the bleaching process will be of the greatest importance and to reach this aim firstly, it is necessary to identify the most important process variables pertaining to the pulp and bleaching conditions and then to study the possibility of building models from them enabling us to predict optical properties of the bleached pulp. This would improve the bleached pulp optical properties by minimizing the effects of the process disturbances and achieve some economical and environmental benefits by reducing the consumption of the bleaching chemicals.

In this case study, statistical modeling of peroxide bleaching process for predicting opacity and brightness of the bleached CMP pulp at MWPI was performed. These models eventually allow optimization of the bleaching conditions for maximum desirable bleached pulp properties.

PROCESS DESCRIPTION

Figure 1 shows a schematic of the one-stage continuous hydrogen peroxide bleaching process of the chemimechanical pulp at MWPI. Pulp form CMP pulp line is blended at about 1% consistency with a chelating agent (DTPA) in latency chest and stored in the unbleached pulp storage tower. Then it is pumped to the first stage twin-roll press, where the pulp is dewatered to a consistency of about 27-30%. After dewatering , the stock is delivered to a Rotomixer in which the bleaching chemicals are mixed. The stock is brought to a bleach tower where the stock is retained for about two hours at a temperature of 60-70 $^{\circ}c$. Afterwards, the bleached pulp is diluted and washed. Then, it is pumped to the second stage twin-roll press and dewatered to a consistency of about 30% and then bleaching reactions are terminated by the addition of SO_2-Water. The pulp pH is lowered by adding sulphur dioxide to prevent alkaline reversion and to decompose the residual peroxide[3]. Finally, the pulp is stored in the CMP pulp storage tower to a consistency of about 12%.

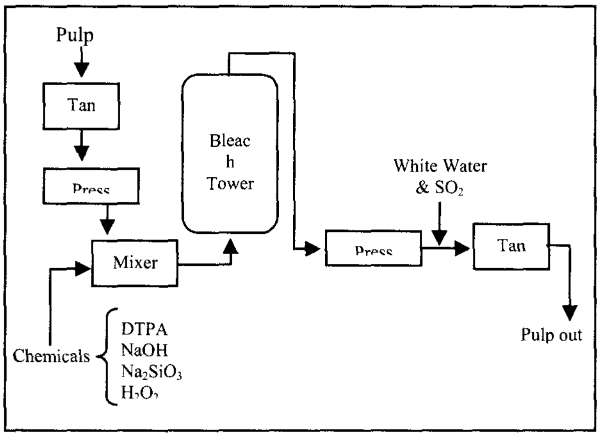

Fig.1. A simplified flowsheet of the continuous high consistency hydrogen peroxide bleaching process at MWPI

METHODS AND MATERIALS

The model building data set were the on-line recorded data of the continuous bleaching plant at MWPI. But the validation data set, were new data collected from bleach plant. The bleaching stock was a pulp blend of two species including hornbeam (75%) and beech (25%). Dependent variables were selected as the bleached pulp brightness and opacity. For opacity, independent variables included: CSF(mL), Shive Content(%), Total $Na^+(gL^{-1})$, Yield(%), Mesh 28(by W %), Mesh 48(by W %), Mesh 100(by W %), Mesh 200(by W %) and Mesh>200(by W %) as pulp variables in the CMP tower.

For brightness, independent variables were: input pulp opacity(%ISO), input pulp brightness(%ISO) and input pulp yellowness(%ISO) as pulp variables, and initial pH, initial NaOH(gL^{-1}), initial $H_2O_2(gL^{-1})$, final pH, residual NaOH(gL^{-1}) and residual $H_2O_2(gL^{-1})$ as bleaching condition variables.

To analyze the data and build models, SPSS software (Proc Multi-variate Linear Regression) and to test for lack of fit, SAS software (Proc Glm) were used to find the best equation, the following subset selection procedures were employed: all combination (r-square), Forward and Backward elimination and Stepwise. A brief explanation of the strategy for building a regression model followed in this study is presented for the pulp brightness. The same procedure was followed for building a model for the pulp opacity.

Scattergrams of the pulp brightness against independent variables were prepared to illustrate the relationship between the independent and dependent variables (trend Y vs. Xs), to find outlier points, and to check whether error-variances are uniform. Scatter plots of the response variable (Y) vs. each predictor variable (X) is useful in determining the nature and the strength of the bivariate relationships between each X and Y variables and for finding gaps in the data points. Scatter plots of each predictor variable against each other are helpful for studying the bivariate relationships among the predictor variables and for identifying gaps and outliers. Analysis is facilitated if these scatter plots are assembled in a scatter plot matrix, as indicated in Figure 2, in which the Y variable for any one scatter plot is the name found in its row, and the X variable is the name found in its column. A scatter plot matrix facilitates the study of the relationships among the variable by comparing the scatter plot within a row or a column [4]. A complement to the scatter plot matrix, that can be helpful, is the correlation matrix (Table 1). It is noted that the correlation matrix is symmetric and that its main diagonal contains 1s.

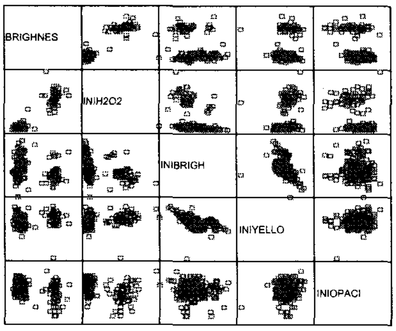

Fig.2. Scatter plot matrix

The plots indicated some outliers. After solving those problems and omitting some serious ones, since some scatterplots were curvilinear, it was decided that X transformations to be carried out. A total of eleven different transformations of X's were tried. $\left(\frac{1}{\text{initial } H_2O_2}\right)$ Was found to be sufficient in addition to the original 3Xs (overall four independent variables, R^2=0.635). There was no significant improvement in R^2 when considering transformation of

Table 1. Correlation matrix (r coefficient)

Correlations

		BRIGHNES	FINPH	RESNAOH	RESH2O2	INIPH	ININAOH	INIH2O2	INIBRIGH	INIYELLO	INIOPACI
BRIGHNES	Pearson Correlation	1	.696**	.608**	.862**	.865**	.887**	.939**	-.215**	.186**	-.408**
	Sig. (2-tailed)	.	.000	.000	.000	.000	.000	.000	.000	.001	.000
	N	295	295	295	295	295	295	295	295	295	295
FINPH	Pearson Correlation	.696**	1	.540**	.586**	.755**	.676**	.692**	-.458**	.195**	-.233**
	Sig. (2-tailed)	.000	.	.000	.000	.000	.000	.000	.000	.001	.000
	N	295	295	295	295	295	295	295	295	295	295
RESNAOH	Pearson Correlation	.608**	.540**	1	.583**	.613**	.644**	.637**	-.348**	.271**	-.207**
	Sig. (2-tailed)	.000	.000	.	.000	.000	.000	.000	.000	.000	.000
	N	295	295	295	295	295	295	295	295	295	295
RESH2O2	Pearson Correlation	.862**	.586**	.583**	1	.765**	.887**	.911**	-.339**	.347**	-.214**
	Sig. (2-tailed)	.000	.000	.000	.	.000	.000	.000	.000	.000	.000
	N	295	295	295	295	295	295	295	295	295	295
INIPH	Pearson Correlation	.865**	.755**	.613**	.765**	1	.848**	.878**	-.368**	.239**	-.304**
	Sig. (2-tailed)	.000	.000	.000	.000	.	.000	.000	.000	.000	.000
	N	295	295	295	295	295	295	295	295	295	295
ININAOH	Pearson Correlation	.887**	.676**	.644**	.887**	.848**	1	.953**	-.391**	.307**	-.249**
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.	.000	.000	.000	.000
	N	295	295	295	295	295	295	295	295	295	295
INIH2O2	Pearson Correlation	.939**	.692**	.637**	.911**	.878**	.953**	1	-.381**	.308**	-.288**
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.	.000	.000	.000
	N	295	295	295	295	295	295	295	295	295	295
INIBRIGH	Pearson Correlation	-.215**	-.458**	-.348**	-.339**	-.368**	-.391**	-.381**	1	-.575**	-.067
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.000	.	.000	.248
	N	295	295	295	295	295	295	295	295	295	295
INIYELLO	Pearson Correlation	.186**	.195**	.271**	.347**	.239**	.307**	.308**	-.575**	1	.105
	Sig. (2-tailed)	.001	.001	.000	.000	.000	.000	.000	.000	.	.072
	N	295	295	295	295	295	295	295	295	295	295
INIOPACI	Pearson Correlation	-.408**	-.233**	-.207**	-.214**	-.304**	-.249**	-.288**	-.067	.105	1
	Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.000	.248	.072	.
	N	295	295	295	295	295	295	295	295	295	295

**. Correlation is significant at the 0.01 level (2-tailed).

other Xs or increasing the number of variables in the model up to 16 Xs (R^2=0.645). According to Neter et al. [4], the two most important assumptions to be tested include normality and uniformity of variance of the error terms. When these two assumptions are not met, transformation of the response variable (Y) is needed in addition to X transformation. Since normality of error terms and uniformity of error variance were not met, transformation of dependent variable (Y) was also examined and $\sin\sqrt{Y}$ (where Y is in radian) was found to make the error variance constant and residuals normal. After the proper transformations were performed, in the SPSS software, the Multi-variate Linear Regression was run to obtain the model parameters.

Following transformation of the Xs, the best combination of Xs (full model) was found to be:

$$\begin{aligned}\sin\sqrt{Y} &= b_0 + b_1(\text{initial } H_2O_2) + b_2(\text{initial Brightness})\\ &+ b_3(\text{initial Opacity}) + b_4(\text{initial Yellowness})\\ &+ b_5(\text{initial } pH) + b_6(\text{initial } NaOH) + b_7(\text{final } pH)\\ &+ b_8(\text{residual } H_2O_2) + b_9(\text{residual } NaOH)\\ &+ b_{10}\left(\frac{1}{\text{initial } H_2O_2}\right) + b_{11}(\text{Log initial } H_2O_2)\\ &+ b_{12}(\text{initial } H_2O_2)^2 + b_{13}(\text{initial Brightness})^2\\ &+ b_{14}(\text{Log initial Brightness})\\ &+ b_{15}(\text{Log initial Opacity}) + b_{16}\left(\frac{1}{\text{initial Yellowness}}\right)\end{aligned}$$

[1]

Next, the best subsets were selected by running F-tests, as well as comparing R^2. In this study, as mentioned earlier, different selection procedures were applied: all combination, Forward, Backward and Stepwise. They were run, because it is always better to run all selection procedures in order to identify all of the good equations and to choose one "best" among all "good" candidates. After comparing the outputs, the best equation was selected from the output of stepwise procedure. After finding the proper model, it is important to examine the aptness of the model. Thus, the model had to be tested for lack of fit to secure the correctness of regression assumptions.

RESULTS

As Table II shows, there is a general significant relationship between the pulp and bleaching conditions variables and the bleached pulp Brightness. Thus, it was possible to develop the Full Model, which contains 16 variables [Eq.1].

Table 2 . Analysis of variance
(Full model , Eq. 1, R^2=0.645)

SOURCE	DF	SS	MS	F-VALUE	PROB>F
MODEL	16	0.181	0.011	30.080	0.0001
ERROR	265	0.1	0.000375		
TOTAL	281	0.281			

1- Selection of the best subset

As mentioned in methodology, the best equation was selected among the several choices given by the stepwise procedure's output. To find the best equation (which could have a different number of independent variables) the value of R^2 was compared and the best model was selected where R^2 was at its peak. This happened to be a model with four independent variables:

$$\begin{aligned}Sin\sqrt{Y} &= 0.7694 - 0.02043(\text{initial } H_2O_2) + 0.0069(\text{initial Brightness})\\ &- 0.01049\left(\frac{1}{\text{initial } H_2O_2}\right) - 0.00171(\text{initial Opacity})\end{aligned}$$

[2]

As the ANOVA Table (Table 3) shows, all four variables including, initial H_2O_2, initial Brightness, initial Opacity and the transformed variable $\left(\frac{1}{\text{initial } H_2O_2}\right)$, are important variables of bleaching process.

Table 3. Analysis of variance
(Reduced model, Eq. 2 , R^2=0.635)

SOURCE	DF	SS	MS	F-VALUE	PROB>F
MODEL	4	0.18075	0.04519	116.89	0.0001
ERROR	277	0.10708	0.00038		
TOTAL	281	0.28783			

2- Test for lack of fit

This is to test the first assumption of the regression analysis, i.e., to assess the appropriateness of the multiple regression function. Formal or statistical evaluation of regression function is F-test which can be performed whenever the observation is replicated. To make sure that, the ANOVA Table is prepared (Table 4), indicating a very low F-value for lack of fit. It implies that at $\alpha = 0.01$ level, there is no significant lack of fit (H_0 is concluded since F-calculated=1.188< F-critical =1.501). in other words, the variation in prediction ($\hat{Y}_i$) is due to the pure error rather than lack of fit from the regression model.

Table 4. General ANOVA table for testing lack of fit

SOURCE	DF	SS	MS	F-VALUE	PROB>F
MODEL	4	0.18	0.045	116.89	0.0001
ERROR	277	0.107	0.00038		
LACK OF FIT	188	0.076	0.00004	1.188	
PURE ERROR	89	0.03	0.0003		
TOTAL	281	0.2878			

3- Test for uniformity of error variance

One method to examine the constancy of the variance of the error terms is to plot standardized residual ($Y_i - \hat{Y}_i$) vs. unstandardized predicted values [5]. The shape of the scattergram (distribution of data points) indicated that the error variance is reasonably homogeneous. As Figure 3 shows, the scattering of data points in this scatterplot nearly follows random pattern.

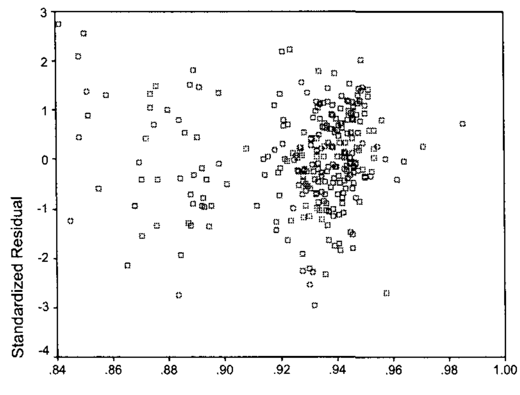

Fig. 3. Scattergram of standardized residuals vs. unstandardized predicted values

4- Test for normality of error terms

It is usually a good strategy to investigate other types of departures first, before concerning with the normality of the error terms. This is because other types of departures can affect the distribution of residuals [4]. For example, residuals may appear to be not normally distributed since an inappropriate regression model was used or because non-constant error variance was involved.

Normal Probability Plot

A good method to examine the normality assumption is using normal probability plots of the residuals. Here each residual is plotted vs. its expected value under normality (Figure 4). A plot that is nearly linear suggests agreement with normality, that is distribution of the error terms does not depart substantially from a normal distribution [4]. In addition to visually assessing the approximate linearity of the points plotted in a normal probability plot, a formal test for normality of the error terms can be conducted by calculating the coefficient of correlation between the residuals ($Y_i - \hat{Y}_i$) and their expected values under normality. A high value of the correlation coefficient can meet the normality assumption.

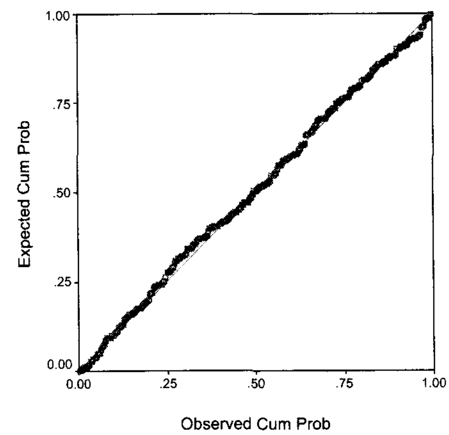

Fig. 4. Normal probability plot of regression standardized residual (residuals vs. expected values).

5- Model validation and predictive ability

The last step in the process of building a model is the validation of the selected regression model. Model validation is a useful and necessary part of the model building process and refers to stability and reasonableness of the regression coefficient, plausibility and usability of the regression function and the ability to generalize inferences draw from the regression analysis. Validation of a regression model usually involves checking the model against independent data [4].

In this study, the model validation was performed using new data set collected from the bleach plant at MWPI.

The second data set were collected under the similar conditions. Then data of each variables included in the selected model were input in the equation 2 and the predicted values were calculated and compared with the measured values.

6- The final model

The final model was developed using overall 282 data point and three variables, one variable related to the bleaching condition and the two more related to the input pulp properties. The final regression model to predict the brightness of the CMP bleached pulp at MWPI is as follows:

$$Sin\sqrt{Y} = 0.7694 - 0.02043\,(\text{initial } H_2O_2) + 0.00691\,(\text{initial Brightness}) - 0.01049\left(\frac{1}{\text{initial } H_2O_2}\right) - 0.00171\,(\text{initial Opacity})$$

[3]

$R^2 = 0.635$

Where,

initial H_2O_2 = the concentration of H_2O_2 in bleach tower prior to bleaching (gL^{-1})

initial brightness = the brightness of unbleached CMP pulp (%ISO)

initial opacity = the opacity of unbleached CMP pulp (%ISO)

$Sin\sqrt{Y}$ = the sine of $\sqrt{Y}$ (Y in radian), when the Y values were transformed. But the predicted values of the bleached pulp brightness should be calculated as follows:

For example: if the calculated value from final equation (equation 3) is $Sin\sqrt{Y} = 0.97 \Rightarrow$ to calculate Y as the bleached CMP pulp brightness:

$ArcSin\,(0.97) = 75.93^\circ$

$(75.93^\circ) + 360^\circ = 435.9^\circ$

$435.9^\circ \times 3.14 = 1368.8$

$\frac{1368.8}{180} = 7.6 \text{ rad} \Rightarrow (7.6)^2 = 57.8$

So, the predicted value of the bleached pulp brightness is 57.8 (%ISO). The units for the parameters (regression coefficients) in the above model are as follows:

$b_1(Lg^{-1})$, $b_2(\%^{-1})$, $b_3(gL^{-1})$, $b_4(\%^{-1})$.

Following the procedures mentioned earlier, another multiple regression model was also developed for predicting the bleached pulp opacity. The resulting predictive model (final model) was found to be:

$$Y = 83.234 - 17.431(\text{Total}Na^+) + 4.459(\text{Total}Na^+)^3 + 0.426(Mesh100) + 0.6072(Mesh200)$$

[4]

$R^2 = 0.61$

where,

Y = opacity of the bleached CMP pulp (%ISO)

Total Na^+ = the total concentration of Na^+ in the bleached pulp when stored in CMP tower (gL^{-1})

Mesh 100 = the bleached or unbleached pulp fibre fraction retained on the 100 mesh screen (by W %).

Mesh 200 = the bleached or unbleached pulp fibre fraction retained on the 200 mesh screen (by W %).

The units for the parameters (regression coefficients) in the above model are as follows:

$b_0(\%)$, $b_1(\%\,Lg^{-1})$, $b_2(\%\,L^3g^{-3})$

Figures 5 and 6 show the actual vs. predicted values of the two dependent variables based on the two models, i.e. equations 3 and 4. As these figures show, the brightness and opacity of the bleached CMP pulp can be predicted on basis of the variables included in the final model. This finding is important because in the model developed to predict bleached pulp brightness for a given brightness value, since input pulp brightness and input pulp opacity are known, so it is possible to control and optimize the hydrogen peroxide charge needed to reach our target pulp brightness.

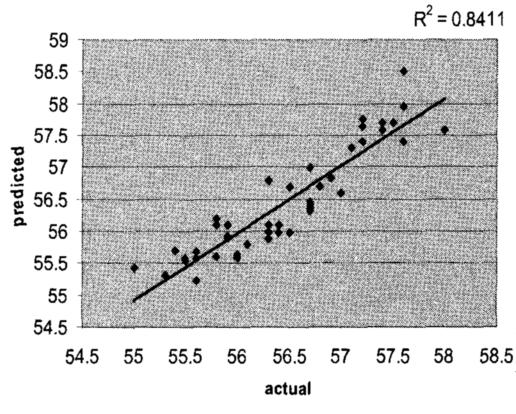

Fig. 5. Actual brightness vs. predicted values of brightness

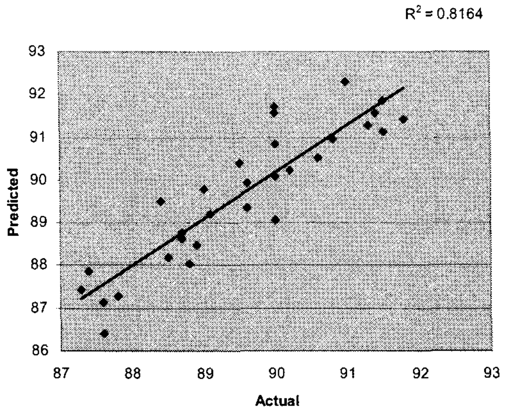

Fig. 6. Actual opacity vs. predicted values of opacity

Also, in the model developed for predicting the pulp opacity, on one hand, the unbleached pulp 100 mesh and 200 mesh fibre fractions are known, and on the other hand it has been demonstrated that there is a linear relationship between sodium hydroxide and hydrogen peroxide charges required in the peroxide bleaching [6]. So, for the optimum pH level in the peroxide bleaching it is possible to optimize sodium hydroxide and sodium silicate charges required and to control the concentration of Total Na^+ in the CMP storage tower as the most important variable reversely influencing the bleached pulp opacity as shown in Figure 7. Consequently controlling the concentration of Total Na^+ will result in to minimize the variations of the pulp opacity after bleaching. It is noted that the high concentration of Total Na^+ in CMP storage tower indicates that the sodium hydroxide and sodium silicate charges are not in the optimum levels.

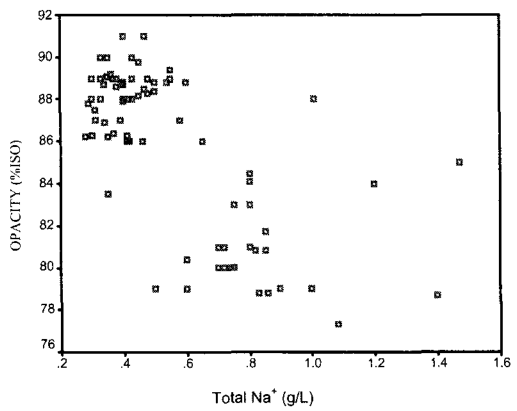

Fig. 7. Scattergram of Total Na^+ vs. opacity

CONCLUSION

Statistical modeling of hydrogen peroxide bleaching process was carried out by means of Multi-variate Regression Analysis. Two multiple regression models developed for predicting the brightness and opacity of the bleached CMP pulp at MWPI. The validation results demonstrated that the models developed can be applied for practical purposes (for process control).

It was found that in addition to hydrogen peroxide charge as the most sensitive controlling variable and the input pulp brightness as the major disturbance to the operation of the bleaching plant [2], input pulp opacity has a statistically significant effect on the final pulp brightness considering F-values at $\alpha = 0.05$. b_4 parameter in the equation 4 shows the reverse relationship between input pulp opacity and final pulp brightness. Because an increase in input pulp opacity implies that less delignification took place during pulping. If all of the other operating conditions are kept constant, an increase in the input pulp opacity will lead to a decrease in the final pulp brightness.

It was also found that the concentration of Total Na^+ in CMP tower was the most effective variable on the final pulp opacity. Because it is an indicator of alkalinity in the bleaching process. A high alkalinity improves fibre flexibility and leads to better fibre bonding. In this condition, mechanical properties of the handsheet made from bleached pulp increase, but the opacity decreases. The other variables included in equation 4 are Mesh 100 and Mesh 200. These classes of fibres are short fibre fractions. Shorter fibres produce better formation [7] and can be considered as fillers inducing improvement in the opacity of the bleached pulp.

REFERENCES:

1. Dence, C.W. and Reeve, D.W., Pulp Bleaching Principles and Practice, 697-716, TAPPI Press (1996).
2. Qian, X. and Tessier, P., Dynamic modeling and control of a hydrogen peroxide bleaching process, pulp and paper Canada 98(9): 81-85 (1997).
3. Persely, J. R. and Hill, R.T., Pulp Bleaching

Principles and Practice, 457- 489, TAPPI Press (1996).

4. Neter, J., Kutner, M.H., Nachtsheim, C.J. and Wasserman, W., Applied Linear Statistical Models, 3rd Ed., Times Mirror Higher Education Group, Inc. Chicago (1996).
5. Rezaee, A.M. and Soltani, A., An introduction to the Applied Regression,1st Ed., 79-85, Publication Center of Esfahan Polytechnic University, Esfahan, Iran, (1988).
6. Lindholm, C.A., Paper Making Science and Technology, vol. 5. , Ed. Jan Sundholm , chapter 11, Finish Pulp and Paper Research Institute (1999).
7. Nazhad, M.M., Homis, E.J., Dodson, C.T.J., Kerekes, R.J., The influence of the formation on tensile strength of paper made from mechanical pulp, TAPPI Conference and Trade Fair Proceedings, 141-146 (2000).