Development of Bleaching Process through Statistical Experimental Design

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ABSTRACT

Paper industry in India is capital intensive in terms of chemical and energy consumption and generates huge pollution loads, thereby considered a threat to the environment. At this present context, therefore, Indian paper industry needs to adopt totally modified process for mere survival point of view. The present study aims towards the optimal and conceptual design of the multi-stage short sequence bleaching process. An attempt has been made to investigate the effect of elemental chlorine free bleaching sequences, namely DE_pD and ODE_pD on the final brightness of the pulp and the extent of environmental parameters such as BOD & COD values. Typical mixed pulp composed of (eucalyptus + bamboo-poplar) used in some mills in India is tried for experimental evaluation. Parallel experiments have been conducted for the conventional sequence (CEHH).. The values are also compared when oxygen pre-bleached pulp is used for usually followed sequence (CEHH) of the mills. Statistical rotatable factorial design for Oxygen delignification stage is carried out at different temperatures, reaction time and alkali doses to develop a non-linear, multivariate statistical model. Multivariate orthogonal regression equations are developed to examine the effect of the various parameters of the oxygen bleaching of the pulp. On comparing the various sequences, it is found that oxygen pre-delignified pulp increases the brightness values and decrease both BOD and COD values. On an average COD reduction is found to be 50% while BOD reduction is about 65%, for same brightness levels.

INTRODUCTION

Paper used as a carrier of information, for packaging, hygienic and many other purposes satisfy many of our daily needs. In spite of the increasing demand of paper the industry suffers from multidirectional problems in India. These include constraints of fibre availability on one hand and water and energy on the other. In addition the industry discharges huge pollution load to the environment in form of effluent containing toxic substances adversely affecting the aquatic life. Thus off late the industry is under strict vigilance of regulatory bodies, both state and central pollution control boards. The environment norms have become more stringent. Therefore, need of totally modified processes and operations arise for mere survival point of view. Hence for sustainable production of paper to meet the demand, conceptual design of systems and equipments are very much needed.

In the process of paper manufacture, with the present day sequences of the bleaching operations adopted, liquid effluents from the bleach plant are considered to be environmentally most hazardous. Traditionally, the elemental chlorine based multistage processes with hypochlorite addition in the brightness stage has been adopted by the mills. This process generates not only BOD (Biological Oxygen Demand), COD (Chemical Oxygen Demand) but also, AOX (Adsorbable Organic Halide), TOCI, EOX (Extractable Organic Halide), POX Persistent Organic Halide), EPOX (Extractable Purgable Organic Halide) and many others. The most dangerous chemicals discharged in the effluent are TCDD, TCDF and chlorinated di-phenyl ether derivatives. To eliminate these acute toxic chemicals in the effluent the treatment costs being prohibitably high, requiring meritoriously planned tertiary treatment, over and above biological secondary treatment of the liquid effluent, Indian Pulp and Paper industry is not well equipped to completely eliminate the above environmentally harmful chemicals. Therefore, it has become an imperative necessity to implement a designed bleach plant which does not induct either elemental chlorine (C) or hypochlorite (H), instead the industry should think of ECF (elemental chlorine free) processes which uses chlorine dioxide (D), hydrogen peroxide (P), Oxygen (O) in the bleaching operation. This not only reduces the environmental load in form of polychloro-organics (AOX, etc.) but also reduce the chemical requirement in the subsequent stages, thereby drastically reducing the formation of unwanted substances. This is corroborated from the fact that AOX generation is reduced to one-fifth if one uses chlorine dioxide in place of elemental chlorine and the substantial reduction in the bleach chemical generates lesser amount of toxic substances. These dual benefits can also be substantiated by using oxygen in the first stage which inevitably reduces the incoming kappa number. This fact stems out from the well known concept that higher the incoming kappa number more is the bleach chemical demand. Therefore, with the above aim in mind the present investigation has been planned with two bleaching sequences, namely, DE_pD and ODE_pD. In order to compare these sequences, experiments are also conducted for the conventional CEHH stage, mostly practiced in Indian mills. To examine the effect of oxygen in the pre-bleaching stage, OCEHH has also been conducted. This enables one to compare the effect of oxygen pre-bleaching on the existing bleaching sequence for the same pulp. Because kappa number is proportional to the environment load, the environmental parameters are determined along with the pulp quality in terms of brightness and viscosity

For the design of the process, mathematical modeling is an extremely important tool. A model is a simplified representation of those aspects of an actual process that are being investigated. The data for an industrial system generally become highly scattered in nature, hence deterministic model is out of the question, resort is made to experimentation and statistics for optimization and simulation.

For the design of the bleach plant, quantitative model is not possible because of complexity of the process and being discrete in nature, rather a statistical correlation could be of immense potential for interrelating the input and output parameters. Even the statistical model cannot be of linear type. The process demands a multivariable non-linear regression equation. Hence an attempt has been made in this investigation to develop these correlations with a specific type of pulp used is the northern Indian paper mills, to benefit both the process engineers as well as the environmentalists to design the effluent treatment plants in a methodical way.

Literature Survey

Extensive work is available regarding the bleaching of pulps with eucalyptus with chlorine dioxide (3), other hardwoods & softwoods (2,4,6), and various sequences including the enzymatic and oxidative treatments for Kraft pulp (2,4,7,9). The effect of variables on the generation of chlorinated organic matter in the effluent was investigated in details (8). As regarding the development of the kinetic model, Edward (8) had reported for the oxygen bleaching stage of a kraft pulp made from softwood species. Though some statistical models are available, these are mostly developed on softwood and hardwood based experimental data. All have been related to the prediction of environmental parameters. Gupta (13) and Gupta et al. (14) have developed improved correlations based on experimental data of the other investigators, that too for softwood and hardwood species. However, no correlations are available for kappa number and viscosity values for the mixture of hardwood+bamboo (85+15) as used by many Paper mills in north India. No other unified equation has been reported till date which can take care of multiple parameters normally encountered in the bleach plant of the large paper mills such that it can estimate or predict the output values during process design of either multi-stage bleach plant. Therefore, it is very important to develop such a correlation using multivariable approach with interaction terms, which could be of immense help

Table 1 Design Matrix

Z_1	Z_2	Z_3	X_0	X_1	X_2	X_3	X'_1	X'_2	X'_3	X_1X_2	X_2X_3	X_2X_3	X_1X_3	$X_1X_2X_3$	Y_{kappa}	$Y_{viscosity}$	$Y_{brightness}$
15	120	1	1	-1	-1	-1	0.27	0.27	0.27	1	1	1	1	-1	21.43	37.8	26.3
15	120	2	1	-1	-1	1	0.27	0.27	0.27	1	-1	-1	-1	1	17.62	34.5	29.5
15	150	1	1	-1	1	-1	0.27	0.27	0.27	-1	-1	-1	1	1	16.22	30.2	31.4
15	150	2	1	-1	1	1	0.27	0.27	0.27	-1	1	1	-1	-1	18.37	26.7	41.7
45	120	1	1	1	-1	-1	0.27	0.27	0.27	-1	1	1	-1	1	12.36	36.5	28.5
45	120	2	1	1	-1	1	0.27	0.27	0.27	-1	-1	-1	1	-1	13.73	29.6	37.1
45	150	1	1	1	1	-1	0.27	0.27	0.27	1	-1	-1	-1	-1	13.67	23.1	39.7
45	150	2	1	1	1	1	0.27	0.27	0.27	1	1	1	1	1	9.46	19.7	45.7
30	135	1.5	1	0	0	0	-0.73	-0.73	-0.73	0	0	0	0	0	14.08	28.9	36.4
15	135	1.5	1	-1.2	0	0	0.75	-0.73	-0.73	1	0	0	0	0	12.44	27.1	32.7
45	135	1.5	1	1.2	0	0	0.75	-0.73	-0.73	0	0	0	0	0	16.23	31.1	39.8
30	120	1.5	1	0	-1.2	0	-0.73	0.75	-0.73	0	0	0	0	0	12.56	24.6	30.8
30	150	1.5	1	0	1.2	0	-0.73	0.75	-0.73	0	0	0	0	0	18.32	34.7	38.3
30	135	1	1	0	0	-1.2	-0.73	-0.73	0.75	0	0	0	0	0	12.78	27.6	28.5
30	135	2	1	0	0	1.2	-0.73	-0.73	0.75	0	0	0	0	0	16.12	31.3	42.2

Table 2 Process conditions of different bleaching sequences.

Stages & Conditions	CEHH	OCEHH	$DE_{OP}D$	$ODE_{OP}D$
Pulp Brightness	24.23	39.01	24.33	39.01
Kappa Number	24.22	12.56	24.22	12.56
1st Stage		**Oxygen**		**Oxygen**
Pressure		5 Kg/cm^2		5 Kg/cm^2
Temperature		120°C		120°C
Retention time		60 min		60 min
NaOH charge		1.5%		1.5%
Consistency		10%		10%
2nd stage	**Chlorination**	**Chlorination**	**Chlorine dioxide**	**Chlorine dioxide**
Temperature	35°C	35°C	70°C	70°C
Retention time	60 min	60 min	60 min	60 min
pH	2	2	5	5
Consistency	3%	3%	10%	10%
Chlorine demand	5.3%	2.5%	5.3%	2.5%
3rd stage	**Extraction**	**Extraction**	**Extraction with oxygen & peroxide**	**Extraction with Oxygen & peroxide**
Temperature	70°C	70°C	70°C	70°C
Retention time	60 min	60 min	60 min	60 min
pH	11	11	11	11
Consistency	3%	3%	10%	10%
Alkali charge	2.95	1.55	2.95	1.55
Oxygen pressure			1 Kg/cm^2	1 Kg/cm^2
Peroxide			0.5%	0.5%
4th stage	**Hypochlorite**	**Hypochlorite**	**Chlorine dioxide**	**Chlorine dioxide**
Temperature	70°C	70°C	70°C	70°C
Retention time	60 min	60 min	60 min	60 min
pH	10.5	10.5	5	5
Consistency	7%	7%	10%	10%
5th stage	**Hypochlorite**	**Hypochlorite**		
Temperature	70°C	70°C		
Retention time	60 min	60 min		
pH	11	11		
Consistency	10%	10%		

to the practicing engineers. Before starting of the experiments, a statistical experimental design is made to optimize the number of experiments.

Statistical design of the experiments

A second order rotatable design is used to derive the estimated regression equation. A full 3^k factorial design involves 27 number of observations. The number could be reduced through the use of composite or sequential designs proposed by Box and Wilson (12). The "kernel" of such a design is a full 2^k factorial design for k<5 or its fractional replicate at k<5. If the estimated regression equation fails the test for the adequacy of fit, the following could be of help:

1. Add 2k "star" points on the coordinate axis of factorial space $(\pm\alpha,0,..,0)$, $(\pm\alpha,..,0)$,.... $(0,0,...\pm\alpha)$, where α is the distance from the center point to the "star" point.

2. Increase the number of observations, n_0, at the center point of the design. The total number of observations in the matrix of a composite design for k factors is given by

$$N = 2^k + 2k = n_0 \qquad k<5.$$

The experimental design matrix is given in Table 1. The property of orthogonality is used to test the experimental matrix. This is followed by proposing a non-linear, multi-variable regression equation and testing the reliability of the coefficients by student-t test and Fischer-F test. The details of the methodology is given in the Appendix. The second order orthogonal design matrix is non-orthogonal because

$\Sigma\ x_{oi}x_{ji}^2 \square 0$

$\Sigma\ x_{ji}^2 x_{ui}^2 \square 0$

The regression equation is assumed to be of the type;

$Y=b_0+b_1+X_1+b_2+X_2+b_3X_3+b_{11}X_1^2+b_{22}X_2^2+b_{33}X_2^2+b_{12}X_1X_2+b_{13}X_1X_3+b_{23}X_1X_2X_3$

where Y is the output parameter (kappa no., viscosity, etc.) and X_1,X_2 and X_3 are the process variables namely operation time (min.), temperature (°C) & alkali dose (% basis) respectively.

EXPERIMENTAL

Procedure to generate the data

The pulp and bleach liquor are collected from the nearby mill. Pulp is known to be the mixture of eucalyptus, bamboo, poplar, saw mill waste in the ratio 66:17:13:4. The pulp is throughly washed in the laboratory to ensure that it is free from the undesirable components. The kappa number of pulp and the bleach liquor are analyzed according to TAPPI standard method (T236, CM-85, OM-76). The range of the parameters are assumed based on literature and practiced data of the mill. The number of experiments are fixed by statistical design given in Table 1. The pulp is subjected to various bleaching sequences like CEHH and DE_pD. The detailed test conditions are given in Table 2. The effluents of the above process are collected and tested for BOD and COD.

The above process is repeated by introducing oxygen in the first stage. The BOD, COD, brightness and viscosity (cupra-ammonium hydroxide method, IS 6213, part 4,1971) are measured according to the TAPPI/ISO standards. The most important part of the entire investigation is the study of the effect of various parameters on the pulp quality (in terms of viscosity, kappa number & brightness) during the oxygen delignification. The environmental paramerters BOD, COD were measured only after the completion of the full bleaching sequence.

Oxygen Delignification

To study the effect of various parameters on the process of oxygen delignification, a number of experiments were carried out at varying conditions of time, temperature alkali doses, at a constant pressure of 5kg/cm². The range for the process variables are given as:

Parameter	Range	Step
Time (min)	15-45	15
Temperature (°C)	120-150	15
Alkali dose (%O.D. basis)	1-2	0.5

The experimental values of kappa number and viscosity are subjected to the statistical design to find the coefficients of the regression equation. From the significance tests, some interacting and/or non-interacting terms are neglected and regression equations are developed, in the later sections.

RESULTS AND DISCUSSION

Experimental data regarding brightness, kappa number and viscosity after the oxygen stage are presented in form of graphs. Effect of various process variables in the Oxygen Delignification are shown in the following paragraphs. The experimental data are plotted as functions of input parameters, namely time, temperature and alkali charge. Graphs are repeated with an aim to examine the relative sensitivities of the different process variables mentioned above.

Effect on the Brightness of the pulp

Brightness variation of the pulp as a function of alkali dose, time and temperature is shown in Fig 1-3. It is clear that brightness increases with the increase in the

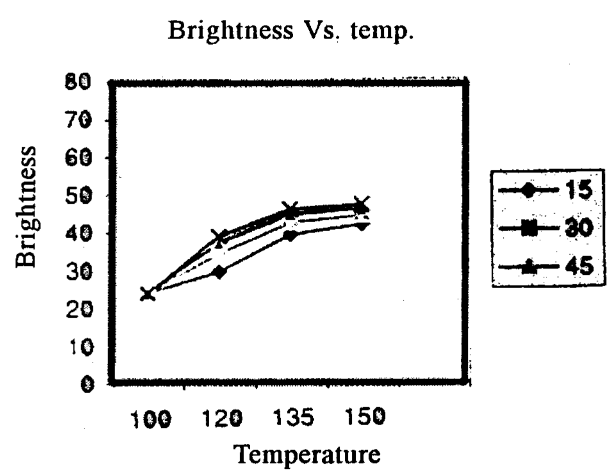

Fig. 1 Effect of temperature on brightness with time as parameter.

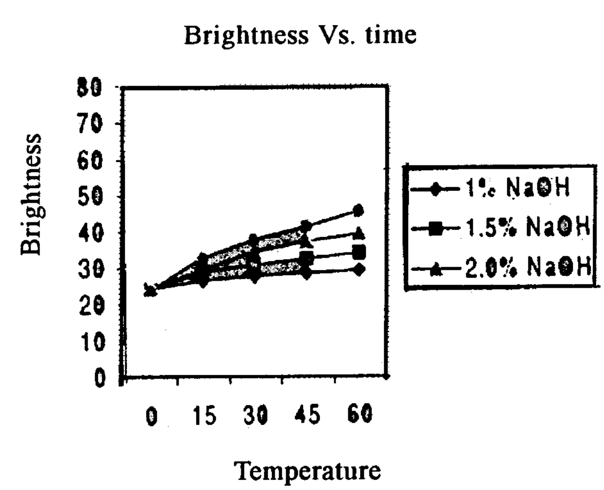

Fig. 2 Effect of time on brightness with alkali dose as parameter.

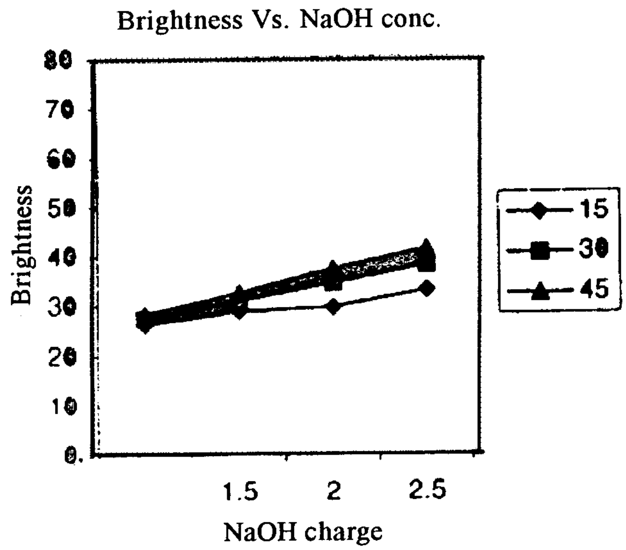

Fig. 3 Effect of time on brightness with time as parameter.

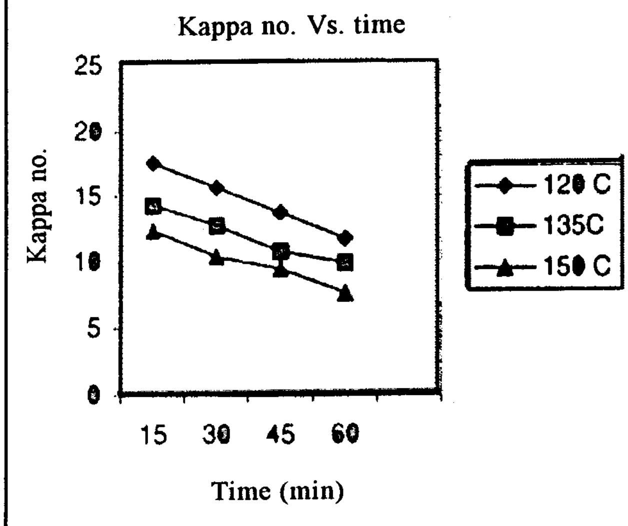

Fig. 5 Effect of reaction time on kappa with time as parameter.

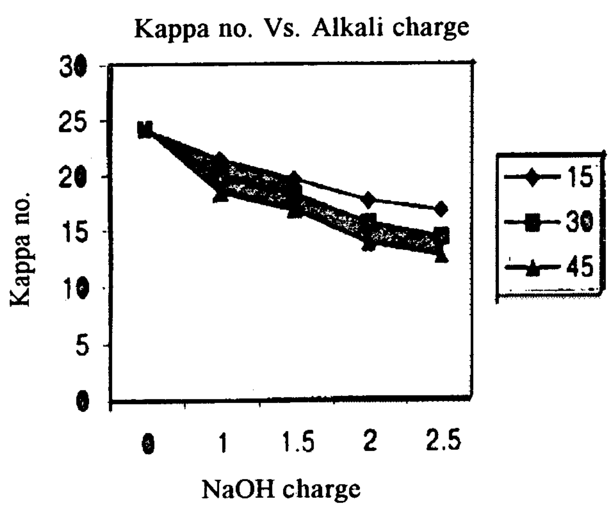

Fig. 4 Effect of alkali charge on brightness with time as parameter.

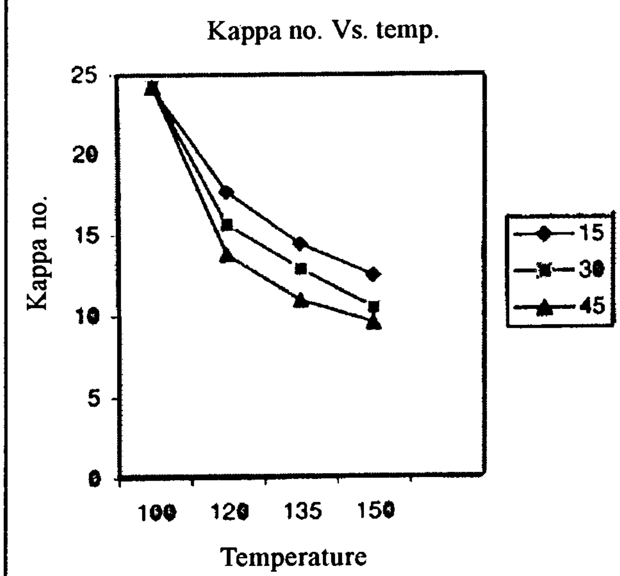

Fig. 6 Effect of temperature on kappa number with time as parameter.

alkali charge, time & temperature within the range specified. It is found that for a 10°C rise in temperature, rate of change of brightness is proportional to the alkali dose.

Effect on the kappa number of the pulp

The variation of kappa number plotted as a function of the above parameters is shown in Fig. 4-6. As anticipated, within the range specified there is a sharp drop in the kappa number with the temperature, time and alkali charge. It is observed that in the initial phase of the experiment, for a 10°C rise in temperature, kappa number changes approximately by 10% independent of the alkali dose variation.

Effect on the Viscosity of the pulp

The reduction of the viscosity of the pulp as a function of alkali dose, time and temperature is shown in Fig. 7-9. The profilers are very much clear and evident stating that increase of temperature, time or alkali dose greatly degrade the pulp strength i.e. reduces the viscosity values of the pulp. It is found that in the phase of the experiment, for a 10°C rise in temperature, viscosity reduction is nearly 10% independent of the alkali dose variation. Also, reduction in pulp viscosity increases with the increase in temperature.

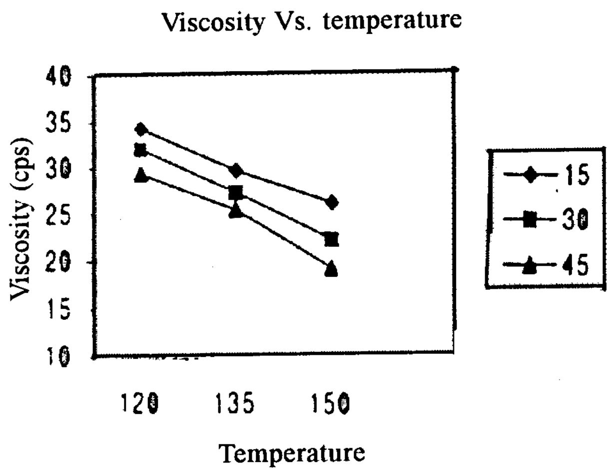

Fig. 7 Effect of temperature on viscosity with time as parameter.

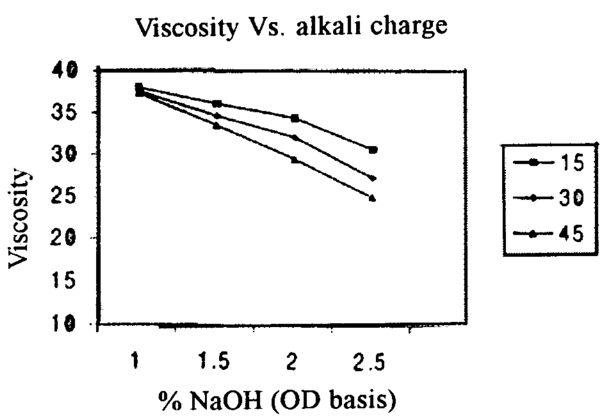

Fig. 8 Effect of alkali dose on pulp viscosity with time as parameter.

Relationship between kappa number and brightness values

It is observed from Fig. 10 that brightenss possesses a nearly straight line relationship with the kappa number of the oxygen delignfied pulp. This is an established fact and does not need explanation.

Development of statistical model and its validation

Statistical non-linear, multivariate regression equations for kappa number and viscosity are developed as per the procedure laid down in the Appendix. The design matrix is given in Table 2. The equations developed through Box Wilson orthogonal rotatable design are given below:

$$Y_{kappa}=70.12-0.1613*Z_1-0.914*Z_2-2.28*Z_3*8.44*10^{-4}*Z_1*Z_2=3.98*10^{-3}*Z_2^2$$

$$Y_{viscosity}=57.2+1.496*Z_{1.}0.466**Z_2-10.12*Z_3+2*10^{-3}*Z_2^2 0.0106*Z_1*Z_2-0.66*Z_1*Z_3$$

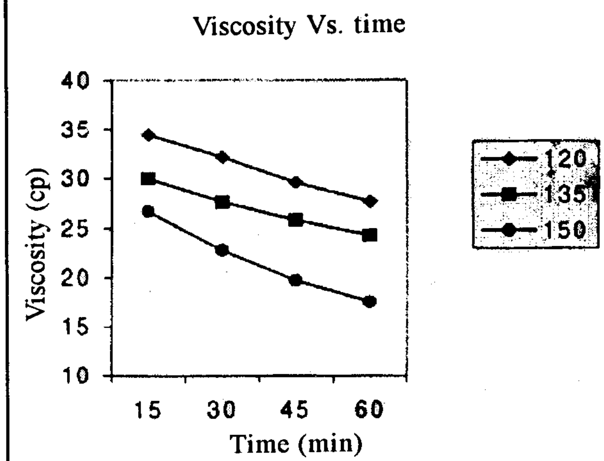

Fig. 9 Effect of time on pulp viscosity with temperature as variable.

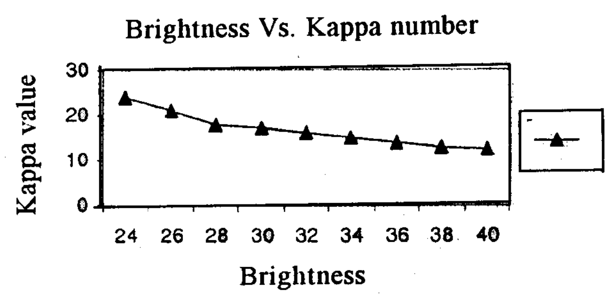

Fig. 10 Variation of brightness with kappa number of the oxygen delignified pulp.

$$0.068*Z_2*Z_3+4.09*10^{-3}*Z_1*Z_2*Z_3$$

where Z_1, Z_2 and Z_3 are the reaction time in minutes, reaction temperature in °C and alkali charge in % respectively.

Validation of the Model

It is an imperative necessity to compare the model with the experimental values to examine the suitability of the model. Within the stipulated data examined in the present investigation, the experimental and model predicted values are compared in Table 3. The difference in experimental values of kappa number and viscosity and those predicted from the model are shown in Fig. 11 and 12. From the spread of the data it is evident that model is quite accurate for the viscosity prediction but the kappa number model shows large deviations at some discrete points. This could be attributed to the following reasons:

- Experimental errors subjected to changing conditions of working temperatures, humidity levels and errors in taking the readings.
- Some of the terms neglected in the regression equation might have some influence.

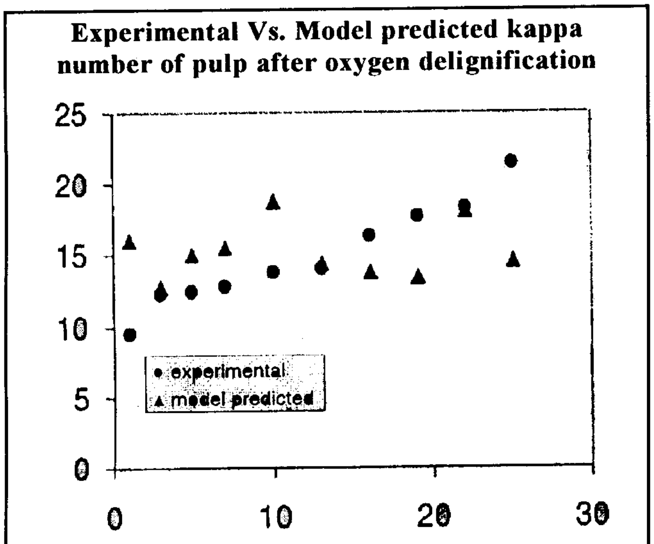

Fig. 11 Comparison of the experimental and model predicted kappa number.

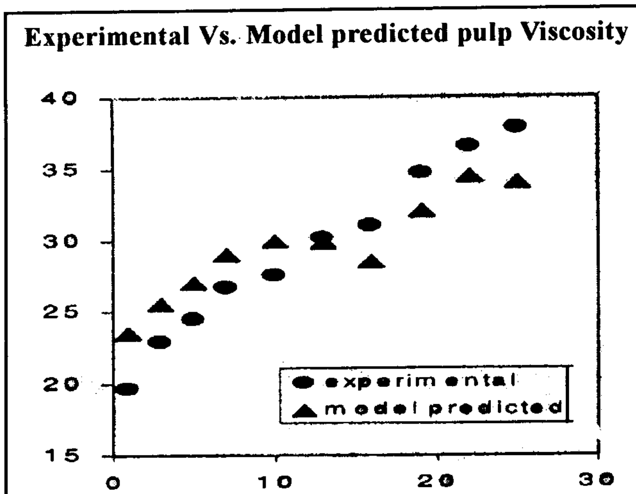

Fig. 12 Comparison of the experimental and model predicted viscosities of the pulp after oxygen delignification.

Comparison of various bleaching sequences

The overall brightness of pulp and effluent parameters like BOD & COD and cost of the bleaching (calculated only on the chemical consumption) are compared in Fig. 13. It is apparent from the data reported that use of oxygen increases the brightness with substantial decrease in the bleaching cost and BOD & COD values. The BOD & COD values are quite high for the conventional sequence (CEHH). With the use of oxygen in the first stage of CEHH sequence (for same brightness level) COD reduction is about 50%, whereas the BOD reduction is close to 64%, while the use of oxygen in the first stage of DE_pD sequence (for the same brightness level) reduces the COD by approx. 50% and BOD by 62%. Use of oxygen also lowers the bleaching cost since oxygen is relatively cheaper than the other bleaching chemicals but the effect of oxygen is significant only in terms of reducing the invironmental impact of the bleach plant. As the cost analysis is made only on the basis of chemical consumption, detailed calculations are required including the effluent treatment costs for the overall optimization of the process.

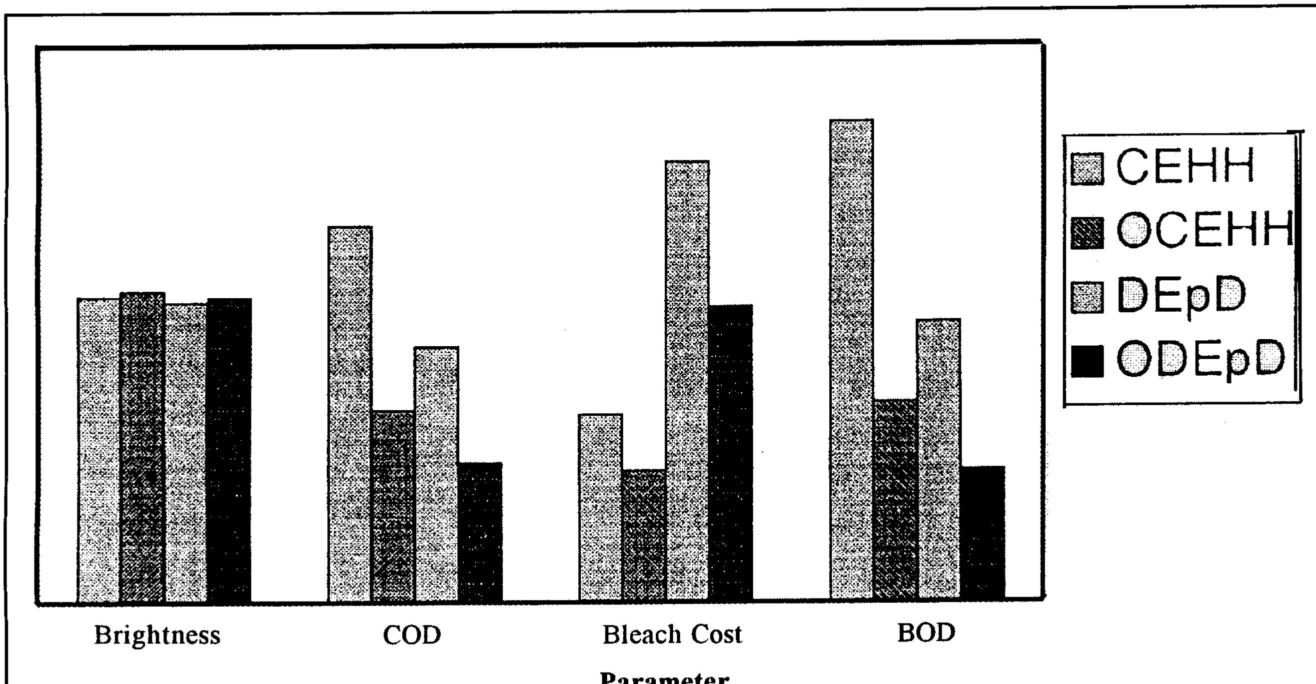

Fig. 13 Comparison of different bleaching sequences

This is just a prelude to the ways of optimizing various bleaching sequence by statistical experimental design which will be attempted in the future.

CONCLUSION

Oxygen delignification is carried out at different temperatures, reaction time and alkali doses to develop a non-linear, multivariate statistical model according to the statistical rotatable factorial design. Multivariable orthogonal regression equations are developed to examine the effect the various parameters of the oxygen bleaching of the pulp. Investigation has been carried out to examine the effect of elemental chlorine free bleaching sequences, namely DE_PD and ODE_PD on the final brightness of the pulp and the extent of environmental parameters such as BOD & COD values. Typical mixed pulp composed of (eucalyptus + bamboo + poplar) is tried for experimental evaluation. The values are also compared when oxygen pre-bleached pulp is used for usually followed sequence (CEHH) by many Indian mills. Parallel experiments have been conducted for the conventional sequence (CEHH). On comparing the various sequences, it is found that oxygen predelignified pulp slightly increases the brightness values while decrease both BOD and COD values. The use of oxygen in the first stage also reduces the cost of the bleach chemicals. COD reduction is found to be 50% while BOD reduction is of the order of 65%. The multi variable orthogonal regression equations developed for the kappa number and the viscosity of the pulp are given below:

$$Y_{kappa}=70.12-0.1613*Z_1-0.914*Z_2-2.28*Z_3*8.44*10^{-4}*Z_1*Z_2=3.98*10^{-3}*Z_2^2$$

$$Y_{viscosity}=57.1.49*Z_{1-}0.466**Z_2-10.12*Z_3+2*10^{-3}*Z_2^2\ 0.0106*Z_1*Z_2-0.66*Z_1*Z_3-0.068*Z_2*Z_3+4.09*10^{-3}*10^{-3}*Z_1*Z_2*Z_3$$

where Z_1, Z_2 and Z_3 are the reaction time in minutes, reaction temperature in °C and alkali charge in % respectively.

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