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INFLUENCE OF COOKING VARIABLES OF CRIMEAN PINE (*PINUS NIGRA* ARNOLD SBSP. *PALLASSIANA*) KRAFT PULP ON THE RESULTING PAPER SHEETS

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ABSTRACT

A central composite factorial design was used to examine the influence of independent variables of kraft pulping of Crimean Pine wood chips at 50 Schopper-Riegler (°SR) level.

Second order polynomial regression equations related each dependent variable to the different independent variables were obtained that reproduced the experimental results for the PFI beating revolutions, breaking length, burst index, tear index, stretch and brightness at 50 °SR obtained at sulphidity, H-factor and active alkali rates over the ranges 15-45%, 800-2400 and 14-22% respectively, with average errors less than %20.

To minimize environmental effects of sulphide and acceptable levels of the properties of the paper sheets, low sulphidity rate, high H-factor and medium alkali concentration can be used.

KEY WORDS: kraft pulping, modelling, *Crimean Pine*, paper properties

INTRODUCTION

Until 1950's sulphite method was the most production rate, but now it has 10% of total pulp production in the world. Currently, the most pulp and paper production is being done with kraft pulping method (Johansson et al. 1987). Kraft pulping of wood is very complex process with several stages in homogeneous phase. There are a lot of factors which effect and determine the process and product quality. Among these, as pulping temperature, time at temperature, sulphidity rate, alkali charge, wood to liquor ratio are the most important independent variables affecting the cooking process (Bojana and Kopitovič 1995).

Most of the annual plant and hardwoods have short fibres; whereas softwoods have generally long fibres. For that reason, it is known that softwoods have a special importance in paper and board industry (Anonym 2000). Resources of Crimean pine (*Pinu negra)* are largely available in the Northwest Region of Turkey. Crimean pine areas are 2.200.000 ha. (Karadağ 1999). Altough modelling of the Crimean pine kraft pulping results did not studied before.

Modelling the pulping process supports decision-making by allowing estimation of pulp quality and calculation of operational costs under different process conditions. The most important process parameters can be determined and used to facilitate process engineering and safety precautions. Especially empirical models describing the influence of the independent variables, on dependent variables, were derived from the experimental data. These models were used to find the optimum conditions for delignification. Many examples of pulping models are found in the literature. Most studies concern mathematical models based on empirical results (Hotton 1973).

These empirical models are to be preferred to theoretical ones as the latter become rather complex when more than two independent variables are involved (Jimenez et al. 2001).

Such a model is most often based on a time-temperature study, resulting in an equation that gives the lignin dissolution as a function of the time and temperature variable known, as Vroom (Vroom 1957) referred to the H-Factor. The result of pulping depends on a great number of variables among which the most important is the time-temperature variable and the alkali concentration in cooking liquor (Masura 1999).

The objective of this work is to develop a mathematical model in which the three important kraft pulping process variables – sulphidity rate, H-factor (combined time and temperature) and active alkali charge – are used to predict paper sheets quality made by Crimean Pine wood. The response variables are beating revolution, breaking length, stretch, burst index, tear index and brightness. Consequently a central composite design was used for the experimental layout.

MATERIAL AND METHODS

Raw Material

Air-dried Crimean Pine woods were (*Pinus nigra* Arnold sbsp. *pallassiana*) obtained from four different geographic zone of West Black sea region of Turkey, the chemical composition of which were presented in Tab. 1.

Tab. 1: Chemical Composition of Crimean Pine Wood

Compositions	Weight content (%) o.d. basis
Holocelluluse	72,34
Cellulose	51,89
α - Cellulose	43,55
Lignin	26,4
Ash	0,18
Solubility in alcohol-benzene	3,45
Solubility in cold water	2,02
Solubility in hot water	3,17
Solubility in %1'lik NaOH	13,0

Analysis of raw material, pulps and paper sheets

The chemical analysis of the untreated wood samples and products were characterized according to the following standard methods: holocellulose (Wise and John 1952), method (Wise and John

1952), lignin (Tappi 211 om-88), cellulose (Kurschner-Hoffer's nitric acid method) (Browning 1967), α-cellulose (Tappi 203 os-61), ash (Tappi 211 om-85), solubility in alcohol-benzene (Tappi 204 om-88), solubility in %1 sodium hydroxide (Tappi 212 om-88), solubility in cold and hot water (Tappi 207 om-88), Shopper-Riegler index (Scan-c 20:65), breaking length and stretch (Tappi 404 om-92), burst index (Tappi 403 om-91), tear index (Tappi 414 om-88) and brightness (Tappi 452 om-92). In order to perform uniform pulping conditions the starting materials were chipped as 20 x 20 x (20-40) mm., air-dried and used for pulping.

Pulping and hand-sheet making

Crimean pine wood chips were pulped in a laboratory type rotary digester that was heated electrically and governed with digital temperature control system. Pulps obtained from the trials were washed, disintegrated in a laboratory type pulp mixer with 2 liters capacity and screened on a Noram type pulp screen with 0.15 mm slotted plate.

Beating of the produced pulp was done in a PFI mill at constant 50 °SR. Then, handsheets were prepared with Frank's Rapid Köthen paper machine according to Zellcheming Marlblat 108 standard method. Handsheets were conditioned according to Tappi T 402 om-88 procedure and their physical and optical properties were tested with relevant standard methods (bursting index: Tappi T 403, tearing index: Tappi T 414 om-88, breaking length and stretch: Tappi T 494 om-88 and brightness: Tappi T 452 om-92).

Experimental design

A central composite experimental design was used to outline the composition of the experimental process condition around a central combination. The tested model uses a series of points (experiments) around a central one (the central experiment) and several additional points (additional experiments) on the axes to allow estimation of the first- and second-order interaction terms of a polynomial. This design satisfy the general requirement that all parameters of a polynomial model can be estimated without the number of observations becoming excessive, and that the observations be spread fairly evenly over the experimental region of interest (Montgomery 1998, Mead 1994).

In this study 2^m central composite design were used with three dependent variables, Sulphidity rate (S), Vroom's H-factor (H) (Vroom 1957) and active alkali charge (A). Based on the following equation (Press et al. 1992);

$$n = 2^m + 2m + 1 \quad (1)$$

Where m is the number of independent variables, the total number of observations (experiments) was found to be 15.

This design allowed determination of the effects of degree two or less on the dependent variables RV (beating revolution), BL (breaking length), ST (stretch), BI (burst index), TI (tear index) and BR (brightness). The experimental data was fitted to the following second-order polynomial;

$$Z = a + bX_S + cX_H + dX_A + eX_S^2 + fX_H^2 + gX_A^2 + hX_SX_H + i\,X_SX_A + jX_HX_A \quad (2)$$

Where Z denotes response variables (dependent variables), X_S, X_H and X_A the normalized values of S, H and A, and letters a - j show constants.

The values of the independent variables were normalized from –1 to +1 by using Eq. (3) in order to facilitate direct comparison of the coefficients and visualising of the effects of the individual independent variables on the response variable;

$$X_n = 2\frac{X - \bar{X}}{X_{max} - X_{min}} \quad (3)$$

Where X_n is the normalized value of *S*, *H* or *A*; *X* is the absolute experimental value of the variable concerned; $\bar{X}$ is the mean of all the experimental values for the variable in question; and X_{max} and X_{min} are maximum and minimum value, respectively, of such a variable. This normalization also results in more accurate estimates of the regression coefficients as it reduces interrelationship between linear and quadratic terms (Aknazarova and Kafarov 1982).

The 15 experiments conducted together with the corresponding normalized values for the independent variables are given in Tab. 2.

Tab. 2: Conditions used in kraft pulping of Crimean Pine and experimental results for the beating revolution and properties of the paper sheets obtained

X_S	X_H	X_A	BR, *%BaSO$_4$*	BL, *km*	BI, *kpa.m^2/g*	TI, *mN.m^2/g*	ST, *%*	RV
-1	-1	-1	21,90	7,23	3,99	11,82	2,91	1000
-1	-1	1	22,20	6,85	3,88	12,53	2,63	855
-1	0	0	22,10	6,24	3,66	10,15	2,23	740
-1	1	-1	15,60	6,65	4,00	10,38	3,50	1010
-1	1	1	25,10	4,22	1,92	7,37	1,68	300
0	-1	0	20,30	6,22	4,08	9,20	2,71	1015
0	0	-1	16,8	6,38	3,72	10,00	3,36	940
0	**0**	**0**	**20,00**	**6,31**	**3,33**	**8,20**	**2,10**	**725**
0	0	1	21,30	5,35	2,81	9,10	1,87	525
0	1	0	19,90	5,87	2,89	9,28	1,79	600
1	-1	-1	15,00	7,02	3,80	9,30	2,80	980
1	-1	1	21,30	6,45	4,34	9,77	2,75	865
1	0	0	19,70	7,28	4,70	8,32	2,84	940
1	1	-1	14,80	7,09	4,43	9,05	3,03	1000
1	1	1	22,10	5,20	2,73	8,60	2,22	655

[a]X_S= Normalized sulphidity concentration; X_H= Normalized H-Factor; X_A= Normalized active alkali charge; BR=Brightness ;BL=Breaking length; ST=Stretch; BI=Bursting index; TI=Tearing index; RV=Beating revolution

RESULTS AND DISCUSSION

To determine the mean values of the independent variables (30% sulphidity rate, 1600 H-factor and 18% alkali charge) a lot of preliminary experiments was conducted. The experimental results obtained in the determinations of the dependent variables are in listed in eight rows, Tab. 2 along with the mean value. The other experiments, corresponding to the experimental design adopted, provided the results shown in the other rows. The independent variables were varied over the following ranges; 15-45% sulphidity rate, 800-2400 H-factor and 14-22% active alkali charge. A constant liquid/solid ratio (1/4) was used in all experiments.

The SPSS 10.0, statistical software package (SPSS Production facility 1997) was used to conduct a multiple linear regression analyses involving all the terms of Eq. (2) using backward method. The coefficients of the terms in the equations, F-values and R^2 values for the fitted lines, are shown in Tab. 3.

Tab. 3: Coefficients of the equations that relate the dependent and independent variables

Coefficients and r^2 and F values of equations	Equations					
	BR	**BL**	**ST**	**BI**	**TI**	**RV**
a	+19,87	+6,03	+2,33	+3,52	+9,54	+810
b	-1,4	-	-	+0,26	-0,72	-
c	-	-0,47	-	-0,41	-0,79	-115
d	+2,79	-0,63	-0,45	-0,43	-	-173
e	-	+0,4	-	+0,53	-	-
f	-	-	-	-	-	-
g	-	-	+0,34	-0,38	-	-
h	-	+0,25	-	-	+0,65	-
ı	-	-	-	-	-	-
j	+1,28	-0,42	-0,29	-0,53	-0,58	-99,38
F	22,75	11,33	8,43	15,30	5,86	14,07
R^2	**0,86**	**0,86**	**0,70**	**0,92**	**0,70**	**0,79**

[a]; BR=Brightness; BL=Breaking length; ST=Stretch; BI=Burst index; TI=Tear index; RV=Beating revolution

For example, calculated brightness values were obtained from the Eq. (4) with errors less than maximum %13.

$$BR = 19,87 - 1,4\,X_S + 2,79\,X_A + 1,28\,X_H X_A \quad (4)$$

The steepest ascent method (Press et al. 1992) was applied to Eq. (Karadağ 1999) in order to determine the maximum brightness value over the ranges studied for the process variables (normalized values from –1 to +1 for all); the maximum brightness value for a high H-factor and alkali charge, in addition to low sulphidity concentration was 25.34% (Tab. 4).

It seems from Tab. 4 that Eq. (Karadağ 1999) allows estimating of the variation of the brightness value with changes in each independent variable over the range considered on constancy of the other two variables. With constant sulphidity rate, H-factor and alkali charge at their normalized values –1, +1 and +1 respectively, the maximum changes in brightness value from variation of the active alkali charge (3,57 units or 14.09% with respect to the maximum value) and the smallest ones from the H-factor (1,28 units or 5,05%) and from the sulphidity charge (1,4 units or 5,52%); the brightness is thus much more sensitive to changes in alkali charge than in H-factor and sulphidity rate (Fig. 1).

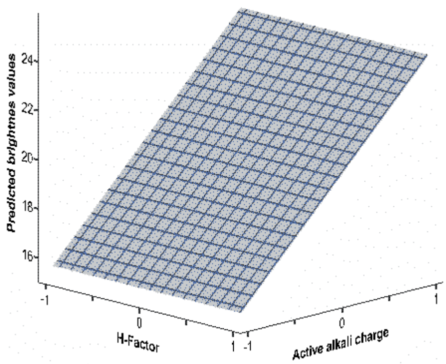

Fig. 1: Brigtness values variations H-factor and active alkali charge at short sulphidity rate (15%)

Tab. 4: Optimum values of the dependent variables and variation with changes in the independent variables in the kraft pulping of Crimean Pine

Dependent variables	Maximum percent errors made in estimating the dependent variables with respect to the experimental values	Optimum (maximum) value	Normalized values of the independent variables leading to optimum values of the dependent variables			Maximum changes in the dependent variables (in units and percentages with respect to the optimum values, which are shown in brackets) with changes in the dependent variables (from –1 to +1)		
			X_S	X_H	X_A	S	H	A
Brightness	13	25,34%	-1	+1	+1	1,4% (5,52%)	1,28%(5,05%)	3,57% (14,09%)
Breaking length	12	7360 m	-1	-1	-1	250 m (3,4%)	300 m (4,08%)	210 m (2,85%)
Stretch	30	3,41%	-	+1	-1	-	0,29% (8,5%)	0,74% (21,7%)
Burst index	11	4,46 kpa.m^2/g	+1	+1	-1	0,26kN/g (5,83%)	0,12 kN/g (2,69%)	0,96 kN/g (21,52%)
Tear index	16	12,28 mNm^2/g	-1	-1	+1	0,07 mNm^2/g (0,57%)	2,07 mNm^2/g (16,45%)	0,58 mNm^2/g (4,72%)
Beating revolution	41	999 rv/min (max)	-	-1	-1	-	31,62rv/min (3,7%)	147,62rv/min (14,78%)
		423 rv/min (min.)	-	+1	+1	-	428,38rv/min(101,27%)	544,38rv/min(128,70%)

From the foregoing it follows that, with a low value of H-factor in addition to a low sulphidity and high alkali charge, the brightness decreases to 24,06%, i.e., by only 5,05% with respect to its highest level (25,34%).

The equations that relate the dependent variables to the independent ones reproduce the results for the former with errors less than 16%, beating revolution and excepted stretch as shown in Tab. 4. Beating revolution didn't effect the sulphidity charge for kraft pulps at the constant °SR. For minimum calculated beating revolution value, it is advisable to use high H-factor and alkali charge (normalized values of +1); thus the lowest revolution value obtained is 423 rv/min. At the lowest beating revolution level, changes in value are more sensitive to variations of H-factor (428.38 units or 101.27%) and active alkali charge (544,38 units or 128,7%) than highest beating revolution value (999 rv/min).

The results of the Tab. 4 were obtained by using a similar procedure with the other dependent variables. Fitted values for burst index, beating revolution and breaking length, calculated from the estimated polynomial equations, were compared with the experimental results for dependent variables and showed in Fig. 2, Fig. 3 and Fig. 4 respectively. When compared with the literature for paper sheet properties, the models give acceptable fit for the pulping data as indicated by R^2 values of 0,79%, 0,86%, 0,70%, 0,92%, 0,70% and 0,86% for beating revolution, breaking length, stretch, burst index, tear index and brightness respectively. The somewhat lower values for some dependent variables are most likely due to the high sensitivity of them dependent to differences in pulping and especially papermaking conditions which were probably not captured by the model.

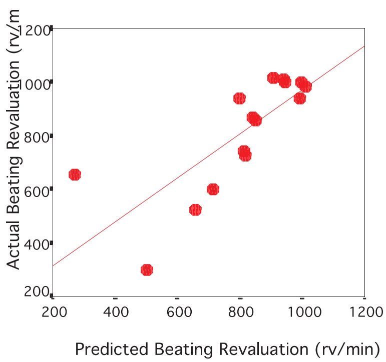

Fig. 2: Actual dependent beating revolution values versus predicted from model equation

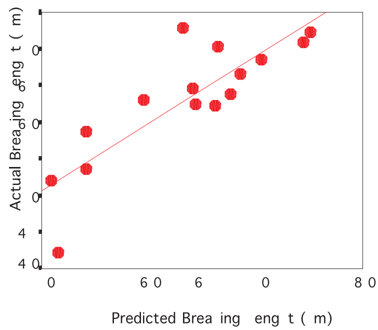

Fig. 3: Actual dependent breaking length values versus predicted from model equation

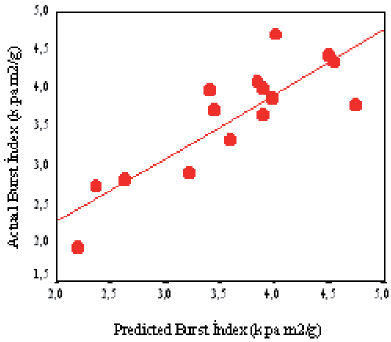

Fig. 4: Actual dependent burst index values versus predicted from model equation

Also the optimum (the highest values except beating revolution) values of the dependent variables, as well as the corresponding values of the independent variables related to them can be seen in Tab. 4. It shows the variation of the dependent variables which changes in each independent variable from –1 to +1 on constancy of all others at the values required obtaining the optimum values of the dependent ones; values are expressed in units of the dependent variable concerned and as percentages relative to the optimum values of the dependent variables.

In Tab. 4, the H-factor level and the active alkali charge are most strongly influencing all the dependent variables, low sulphidity charge or not must be used in order to ensure optimal resulting paper properties. Also, the use of a high H-factor is recommended except tear index and breaking length as can be seen in Fig. 5 and Fig 6. To obtain maximum tear index, low sulphidity rate and H-factor level and high alkali charge is recommended. Besides for minimum beating revolution and maximum breaking length, stretch and burst index, low active alkali concentration is more effective.

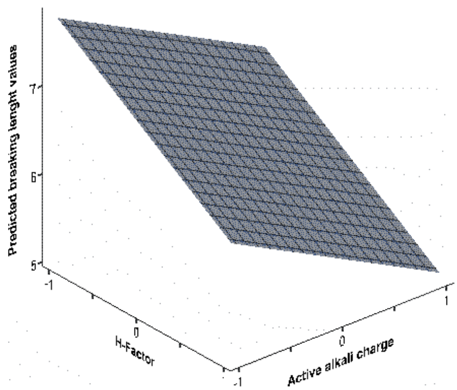

Fig. 5: Breaking lenght variations H-factor and active alkali charge at short Sulphidity rate (15%)

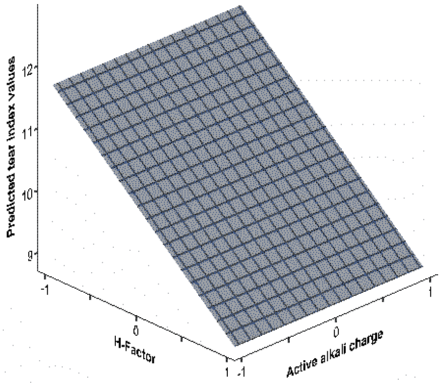

Fig: 6. Tear index variations H-factor and active alkali charge at short sulphidity rate (15%)

CONCLUSIONS

Obtaining the optimum burst index, brightness, stretch of the paper sheets and beating revolution (4.46 k.Pa.m2/g, 25.34 %, 3.41 % and 423 rv/min. respectively) entails using maximum H-factor. The optimum tear index (12.28 mNm2/g) is achieved with a minimum sulphidity, low H-factor and high alkali charge. Maximum breaking length (7360 m) of the paper sheets was obtained at low sulphidity rate, H-factor level and alkali charge. While PFI beating revolution isn't affected by sulphidity changes, the high Sulphidity rate (45 %) was recommended for obtaining the best burst index.

It is clearly stated that to minimize environmental effects of sulphide and acceptable levels of the properties of the paper sheets, low sulphidity rate, high H-factor and medium alkali concentration can be used.

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REFERENCES

1. Aknazarova S., Kafarov, V., 1982: Experiment optimisation in chemistry and chemical engineering, Moscow, Mir Publisher
2. Anonim, 2000: Devlet Planlama Teşkilatı, 8. Beş Yıllık Kalkınma Planı Kağıtçılık Özel İhtisas Komisyonu Raporu, Yayın No: DPT: 2525-OIK: Ankara, 541 pp.
3. Bojana,K., Kopitovič, S., 1995: Mathematical model of sulphate pulping of poplar wood, Drevársky Výskum (Wood Research), 1: 35-47
4. Browning, B.L., 1967: Methods of wood chemistry, Vol:II, Interscience Publishers, New York

5. Hotton, J.V., 1973: Process control in kraft pulping, Tappi Journal, 56(7): 97-100
6. Jimenez, L., Garcia, J.C., Perez, I. and Ferrer, J.L., 2001: Chica, A., Influence of the operating conditions in the asetone pulping of wheat straw on the properties of the resulting paper sheets, Bioresource technology, 79: 23-27
7. Johansson, A., Altonen, O. and Ylinen, P., 1987: Organosolv pulping methods and pulping properties, Biomass, 13: 45-45
8. Karadağ, M., 1999: Batı Karadeniz Bölgesinde Karaçam Doğal Gençleştirme Koşulları Üzerine Araştırmalar, Batı Karadeniz O. A. E. Yayınları, Teknik Bülten no: 4, Bolu
9. Masura, V., 1999: A mathematical model of kraft pulping related to the alkali concentration in the cooking liquor, Wood science of technology, 33: 381-389
10. Mead, R., 1994: The design of experiments, Cambridge University Press, Cambridge, Pp. 538-576
11. Montgomery, D.C., 1998: Design and analyses of experiments, John Willey and Sons, Inc., New York
12. Press, W.H., Teukolsky, S.A., Vetterling, W.T. and Flannery, B.B., 1992: Numerical recipes in C: The art of scientific computing, Cambridge University Press, Cambridge
13. SPSS Production facility (1997) Release 10.0, Copyright (c) SPSS Inc.
14. Vroom, K.E., 1957: Computing of H-Factor, Pulp and Paper Magazine of Canada, 58: 228-231
15. Wise, L.E., John, E.C., 1952: Wood Chemistry, 2. Ed. Vol:1-2, Reinhold Publication Co., New York, USA

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