INFLUENCE OF PULPING CONDITIONS ON THE PROPERTIES OF ANATOLIAN BLACK PINE (*PINUS NIGRA* ARNOLD SSP. *PALLASSIANA*) KRAFT PULPS

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ABSTRACT

Anatolian Black Pine wood chips were pulped using kraft method in laboratory scale batch digester. A series of experimental kraft pulping was carried out according to Central Composite Design (CCD) to investigate the pulping process and to study the effect of its variables (active alkali rate, sulphidity rate and Vroom’s H-factor combining temperature and time) on pulp quality and yield. Second order polynomial regression equations using three independent process variables, were found to be appropriate for describing kraft pulping of Anatolian Black Pine wood fibers. The derived equations were able to predict the kappa number, viscosity, yield, holocellulose and α-cellulose content of the pulp with adjusted $R^2$ values of 96.1%, 96.8%, 86.3%, 62.3%, 96.1% and 92.2% respectively. H-factor level and the active alkali charge are the most strongly influencing all the dependent variables. In order to obtain acceptable levels of the pulp properties, high sulphidity rate (45%), medium H-factor (1600) and medium alkali concentration (18 %) can be used in kraft pulping of Anatolian Black Pine woods.

Keywords: kraft pulping, modelling, Anatolian Black Pine, Pulp Properties

Introduction

Kraft method is a common pulping technology all over the world. Nowadays, most of the chemical pulp used in the papermaking was made kraft process (%90 of the total production) in the world (7). Kraft pulping of wood is very complex process with several stages in heterogeneous phase. There are a lot of factors effecting and determining the process and product quality. However, independent variables are the main technological parameters of the process (pulping temperature, time at temperature, sulphidity rate, alkali charge, wood to liquor ratio, etc.) (3-19).

Anatolian Black Pine forests have the largest spread area after Calabrian Pine (approximately 2.200.000 ha. of total forest area) and its using in pulp and paper industry is insufficient and there is no study about suitability of this wood species for domestic paper industry in Turkey (15). On the other hand, soft woods having long fibers have a special importance in paper and board industry, whereas hardwoods and the most annual plants give short fibers (2).

In a pulping operation, the control of production and quality starts first with modelling of processes. Modelling of a system supports decision making by allowing estimation of pulp quality and calculation of operational costs under different process conditions (29). 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 (4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, 18, 20, 22, 25, 26, 27, 28, 29). Obtained empirical models are to be preferred to theoretical ones as the latter become rather complex when more than two independent variables are involved (13).

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 temperature variable known, according to Vroom 1957 (30), as 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 (21).

In this study, a central composite design was developed to predict of six different pulp properties (kappa number, viscosity, screened yield, total yield, holocellulose and α-cellulose contents of pulp) and, sulphidity, H-factor and active alkali ratio were chosen as depended variables.

Materials and Methods

Raw material

Anatolian Black Pine (*Pinus nigra* Arnold ssp. *pallassiana*) wood specimens were obtained from four different geographic zone of West Blacksea region of Turkey. In the previous study, the chemical composition of the wood was determined to be Holocellulose; 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% NaOH; 13.0% (17).
Pulping and pulp properties

Pulping trials were carried out in a 15 l. batch cylindrical reactor which was heated electrically. Temperature was controlled by Omron E5CK type digital controller unit in the range of ±0.2 °C, cooked material was disintegrated by a laboratory type 2 l. pulp mixer for 10 min. at 2% consistency. Then, the pulp was fractionated on a Noram type laboratory type pulp screen with 0.15 mm slots. Reject ratios, screened pulp yields and total yields were calculated on oven dry wood chips.

Experimental design

A central composite 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 satisfies the general requirement that all parameters of a polynomial model can be estimated without the number of observations becoming excessive, and that the observations can be spread fairly evenly over the experimental region of interest (23, 24).

In this study a 2^m central composite design was used with three dependent variables, Sulphidity rate (S), Vroom’s H-factor (H) (30) and active alkali charge (A). Based on the following equation /1/;

\[ n = 2^m + 2m + 1 /1/ \]

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 VS= viscosity, KN= kappa no, TY= total yield, SY= screened yield, HO= holocellulose, \( \alpha \)-C= \( \alpha \)-cellulose. The experimental data was fitted to the following second-order polynomial;

\[ Z = a + bX_s + cX_H + dX_A + eX_s^2 + \]
\[ + fX_H^2 + gX_A^2 + hX_sX_H + iX_sX_A + jX_HX_A /2/ \]

Where \( Z \) denotes response variables (dependent variables), \( X_s \), \( X_H \) and \( X_A \) the normalized values of S, H and A, and than a to 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 visualization of the effects of the individual independent variables on the response variable;

\[ X_n = 2 \frac{X - \bar{X}}{X_{\text{max}} - X_{\text{min}}} /3/ \]

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 \( X_{\text{max}} \) and \( X_{\text{min}} \) are maximum and minimum value, respectively, of such a variable. This normalization also result in more accurate estimates of the regression coefficients as it reduces interrelationship between linear and quadratic terms (24).

The 15 experiments conducted, together with the corresponding normalized values for the independent variables are given in Table 1. Obtained experimental data, as shown in the table, was duplicated for calculating standart errors.

Results and Discussion

To determine the mean values of the independent variables (30% sulphidity rate, 1600 H-factor and 18% alkali charge) a lot

<table>
<thead>
<tr>
<th>Trial no</th>
<th>( X_s )</th>
<th>( X_H )</th>
<th>( X_A )</th>
<th>VS, cm³/g</th>
<th>KN</th>
<th>TY, %</th>
<th>SY, %</th>
<th>HO, %</th>
<th>( \alpha )-C, %</th>
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<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>983</td>
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<td>2.98</td>
<td>81.13</td>
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<td>-1</td>
<td>1</td>
<td>801</td>
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<td>45.4</td>
<td>44.31</td>
<td>91.54</td>
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<td>0</td>
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<td>0</td>
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<td>812</td>
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<td>46.0</td>
<td>45.62</td>
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<td>0</td>
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<td>43.75</td>
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<td>910</td>
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<td>44.60</td>
<td>92.42</td>
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<td>1</td>
<td>1</td>
<td>577</td>
<td>20.8</td>
<td>41.9</td>
<td>41.86</td>
<td>95.82</td>
<td>83.17</td>
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</tbody>
</table>

\( X_s \)= Normalized sulphidity concentration; \( X_H \)= Normalized H-Factor; \( X_A \)= Normalized active alkali charge; VS= Viscosity, KN= Kappa no, TY= Total yield, SY= Screened yield, HO= Holocellulose, \( \alpha \)-C= \( \alpha \)-Cellulose
Coefﬁcients of the equations that relate the dependent and independent variables

<table>
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<th>Coefﬁcients and r², adjusted r² and standard error values of equations</th>
<th>Equations</th>
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<td></td>
<td>KN (1)</td>
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<tr>
<td>a</td>
<td>+39.089</td>
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<tr>
<td>b</td>
<td>-5.7</td>
</tr>
<tr>
<td>c</td>
<td>-13.4</td>
</tr>
<tr>
<td>d</td>
<td>-26.94</td>
</tr>
<tr>
<td>e</td>
<td>-</td>
</tr>
<tr>
<td>f</td>
<td>+8.53</td>
</tr>
<tr>
<td>g</td>
<td>+13.23</td>
</tr>
<tr>
<td>h</td>
<td>-</td>
</tr>
<tr>
<td>i</td>
<td>-</td>
</tr>
<tr>
<td>j</td>
<td>-</td>
</tr>
</tbody>
</table>

Standard Error

| | 5.44 | 41.39 | 2.41 | 7.03 | 0.83 | 0.94 |

\[
R^2 = 0.975 \quad 0.980 \quad 0.893 \quad 0.706 \quad 0.975 \quad 0.950 \\
\text{Adjusted } R^2 = 0.961 \quad 0.968 \quad 0.863 \quad 0.625 \quad 0.961 \quad 0.922 \\
\]

\[a = \text{Constant}, \quad b = \text{Sulphidity (S)}, \quad c = \text{H-factor (H)}, \quad d = \text{Active alkali rate (A)}, \quad e = S^2, \quad f = H^2, \quad g = A^2, \quad h = SxH, \quad i = SxA \text{ and } j = HxA, \quad \text{VS= Viscosity, KN= Kappa no, TY= Total yield, SY= Screened yield, HO= Holocellulose, } \alpha-C= \alpha-\text{Cellulose} \]

of preliminary experiments were conducted. The experimental results obtained in the determinations of the dependent variables different from the mean values are given in the eighth row of Table 1. The other experiments, corresponding to the experimental design adopted, provided the results as shown in the other rows. The independent variables 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 statistical packet program was used to conduct a multiple linear regression analyses involving all the terms of Eq. /2/ using stepwise method. The coefﬁcients of the terms in the equations, F-values and R² values for the ﬁtted lines, are shown in Table 2. To survive in the ﬁnal model, all terms should be signiﬁcant at a conﬁdence level of 95 % or higher. Consequently, the insigniﬁcant terms at a level of 0.05 were eliminated. The following equations /4, 5, 6, 7, 8 and 9/ are reduced models for each response.

Kappa no = 30.09 - 5.7b - 13.4 c - 26.94d + 8.53f + 13.23g /4/ 
Viscosity = 822.4 + 98.1b - 115.8c - 214.2d + 53.7 e - 6.79j /5/ 
Total yield = 46.04 - 3.49c - 6.1d + 3.26g /6/ 
Screened yield = 44.76 + 7.85d - 9.81i - 6.79 j /7/ 
Holocellulose content = 93.22 + 0.75b + 1.98c + 4.09d - 1.68f - 1.89g /8/ 
α-cellulose content = 80.236 + 0.93b + 1.47c + 3.12 d - 1.6 f - 1.43 g /9/ 

For example, calculated kappa number values were obtained from the Equation 1 with R²= 0.975 and 5.44 standard error value (Fig. 2). The interaction effect of active alkali charge and H-factor on kappa number in form of a response surface graph was shown in Fig. 6. 

Fig. 1 Relationship between predicted and observed viscosity values

Fig. 2 Relationship between predicted and observed kappa number
The lowest kappa number value was determined over the ranges of process variables studied (normalized values from –1 to +1 for all), thus minimum kappa number value calculated for a high H-factor, alkali charge and sulphidity concentration. It was obtained as 14.8.

Eq. 4 allows for the estimation of the variation of the kappa numbers with changes in each independent variable over the range considered on constancy of the other two variables. Maximum kappa number was obtained holding the sulphidity rate, H-factor and active alkali charge at their normalized values +1, +1 and +1 respectively within the limit of this study.

As can be seen in Table 3, changes at kappa number arising from active alkali variation were calculated maximum with 53.9 unit (or 364.2%). However, changing of H-factor and sulphidity charge from –1 to +1 effects on kappa number value at low degrees with 26.8 unit (or 181.2%) and 11.4 unit (or 77.02%) respectively. As a result, it can be stated that, %; the kappa number is thus much more sensitive to changes in alkali charge than in H-factor and sulphidity rate.

Total yield and screened yield values were not influenced from changing the sulphidity rate. Within the limit of this study, screened yield ranged from about 2.98% to 45.62% (Table 1) and total yield from about 40.0% to 64.7, typical for chemical pulping of wood. Inter-relationship of experimental total yield results and calculated from Equation 3 are given in Fig. 3 ($R^2 = 0.893$) and a response surface graph showing the
interaction effects of alkali charge and H-factor on total yield is presented in Figure 7.

Fig. 8 Variation of the holocellulose content with the active alkali charge and H-factor

The results of the Table 3 were obtained by using a similar procedure with the other dependent variables. Fitted values calculated from the estimated polynomial equations were compared with the experimental results for dependent variables in Figures 1, 2, 3, 4 and 5. When compared with the literature for pulp properties, the models give acceptable fit for the pulping data as indicated by $R^2$ value of 0.975%, 0.98%, 0.893%, 0.706%, 0.975% and 0.95% for kappa number, viscosity, total yield, screened yield, holocellulose rate and $\alpha$-cellulose rate respectively. The somewhat lower values for some dependent variables are most likely due to the high sensitivity of them dependent on differences in papermaking conditions which were probably not captured by the model. Because there are very extreme pulping condition in the used experimental plan, low explained variability of the screened yield were obtained ($R^2=0.706$ $P<0.05$).

The equations in Table 3 that relate the dependent variables to the independent ones reproduce the results for the former with errors less than 37%, screened yield excepted.

The optimum (highest) values of the dependent variables, as well as the corresponding values of the independent variables related to them are given in Table 3. It also 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.

As can be seen in Table 3, for optimum dependent variables, high sulphidity charge must be used in order to ensure optimal resulting pulp properties. But changing sulphidity rate is not affecting the yield values. High active alkali charge is recommended for optimum kappa no, screened yield, holocellulose and $\alpha$-cellulose content. But for maximum viscosity and total yield, lower alkali charge (-1) must be used. To obtain minimum kappa number and maximum holocellulose content, high H-factor is recommended. Variation of the holocellulose content with the active alkali charge and H-factor is shown in Fig. 8.

Table 3 also shows that as the independent variables the H-factor level and the active alkali charge are the most strongly influencing all the dependent variables. However high sulphidity rate is affecting the dependent variables except total and screened yield. In order to obtain acceptable levels of the pulp properties, high sulphidity rate (+1), medium H-factor (0) and medium alkali concentration (0) can be used in kraft pulping of Anatolian Black Pine woods.

**TABLE 3**

<table>
<thead>
<tr>
<th>Dependent variables</th>
<th>M.P.E</th>
<th>Optimum (maximum) value</th>
<th>Normalized values of the independent variables leading to optimum values of the dependent variables</th>
<th>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 independent variables (from –1 to +1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kappa number</td>
<td>31</td>
<td>14.8 (min.) +1 +1 +1</td>
<td>11.4 (%77.02) 26.8 (181.08) 53.9 (364.19%)</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>37</td>
<td>1233 cm$^3$/g +1 -1 -1</td>
<td>196 (%15.9) 89 (7.22%) 286 (23.2%)</td>
<td></td>
</tr>
<tr>
<td>Total yield</td>
<td>10</td>
<td>58.9 - -1 -1</td>
<td>7% (11.88%) 12.2% (20.71%)</td>
<td></td>
</tr>
<tr>
<td>Screened yield</td>
<td>672</td>
<td>%49.6 - -1 +1</td>
<td>13.6% (29.42%) 28.9% (58.27%)</td>
<td></td>
</tr>
<tr>
<td>Holocellulose content</td>
<td>2</td>
<td>%96.5 +1 +1 +1</td>
<td>1.5% (1.55%) 4% (4.15%) 8.2% (8.49%)</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Cellulose content</td>
<td>2</td>
<td>%82.9 +1 0 +1</td>
<td>1.9 (2.29%) 2.9% (3.5%) 6.3% (7.6%)</td>
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</tr>
</tbody>
</table>

M.P.E: Maximum percent errors made in estimating the dependent variables with respect to the experimental values
REFERENCES


