Effects of pulping conditions and black liquor on viscosity of softwood kraft black liquors: predictive models

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ABSTRACT: The effects of pulping conditions and black liquor composition on the kinematic viscosity of slash pine kraft black liquors from statistically designed pulping experiments have been studied. Very accurate predictive equations requiring five parameters at most were obtained using nonlinear regression procedures. These correlations can be used to estimate the viscosity of slash pine black liquors at process conditions from knowledge of pulping variables or black liquor solids composition. The analysis, using a quadratic response model, indicates that the viscous response of black liquor to both pulping variables and black liquor solids composition is highly nonlinear, and higher-order interactions are important when a predictive model is needed. Predictive models (of ten parameters) for viscosity behavior of slash pine black liquors at low solids concentrations (≤50% solids) as a function of the cooking conditions and composition of the liquors were obtained by using general linear regression models and using different statistical criteria.

KEYWORDS: Black liquors, cooking liquor composition, kraft liquors, lignins, models, pinus, *statistical analysis, statistical methods, variability, viscosity.*

In an earlier paper *(1),* two-dimensional viscosity plots were used to study the effects of black liquor composition on viscosity, and it was concluded that lignin concentration, lignin molecular weight, and sodium ion and other inorganic ion concentrations in black liquor make a significant contribution to viscosity. The effect of carbonates at low levels is not important and can be ignored. It was also shown that black liquor at low solids concentrations (≤ 50%) can be treated as a polymer solution *(2),* and theories developed for dilute polymer solutions were used to define the viscosity behavior of black liquors at concentrations lower than 50% solids. Because of the strong dependency of viscosity on temperature and solids concentration, it is difficult to use response surface methods to study the joint effect of variables on viscosity at every temperature and solids content. Since the effects of temperature and solids concentration on viscosity can be combined into a single variable by application of the correlation method based on corresponding states *(2)* for any black liquor of constant solids composition, data for individual liquors were used to develop such correlations for each liquor individually. Differences in such correlations for different liquors are the result only of differences in pulping conditions or of differences in the solids composition arising from differences in pulping conditions. In this manner, the effects of solids composition arising from differences in pulping conditions can be partitioned and correlated separately.

The correlations of reduced kinematic viscosity as a function of the combined variables for solids con-

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I. Constants of Eq. 1 for slash pine black liquors

Black liquor	$a_1 \times 10^{-2}$, °K	$a_2 \times 10^{-4}$, °K²	r^2	$a_2 \times 10^{-4}$ when a_1 is fixed, °K²	r^2
ABAFX011,12	1.943	184.71	0.997	164.59	0.996
ABAFX013,14	6.153	175.67	0.999	190.40	0.994
ABAFX015,16	4.760	168.04	0.998	174.06	0.993
ABAFX017,18	5.333	159.82	0.999	165.24	0.997
ABAFX019,20	5.403	172.09	0.999	177.04	0.998
ABAFX021,22	4.174	199.13	0.998	190.78	0.996
ABAFX023,24	5.835	151.63	0.999	161.10	0.998
ABAFX025,26	3.508	135.78	0.999	126.16	0.997
ABAFX027,28	5.590	164.27	0.999	170.71	0.998
ABAFX029,30	7.100	161.26	0.999	184.38	0.998
ABAFX031,32	5.490	146.08	0.998	154.06	0.992
ABAFX033,34	3.616	172.31	0.998	162.81	0.997
ABAFX035,36	5.300	144.44	0.998	151.16	0.996
ABAFX037,38	4.035	167.73	0.999	162.98	0.998
ABAFX039,40	4.635	164.28	0.999	162.71	0.997
ABAFX041,42	3.842	167.36	0.999	159.71	0.998
ABAFX043,44	6.100	160.00	0.998	173.79	0.995
ABAFX051,52	1.585	162.60	0.999	141.46	0.996
ABAFX053,54	5.232	174.73	0.999	180.30	0.998
ABAFX055,56	4.970	170.75	0.999	170.48	0.996
ABAFX057,58	7.818	145.92	0.997	183.27	0.995
ABAFX059,60	3.217	174.25	0.999	161.38	0.997
ABAFX069,70	6.280	130.31	0.999	144.73	0.995
ABAFX073	1.553	178.50	0.998	154.43	0.995
ABAFX075,76	3.120	186.01	0.998	173.02	0.997

centration and temperature, S/T, for individual liquors (≤ 50% solids) were fitted to a power series as:

$$\log \frac{\mu}{\mu_w} = \sum_{i=1}^{n} a_i \left(\frac{S}{T}\right)^i \qquad (1)$$

where

μ = liquor kinematic viscosity

μ_w = water kinematic viscosity

S = solids concentration

T = absolute temperature

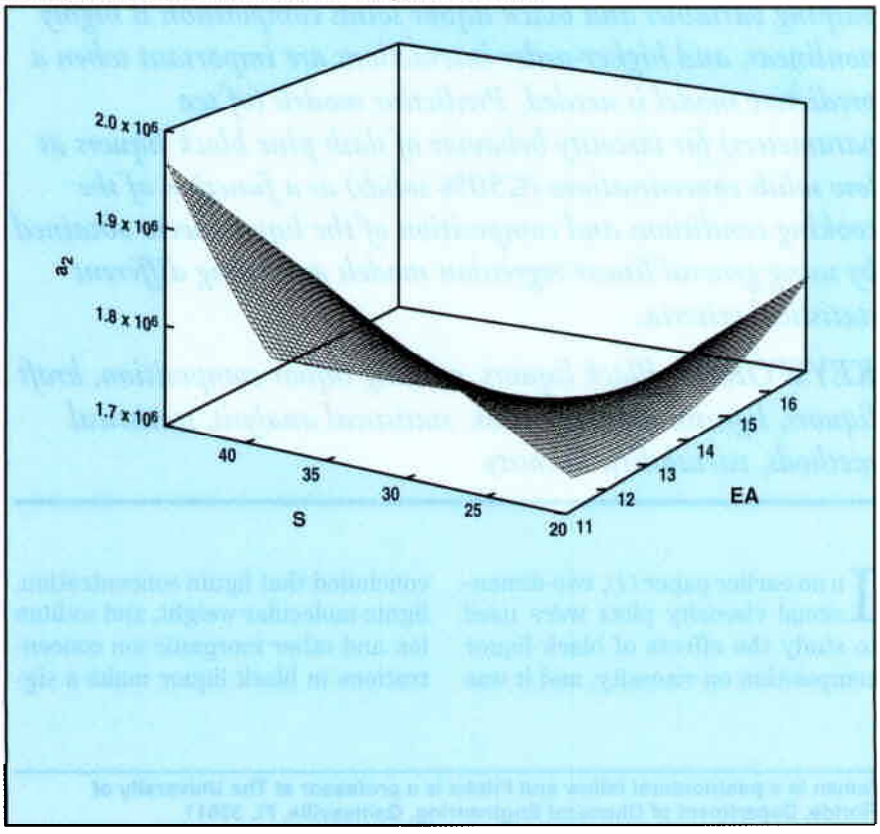
a_i = constants.

Extensive trials demonstrated that the viscosity of most liquors could be fitted with good accuracy by using two constants as:

$$\log \frac{\mu}{\mu_w} = a_1 \left(\frac{S}{T}\right) + a_2 \left(\frac{S}{T}\right)^2 \qquad (2)$$

The initial slopes of all correlations for kraft black liquors derived from pulping the same species were identical or nearly so. Therefore, a_1,

1. Three-dimensional plot for a_2 as a function of sulfidity and effective alkali at constant cooking temperature (440°K) and cooking time (80 min)

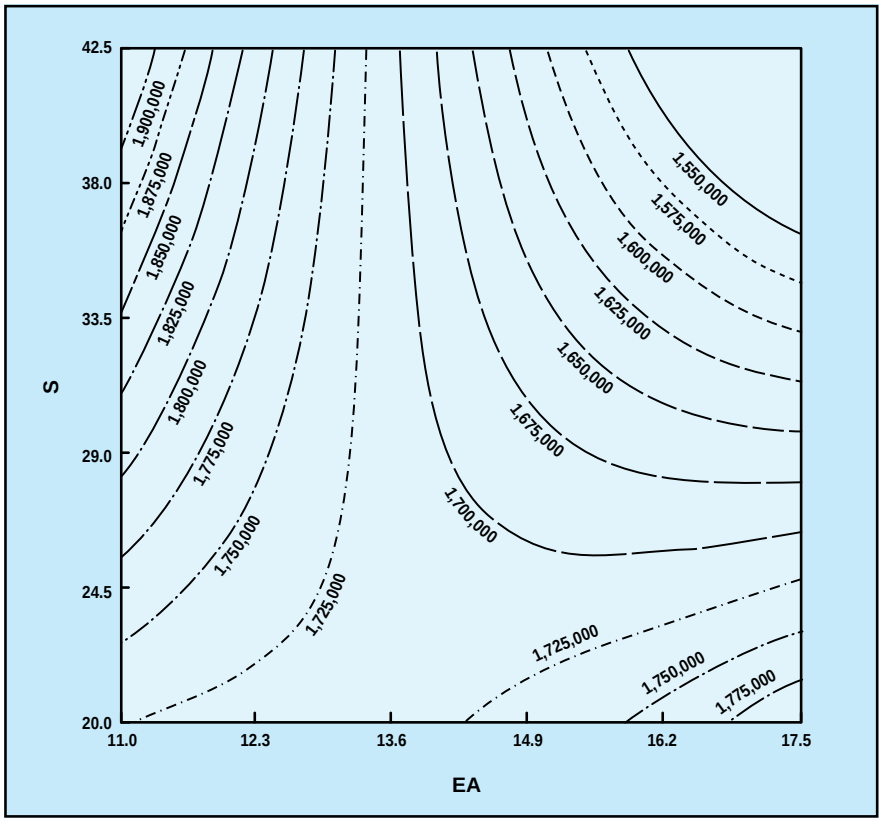


II. Pulping conditions and H factor for slash pine black liquors*

Cook no.	*t, min*	*T, °C*	*EA, %*	*S, %*	*h*
ABAFX011,12	40.0	165.6	13.0	20.0	555.5
ABAFX013,14	80.0	176.7	13.0	20.0	2731.7
ABAFX015,16	80.0	165.6	16.0	20.0	893.0
ABAFX017,18	40.0	176.7	16.0	20.0	-
ABAFX019,20	80.0	165.6	13.0	35.0	838.5
ABAFX021,22	40.0	176.7	13.0	35.0	1499.5
ABAFX023,24	40.0	165.6	16.0	35.0	631.2
ABAFX025,26	80.0	176.7	16.0	35.0	2594.7
ABAFX027,28	80.0	165.6	13.0	20.0	982.0
ABAFX029,30	40.0	176.7	13.0	20.0	1401.5
ABAFX031,32	40.0	165.6	16.0	20.0	473.3
ABAFX033,34	80.0	176.7	16.0	20.0	2606.2
ABAFX035,36	40.0	165.6	13.0	35.0	574.7
ABAFX037,38	80.0	176.7	13.0	35.0	2421.7
ABAFX039,40	80.0	165.6	16.0	35.0	977.1
ABAFX041,42	40.0	176.7	16.0	35.0	1433.0
ABAFX043,44	60.0	171.1	14.5	27.5	1270.1
ABAFX051,52	60.0	182.2	14.5	27.5	3066.9
ABAFX053,54	60.0	171.1	11.5	27.5	1236.8
ABAFX055,56	60.0	171.1	17.5	27.5	1234.1
ABAFX057,58	60.0	171.1	14.5	12.5	1248.5
ABAFX059,60	60.0	171.1	14.5	42.5	1178.7
ABAFX069,70	60.0	160.0	14.5	27.5	561.1
ABAFX073	100.0	171.1	14.5	27.5	1993.3
ABAFX075,76	20.0	171.1	14.5	27.5	513.66

*t=cooking time, T=cooking temperature, EA=effective alkali, S=sulfidity, h=H factor

2. Contour plot for a_2 as a function of sulfidity and effective alkali at constant cooking temperature (440°K) and cooking time (80 min)



which represents this slope in the limit, was set constant at the average value (466.4°K) determined from best correlations of each reduced-viscosity curve, and the reduced-viscosity curves were correlated again with a_1 treated as a universal constant. In this manner, the liquor viscosity variations due to variations in solids composition arising from differences in pulping conditions can be represented by differences in the constant a_2. The values of a_1 and a_2, and the new values of a_2 with a_1 treated as a universal constant, are summarized in **Table I.**

As described earlier *(1, 2),* the liquors used in this work to determine the effects of pulping conditions or solids compositions on liquor viscosity quantitatively are from a two-level, four-variable factorially designed experiment with center and star points for kraft pulping of slash pine. The resulting rotatable composite design, with a total of 25 separate pulping conditions, supplies

information suitable for determining nonlinear responses. The range of independent variables was set to include virtually all pulping conditions that could be used commercially within the experimental space.

The objectives of this work were to (a) study the effect of pulping variables and black liquor solids composition on viscosity (constant a_2 in the reduced correlation) by surface response methods and (b) represent proper correlations for viscosity behavior of slash pine black liquors as a function of the cooking conditions or composition of the liquor solids using a_2, as described earlier. These correlations will be useful in estimating the viscosity of black liquors at operating conditions from knowledge of the pulping conditions or the black liquor solids composition. Prior to this work, no similar study has been reported in the literature.

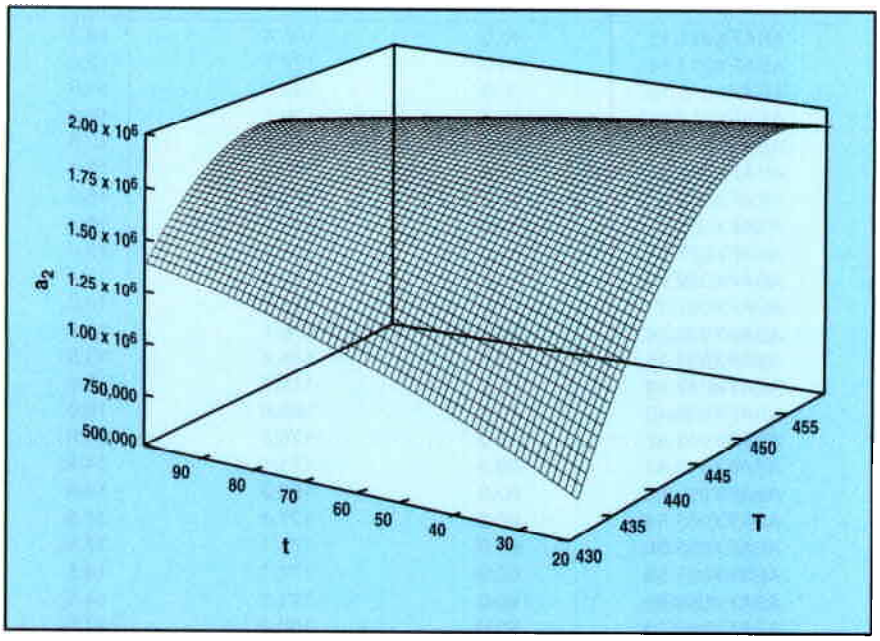
The effect of the cooking conditions on the viscosity of black liquor

To investigate the influence of the cooking conditions [effective alkali (EA), sulfidity *(S)*, cooking time *(t)*, and cooking temperature *(T)*] on viscosity, response surface methods were used to analyze the response of viscosity *(a_2)* to the pulping variables, and then different statistical approaches were used to establish proper models for a_2 as a function of the cooking conditions. Since, in the design of the pulping experiments, center point and star points (extreme axes) are added to the 24 factorial, quadratic, and interaction terms are considered in addition to the main effects and their interactions. The pulping conditions for the liquors used in this study, along with H factors for the cooks, are summarized in **Table II.**

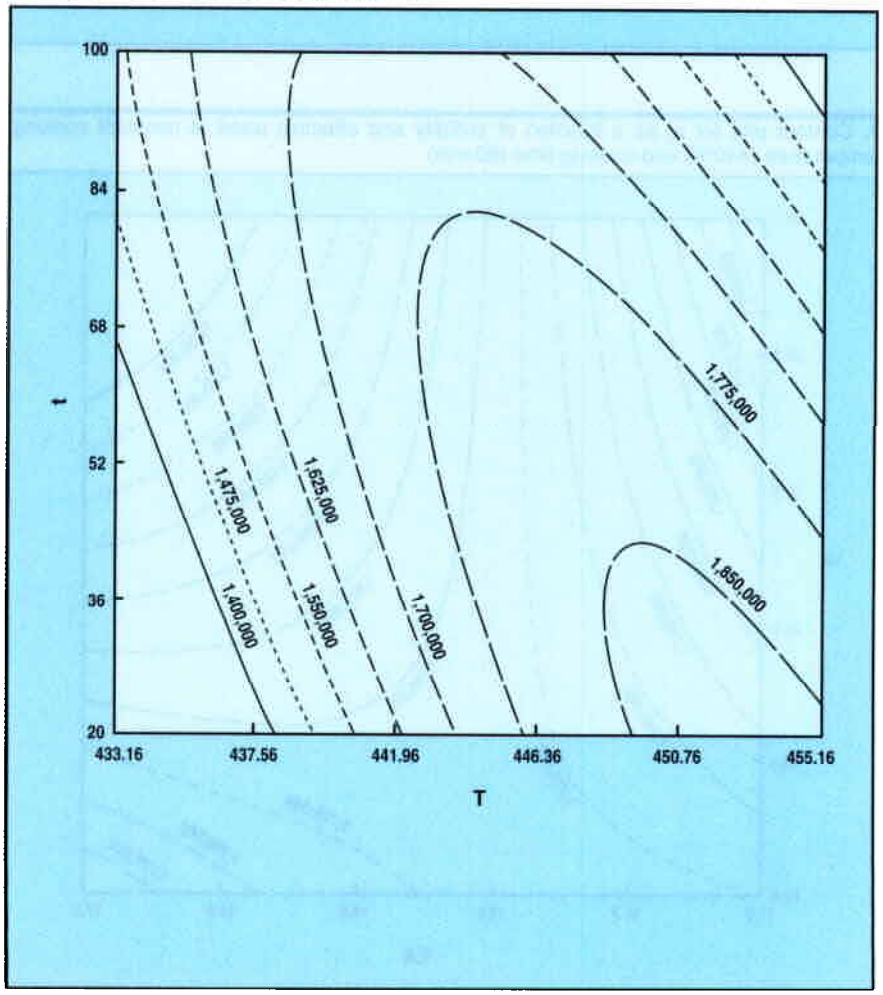
Response surface methods

Response surface methodology, as suggested by Box *(3)*, was used to

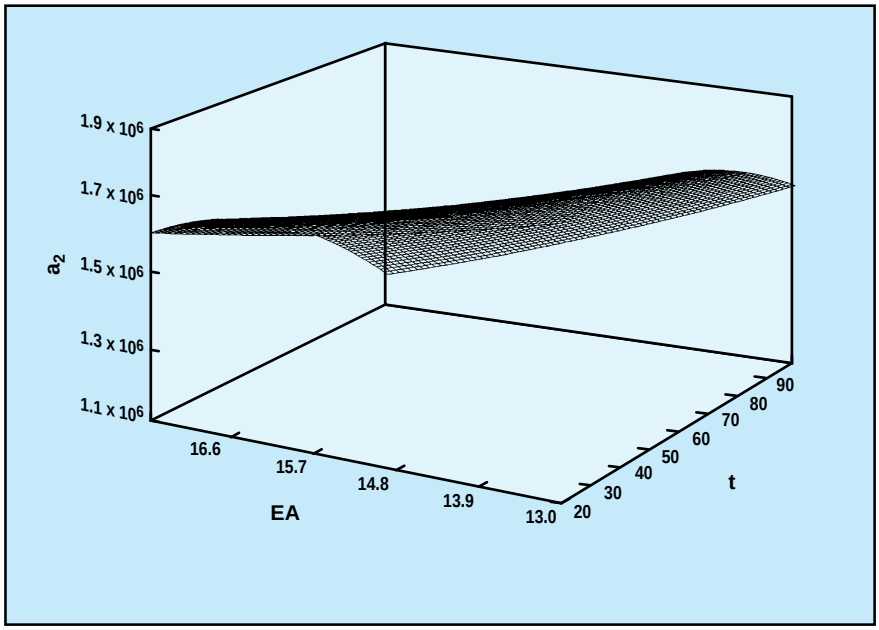
3. Three-dimensional plot for a_2 as a function of cooking time and cooking temperature at constant sulfidity (27.5%) and effective alkali (13%)



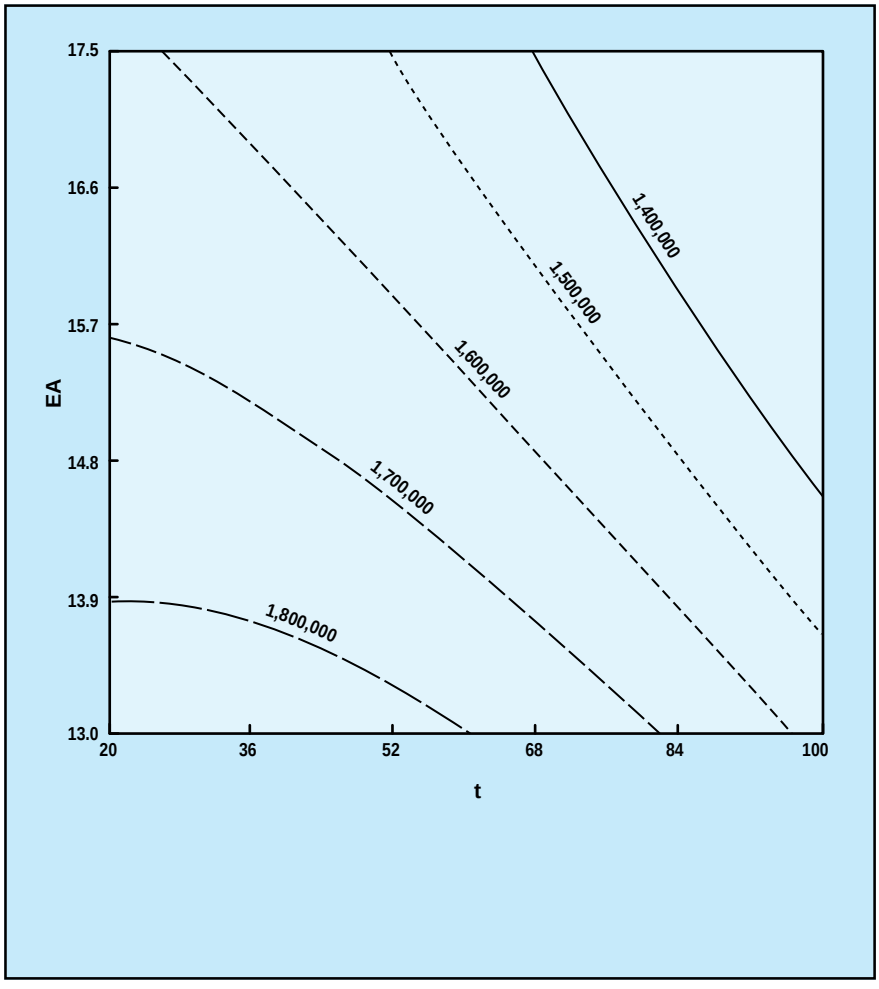
4. Contour plot for a_2 as a function of cooking time and cooking temperature at constant sulfidity (27.5%) and effective alkali (13%)



5. Three-dimensional plot for a_2 as a function of effective alkali and cooking time at constant cooking temperature (450°K) and sulfidity (27.5%)



6. Contour plot for a_2 as a function of effective alkali and cooking time at constant cooking temperature (450°K) and sulfidity (27.5%)



perform the empirical study between the viscosity (constant a_2) as the measured response to the input variables of pulping, which consist of effective alkali, sulfidity, and cooking time and temperature. With this technique, the effect of a given set of variables on a particular response can be studied, the setting of inputs (if any) that satisfies the desired specification can be recognized and, finally, the values of the inputs belonging to the stationary points of the response surface can be specified.

To develop plots of the response surface and contours, the following general multiple regression linear model, which consists of the main effects, interactions, and quadratic terms, was used:

SEE PAGE 116 FOR EQUATION 3

where Y is the estimate for the dependent variable (response a_2), and the X_i's are independent variables (here, EA, S, T, and t) that are known for each experimental run. The constants $ß_o$, $ß_i$, $ß_{ij}$, $ß_{ijk}$, $ß_{ijkl}$, and $ß_{ii}$ are the regression parameters. The parameter $ß_o$ is the y intercept and is used as part of the predictive equation. The other parameters ($ß_i$...$ß_{ii}$) in the multiple regression model are partial slopes, and these represent the expected change in y for a unit increase in the corresponding independent variable *(4)*. X_i's are the main (linear) effect terms for each of the qualitative independent variables, X_iX_j's account for the two-variable interactions, $X_iX_jX_k$'s specify three-variable interactions, $X_iX_jX_kX_l$'s indicate four-variable interactions, and the X_i^2 terms indicate quadratic effects. The above model consists of four linear terms; six two-variable interactions, four three-variable interactions, one four-variable interaction, four quadratic terms, and the constant $ß_o$, a total of twenty parameters.

Before using Eq. 3 for surface response and contour analysis, we used the least squares regression (LSREG) procedure *(5)*, which

III. Chemical analysis of slash pine black liquors

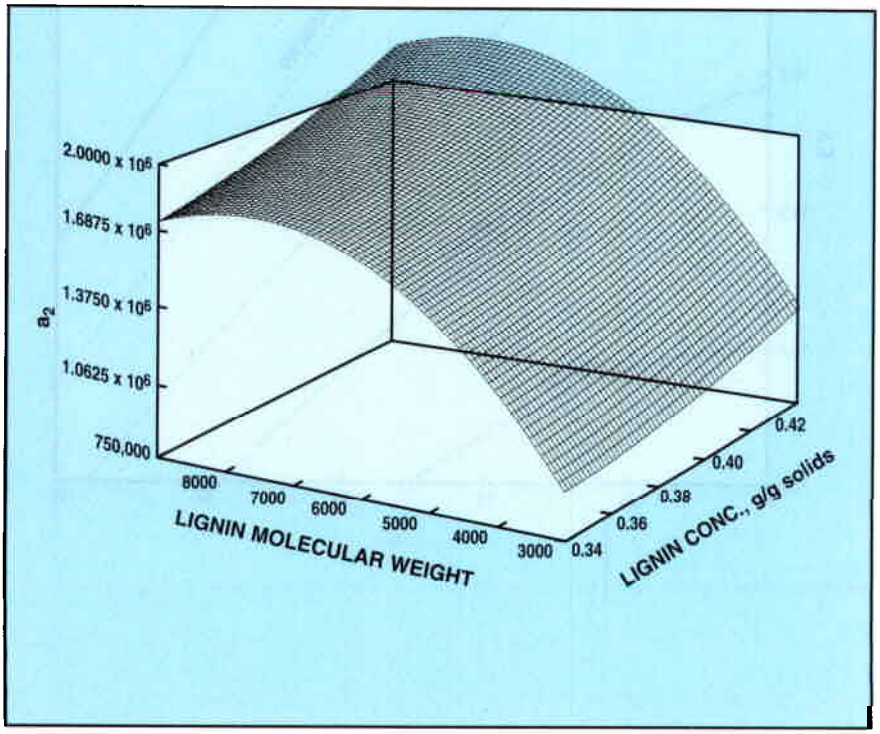
Cook no.	Lignin, g/g solids	$\overline{M}_w$	Sodium, g/g solids	Carbonates, g/g solids	Organics, g/g solids	Inorganics, g/g solids
ABAFX011,12	0.350	6411.0	0.152	0.0289	0.544	0.237
ABAFX013,14	0.435	6618.0	0.145	0.0537	0.613	0.243
ABAFX015,16	0.380	8687.0	0.177	0.0288	0.561	0.262
ABAFX017,18	0.409	6422.0	0.169	0.0612	0.587	0.281
ABAFX019,20	0.421	6544.0	0.162	0.0545	0.594	0.307
ABAFX021,22	0.417	6931.5	0.149	0.0558	0.627	0.280
ABAFX023,24	0.384	7528.5	0.188	0.0635	0.566	0.352
ABAFX025,26	0.393	3910.0	0.175	0.0656	0.619	0.334
ABAFX027,28	0.408	7960.0	0.142	0.0465	0.613	0.245
ABAFX029,30	0.427	9358.0	0.145	0.0617	0.628	0.262
ABAFX031,32	0.344	5046.5	0.166	0.0691	0.526	0.304
ABAFX033,34	0.440	6023.5	0.162	0.0454	0.607	0.269
ABAFX035,36	0.376	5995.5	0.189	0.0242	0.561	0.299
ABAFX037,38	0.423	5589.0	0.136	0.0154	0.557	0.202
ABAFX039,40	0.406	7571.5	0.168	0.0064	0.473	0.211
ABAFX041,42	0.404	5693.0	0.166	0.0226	0.554	0.283
ABAFX043,44	0.419	9672.0	0.163	0.0602	0.630	0.304
ABAFX051,52	0.430	5181.0	0.150	0.0354	0.680	0.258
ABAFX053,54	0.417	7154.0	0.145	0.0546	0.581	0.265
ABAFX055,56	0.406	7149.0	0.167	0.0603	0.519	0.307
ABAFX057,58	0.397	9582.0	0.159	0.0642	0.565	0.268
ABAFX059,60	0.413	6470.0	0.158	0.0448	0.561	0.325
ABAFX069,70	0.339	4820.5	0.166	0.1280	0.485	0.420
ABAFX073	0.430	5002.5	0.173	0.0931	0.552	0.360
ABAFX075,76	0.365	6279.5	0.169	0.0592	0.440	0.290

builds quadratic response-surface regression models. This is useful in searching for factor values that optimize a response *(5)* and was used to generate quadratic effects, to perform a lack-of-fit test, to find the solution for critical values of the surface, and to find the eigenvalues of the associated quadratic form. The quadratic response surface model for the response variable Y can be written as:

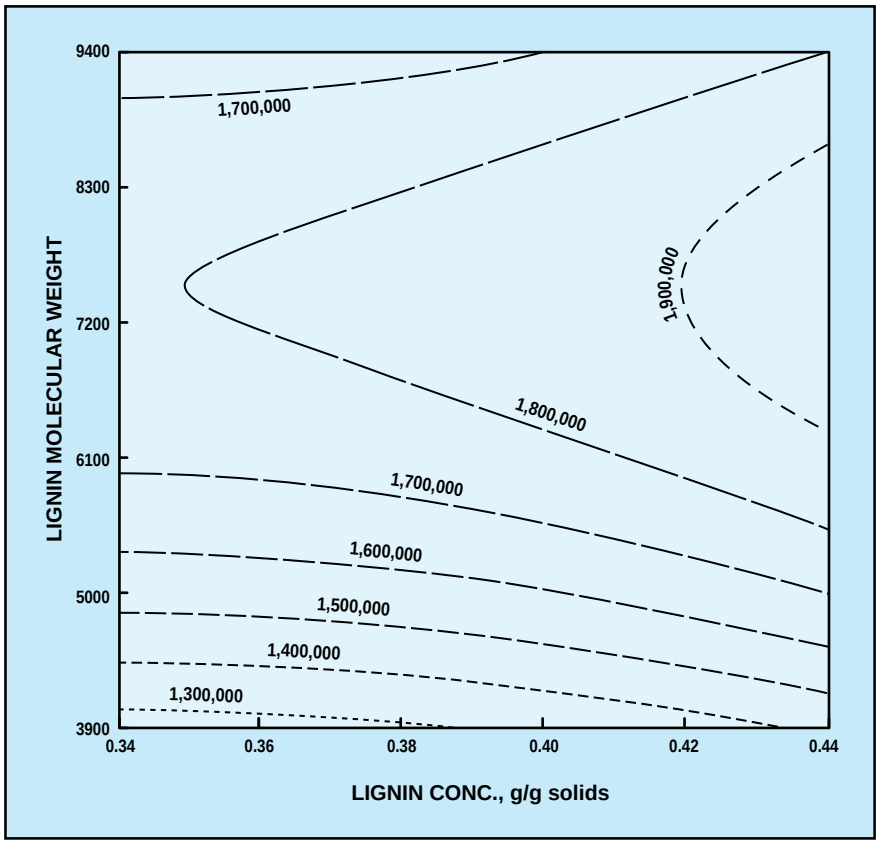
$$Y = \beta_o + \sum_{i=1}^{4} \beta_i X_i + \sum_{i<j}^{4} \beta_{ij} X_i X_j + \sum_{i=1}^{4} \beta_{ii} X_i^2 \quad (4)$$

The results of the RSREG routine in the statistical analysis system (SAS) *(5)* indicates that r^2 for Eq. 4 is 0.852, which indicates a good fit. The analysis also indicates that main (linear) effects on viscosity response (a_2) are significant at a level of 0.022 (at a confidence interval of 95%), the quadratic effects are sig-

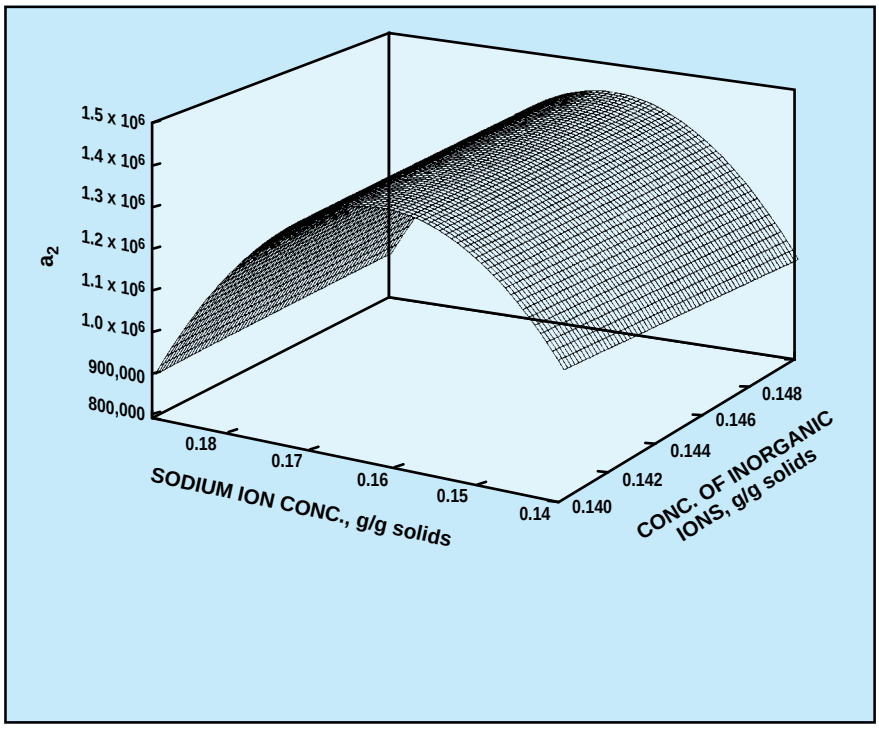
7. Three-dimensional plot for a_2 as a function of lignin molecular weight and lignin concentration at constant sodium ion concentration (0.145 g/g solids) and inorganics ion concentration (0.04 g/g solids)



8. Contour plot for a_2 as a function of lignin molecular weight and lignin concentration at constant sodium ion concentration (0.145 g/g solids) and inorganics ion concentration (0.04 g/g solids)



9. Three-dimensional plot for a_2 as a function of sodium ion concentration and inorganics concentration at constant lignin concentration (0.4 g/g solids) and constant lignin molecular weight (9580)



nificant at a level of 0.034, and the cross products (two-variable interactions) are significant at a level of 0.030. The total regressors are significant at a level of 0.015. These results indicate that the viscosity response of black liquor to the pulping variables is highly nonlinear. Although the linear terms make the largest contribution to the response, the quadratic terms and cross products are also important. This indicates that, in addition to these terms, higher-order interactions should be included when a predictive model is chosen. Therefore, Eq. 3 was chosen for analysis of the response.

The canonical analysis of the response surface indicates that the stationary point (maximum, minimum, saddle point, or flat area) is a saddle point, and the predicted value of a_2 at the stationary point is equal to 1.670×10^6, which is approximately in the center of the a_2 values. The input variables at the stationary point are S = 34.56%, EA = 17.38%, T = 442.96°K, and t = 28.64 min; these fall in the input space of the pulping experiments. The four eigenvalues and the corresponding eigenvectors were also determined using the RSREG procedure. The eigenvalues corresponding to the cooking time and cooking temperature (with a larger absolute value for cooking time) have negative signs, while eigenvalues corresponding to sulfidity and effective alkali are positive (with a larger value for sulfidity). The order of the absolute value of the eigenvalues is:

$$|\lambda_t| > |\lambda_S| > |\lambda_T| > |\lambda_{EA}|$$

This indicates that eigenvectors corresponding to cooking time and sulfidity give a direction of steepest ascent, and the eigenvectors corresponding to cooking temperature and effective alkali give a direction of steepest descent.

Three-dimensional surface and contour plot analysis

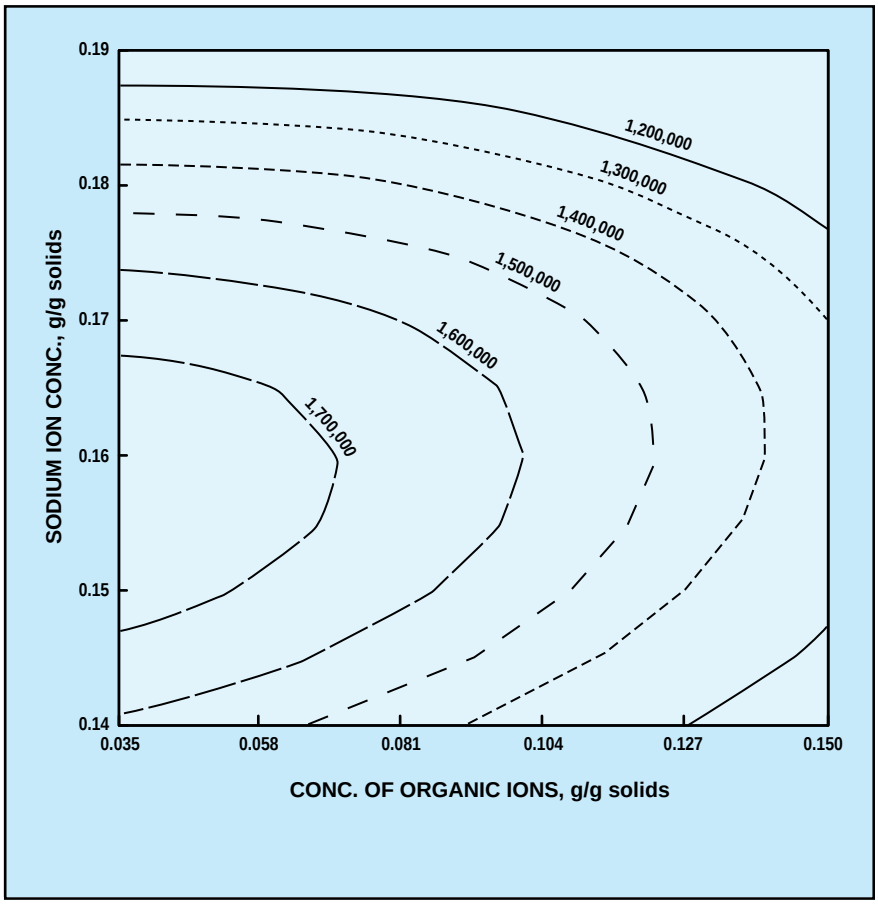
Since higher-order interactions are important in terms of viscosity, Eq. 3 was used to perform geometric representation of the response variable at different input conditions. The regression (REG) procedure in SAS *(5)* was used to estimate the model parameters of Eq. 3. For this model $r^2 = 0.94$, which is a very good fit, and the model residuals are very low. Since there are four independent variables, two of them must be fixed to perform a three-dimensional surface response or a contour plot.

Figures 1 through 6 are examples of the response surfaces and their contour plots. Figures 1 and 2 represent the three-dimensional response surface and contours for a_2 as a function of effective alkali and sulfidity at a constant cooking temperature of 440°K and a cooking time of 80 min. The viscosity response is a falling/rising ridge with respect to sulfidity and effective alkali. The contour plot (Fig. 2) indicates that, at a sulfidity level above 25.8%, an increase in effective alkali reduces the viscosity. Below this sulfidity level, an increase in the effective alkali level up to 13.4% reduces the viscosity; after that, viscosity increases with the effective alkali level. Also, when the effective alkali level is lower than 13.4%, increasing sulfidity increases the viscosity; however, above this effective alkali level, the viscosity decreases as the sulfidity level is increased. Note that this is true for the specific levels of cooking time and cooking temperature. The behavior of the response variable as a function of sulfidity and effective alkali may be different at other cooking time and cooking temperature levels.

Figure 3 represents the effects of cooking time and temperature on viscosity at a constant effective alkali of 13% and sulfidity of 27.5%. The viscosity response to cooking time and temperature is a rising/falling ridge. The contour plot (Fig. 4) at this level of effective alkali and sulfidity indicates that, at cooking temperatures below about 445°K, increasing the cooking time decreases the liquor viscosity. Also, at any cooking time, the viscosity response increases with the cooking temperature up to a point; after that, the viscosity decreases with further increase in cooking temperature. In general, the higher the cooking time, the lower the cooking temperature at which the viscosity response starts to decrease with cooking temperature.

Figures 5 and 6 are the response surface and the contour plots of viscosity with respect to effective alkali and cooking time at a constant cooking temperature of 450°K and a sulfidity of 27.5%. The surface is a falling ridge with respect to both effective alkali and cooking time; an increase in the cooking time reduces the viscosity at any level of effective alkali. Also, the viscosity decreases with increases in the effective alkali level at all cooking time levels.

10. Contour plot for a_2 as a function of sodium ion concentration and inorganics concentration at constant lignin concentration (0.4 g/g solids) and constant lignin molecular weight (9580)



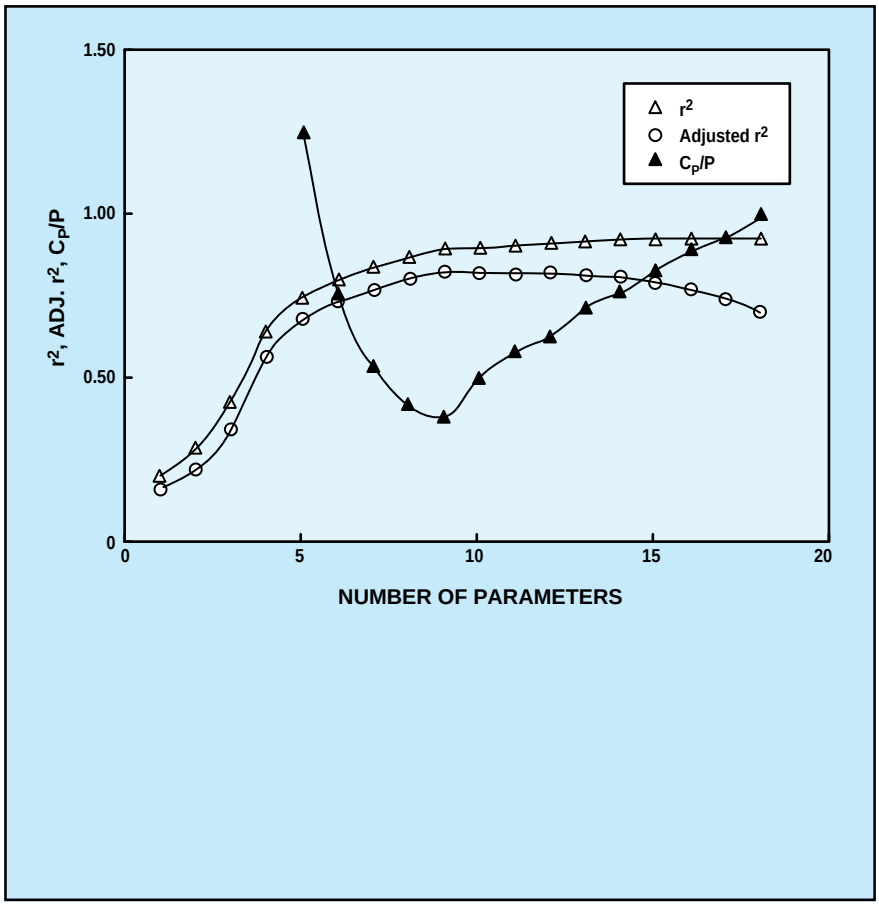
Models and residual analysis

The predictive models for a_2 were chosen using the procedures discussed in the appendix, and predicted values and the corresponding residuals were calculated using regression procedures in the statistical analysis system. These models, which are based on different statistical criteria, are as follows:

- Model (A) based on RSQUARE (r^2):

$$a_2 = -461792363.0 - (1124009.0 \times S) - (387355.0 \times t) + (2115158.0 \times T) + (2557.96 \times S \times T) + (906.1 \times T \times t) + (1681.32 \times S \times$$

11. r^2, adjusted r^2, and C_p/P for the effect of cooking conditions on the viscosity (a_2) of black liquor



EA x *t*) – (3.83 x *S* x EA x *t* x *T*) – (2415.04 x *T* x *T*) – (60.99 x *t* x *t*) (5)

where r^2 = 0.89 and adjusted r^2 = 0.83.

- Model (B) based on backward elimination:

a_2 = –442013331.0 – (2089669 x *S*) + (1973908.0 x *T*) + (122597 x *S* x EA) + (10846.0 x *S* x *t*) + (4770.36 x *S* x *T*) + (14.47 x *t* x *T*) – (279.12 x *S* x EA x *T*) – (25.0 x *S* x *t* x *T*) – (2195.92 x *T* x *T*) (6)

where r^2 = 0.86 and adjusted r^2 = 0.79.

- Model (C) based on maximum r^2:

a_2 = –490926526.0 + (13826.0 x *t*) + (2180913.0 x *T*) – (17315.0 x *S* x *t*) + (21.54 x *S* x *T*) + (1795.15 x *S* x EA x *t*) + (39.15 x *S* x *t* x *T*) – (4.1 x *S* x EA x *t* x *T*) – (2415.04 x *T* x *T*) – (60.99 x *t* x *t*) (7)

where r^2 = 0.87 and adjusted r^2 = 0.79.

The residuals (actual values of a_2 minus predicted values of a_2) of these three models were plotted with respect to predicted values of a_2. All of the residuals scatter around zero and are independent of the predicted values. The residuals for Models A and C are slightly smaller than that for Model B. However, these models can be used to predict values of a_2 at different cooking conditions, which can then be used to determine the viscosity of the corresponding liquor at low solids content (≤ 50%) at various temperatures and solids concentrations. Calculated values should be accurate to within about ± 6% (except one point) or better for a_2 and ± 13% or better for viscosity.

Empirical correlation with sulfidity, effective alkali, and H factor

As previously mentioned *(1)*, the pulping variables of cooking time and cooking temperature are commonly combined in the pulp and paper industry into one variable known as H factor *(6, 7)*. In this work, H factors were calculated from the time-temperature profiles recorded for each cook and are reported in Table II. An empirical correlation between effective alkali, sulfidity, and H factor and the response variable (a_2) was found using SAS procedures.

The independent variable terms that were considered in the model were: *S*, EA, *h* (H factor), *S* x EA, *S* x *h*, EA x *h*, *S* x EA x *h*, *S* x *S*, EA x EA, *h* x *h*, *S* x *S* x EA, *S* x *S* x *h*, EA x EA x *S*, EA x EA x *h*, *S* x *h* x *h*, and EA x *h* x *h*. The analysis of r^2 and C_p (r^2 procedure) showed that a model of nine parameters was the best. The stepwise procedure with maximum r^2 and backward elimination strategies was used for model screening. The nine-parameter model based on a maximum r^2 strategy is as follows:

a_2 = 1603552.0 + (1360.83 x *h*) – (214.38 x EA x *h*) + (482.1 x *S* x *S*) + (0.476 x *h* x *h*) – (0.224 x *S* x *S* x *h*) – (84.53 x EA x EA x *S*) + (10.48 x EA x EA x *h*) – (0.04 x EA x *h* x *h*) (8)

where r^2 = 0.75.

Although r^2 for this model is lower than for earlier models, the residual analysis indicates that the model is accurate to within ± 10%. All of the residuals with respect to the predicted value of the response variable are scattered around zero.

Effect of black liquor composition on viscosity

We previously showed *(1)* that carbonates at low levels have an insignificant effect on black liquor viscosity. Also, for slash pine black liquors, organics other than lignin are not important in terms of viscosity variation. Therefore, the task is

reduced to investigating the influence of lignin molecular weight, lignin concentration, sodium ion concentration, and other inorganic ion concentrations (except carbonates) on the viscosity response of slash pine black liquors. Methods for chemical analysis of the liquors, lignin purification, and determination of lignin concentration and molecular weight [note that lignin molecular weights were measured using gel permeation chromatography (GPC)] can be found elsewhere *(8–12)*. The concentrations of lignin and organics, sodium, carbonate, and organic ions are summarized in **Table III.** In this part of the work, also, response surface methods and different statistical criteria were used to analyze the response of viscosity (a_2) and establish proper models for a_2 as a function of black liquor composition. The data were fitted to a quadratic response-surface model (Eq. 4) by using the RSREG procedure, and the results indicate that main effects are significant at a level of 0.001, the quadratic effects are significant at a level of 0.08, the cross products are significant at a level of 0.7, and total regressors are significant at a level of 0.016. r^2 for the model is 0.85, which indicates a good fit.

The canonical analysis of the response surface indicates that the stationary point is a saddle point, and the predicted value of a_2 at the stationary point is 1.670×10^6, which is very close to the value found for response to the pulping conditions. The input variables at the stationary point are: lignin concentration = 0.414 g/g solids, lignin molecular weight = 5884.0, inorganics concentration = 0.495 g/g solids, and sodium concentration = 0.185 g/g solids. The inorganics concentration at the stationary point falls outside of the input space region.

For three-dimensional surface and contour plot analysis, the REG procedure in SAS was used to determine the model parameters of Eq. 3. r^2 for this model was 0.92. **Figures 7 and 8** indicate the three-dimensional response surface and contours for a_2 as a function of lignin molecular weight and lignin concentration at a constant sodium ion concentration of 0.145 g/g solids and inorganics ion concentration of 0.04 g/g solids. The contour plot indicates that a_2 is affected by both lignin molecular weight and lignin concentration. a_2 is an increasing function of the lignin concentration at any level of lignin molecular weight. At a fixed level of lignin concentration, a_2 increases with lignin molecular weight to a level of 7500.0 and then decreases slightly with a further increase in lignin molecular weight. However, this is a response for these conditions only, and it may change at other levels of sodium and inorganics.

Figures 9 and 10 are the response surface and contour plot of a_2 with respect to sodium and inorganic ions at a constant lignin concentration of 0.4 g/g solids and lignin molecular weight of 9580.0. The surface is a falling ridge with respect to inorganics and a rising/falling ridge with respect to sodium. An increase in the inorganics level reduces the viscosity at any level of sodium ion concentration. Also, at a fixed inorganics level concentration, a_2 shows an increase with increasing sodium ions up to 0.16–0.165 g/g solids and then decreases with a further increase in the sodium concentration level. Again, these are typical results, and results may be different at other levels of lignin concentration and lignin molecular weight.

Equation 3

$$Y = \beta_o + \sum_{i=1}^{4} \beta_i X_i + \sum_{i<j}^{4} \beta_{ij} X_i X_j + \sum_{i<j<k}^{4} \beta_{ijk} X_i X_j X_k + \sum_{i<j<k<l}^{4} \beta_{ijkl} X_i X_j X_k X_l + \sum_{i=1}^{4} \beta_{ii} X_i^2 \qquad (3)$$

Predictive model and residual analysis

The r^2 procedure in SAS was used for variable selection as in Eq. 3. The analysis of r^2, adjusted r^2, and C_p/P, with respect to the number of parameters in the model (P), indicated a ten-parameter model was the best. The stepwise procedure with maximum r^2 and backward elimination strategies was used for model screening. The ten-parameter model based on backward elimination is:

$$a_2 = 2331959.0 - (1327.75 \times X_1) - (258143870.0 \times X_2) + (69528231.0 \times X_3) + (11663.0 \times X_1 \times X_3) + (1569590311.0 \times X_2 \times X_3) + (77236.0 \times X_1 \times X_2 \times X_4) - (469639 \times X_1 \times X_2 \times X_3 \times X_4) - (0.036 \times X_1 \times X_1) - (531279901.0 \times X_3 \times X_3) \qquad (9)$$

where $r^2 = 0.85$, adjusted $r^2 = 0.8$, and

X_1 = lignin molecular weight

X_2 = inorganics concentration

X_3 = sodium ion concentration

X_4 = lignin concentration.

The residual analysis of the model indicated that all of them are scattered around zero, and the model can be used to predict the values of a_2 accurately to within ± 7% or lower.

Nonlinear regression models

Our goal in this work was not only to correlate the viscosity to the pulping conditions and black liquor composition, but also to determine predictive models requiring the fewest

parameters. By using the general multiple regression linear model (Eq. 3) and applying different statistical criteria, we were able to find several predictive models for viscosity response of black liquor. Using these methods, the response surface can be defined with models of at least 9–10 parameters. Therefore, at least 10–11 experimental conditions are required to define the parameters of the model. Attempts were made to find models with fewer parameters for describing the surface response as a function of the independent variables. The nonlinear (NLIN) procedure in SAS was used to search for different nonlinear regression models that can be used to define the viscosity response as a function of the cooking variables and black liquor composition. The NLIN procedure produces least-squares or weighted least-squares estimates of the parameters of a nonlinear model. Nonlinear models are more difficult to specify and estimate than linear models. The nonlinear predictive models that were obtained using the NLIN procedure are:

Model for a_2 as a function of *S*, EA, *T*, and *t*. The following nonlinear regression model fits the experimental data as a function of sulfidity, effective alkali, cooking time, and cooking temperature with very good accuracy:

$$a_2 = 0.272T^{2.72}\, t^{-0.0012}\, S^{-0.0712}\, (\mathrm{EA})^{-0.2644} \quad (10)$$

where $r^2 = 0.997$.

The residual analysis for this model indicates that all residuals are scattered around zero, and the model is accurate enough to predict the values of a_2 within ± 8% or better (± 15% for viscosity). This model indicates that cooking temperature and effective alkali have more significant effects than cooking time and sulfidity.

Correlation with sulfidity, effective alkali, and H factor. The nonlinear regression model that fits the response variable as a function of sulfidity, effective alkali, and H factor is:

$$a_2 = 1{,}910{,}000 - 13.74\, (\log_e)\, h\, (\mathrm{EA})^{2.02} S^{0.746} \quad (11)$$

where $r^2 = 0.994$.

The residual analysis for this model indicates that all residuals are scattered around zero, and the model is accurate enough to predict the values of a_2 within ± 9% or better.

Correlation with black liquor composition. The data for the response variable were correlated to the liquor composition by:

$$a_2 = 11.165\, (M_w)^{0.297}\, (C_{\mathrm{lignin}})^{0.054}\, (\mathrm{Inorganics})^{-0.015}\, (\mathrm{Sodium})^{-0.303} \quad (12)$$

where $r^2 = 0.999$.

In the above correlation and in the previous model for a_2 as a function of black liquor composition, the carbonates were not included; however, if one includes the carbonates as inorganics (all inorganics except sodium ions), the model becomes:

$$a_2 = 11.042\, (M_w)^{0.312}\, (C_{\mathrm{lignin}})^{0.056}\, (\mathrm{Inorganics})^{0.019}\, (\mathrm{Sodium})^{-0.34} \quad (13)$$

where $r^2 = 0.999$.

The accuracies of Eqs. 12 and 13 are nearly the same, and they have the same predictive power, which means that carbonates at a low level are not important in terms of viscosity. However, when they are included, there is a small change in the parameters of the model. Both Eqs. 12 and 13 indicate that the lignin molecular weight and sodium ion concentration make the greater contributions to the viscosity of black liquor. The residuals of these two equations are all scattered around zero and indicate that the models should be accurate to within ± 8% or better.

Conclusions

The effects of cooking variables and black liquor composition on the viscosity were studied both qualitatively and statistically by surface response methodology and different statistical criteria. The analysis of a quadratic response model indicates that the viscosity response of black liquor to both pulping variables and black liquor composition is highly nonlinear, and higher-order interactions should be included when a predictive model is chosen.

For this reason, the general multiple regression linear model (Eq. 3) (which consists of the main effects; two-, three-, and four-variable interactions; and quadratic terms) was used to perform geometric representation of the response variable at different input conditions and to search for statistically based predictive models for defining the response variable as a function of the cooking variables and composition of the liquor. The three-dimensional response surfaces and their contours with respect to the cooking variables indicate that, at high sulfidity levels, an increase in the effective alkali level reduces the liquor viscosity, while at low sulfidity levels, viscosity increases with the effective alkali level. At lower cooking temperature levels, the viscosity is an increasing function of the cooking time, while at higher cooking temperature levels, the viscosity decreases as the cooking time is increased.

The response surfaces and their contours with respect to black liquor composition indicate that the viscosity response of black liquor is a strong function of lignin molecular weight. At any level of lignin molecular weight, the viscosity increases as the lignin concentration is increased in the liquor. However, the viscosity increase is more significant at lower lignin molecular weights. As the lignin molecular weight is increased at a fixed lignin concentration, the viscosity increases rapidly, reaches a maximum at a high molecular weight, and then starts to decrease slightly (or stays constant) with further increase in the level of lignin molecular weight. The response surface and its contour plot with respect to sodium and other inorganic ions at a constant lignin concentration and molecular weight show that the viscosity is highly affected by sodium ion concentration.

The viscosity decreases at any sodium concentration level as the inorganics concentration is increased.

The r^2 procedure in SAS showed that a ten-parameter model can be used to define the viscosity response of black liquor as a function of the pulping variables and composition of black liquor. The predictive models based on different statistical criteria should be accurate to within ± 10% or better for a_2 and ± 15% or better for viscosity. The nonlinear regression procedure was used to find predictive models with fewer parameters to describe the surface response as a function of the pulping variables and black liquor composition. The response variable could be defined with equations of at most five parameters. The models based on this approach are generally more accurate and can be used to calculate the values of a_2 with an accuracy of ± 8% or better. The calculated values of viscosity should be accurate to within ± 13% or better for a range of viscosity of three orders of magnitude.

The methods developed and the demonstration of general applicability significantly reduce the quantity of data necessary to describe the viscosity behavior of the liquors from other wood species. TJ

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The authors are grateful for the financial support provided by a number of industrial firms and the U.S. Department of Energy under Grant No. DE-FG02-85ER40740. We are also grateful for the assistance of Barbara Speck.

Received for review Aug. 12, 1994.

Accepted Jan. 6, 1995.

Appendix

Statistical modeling

The objective of the work described here was not only to study the effects of cooking variables on the viscosity response of black liquors, but more importantly, to find appropriate models that could be used to predict the viscosity of mill black liquors at process conditions. The 20-parameter model of Eq. 3 could be used to fit the experimental data of the present study with good accuracy. However, this does not mean that all the variables in this model are reasonable candidates as independent variables (i.e., all of them are significant at a level of 0.05). In addition, as the number of parameters in the model is increased, more experimental data are required to estimate the parameters of the predictive model. This would be more time-consuming and unreasonable. On the other hand, the problem of selecting reasonable candidate independent variables can be a difficult task and time-consuming. In this section, different statistical methods for model selection are discussed, the regression models are selected, and model assumptions are checked.

Selecting the variables

Different selection procedures can be used to select the proper independent variables among the candidates for a predictive model. The first selection procedure involves performing all possible regressions with the dependent variable and one or more of the independent variables used in Eq. 3. Obviously, this approach requires running a large number of regression models and can be time consuming. Before running all possible regressions, one must consider what criteria should be used to select the best-fitting equation from all possible regressions. Among the various criteria *(4)* for selecting the best regression equation from the set of all possible regression equations, the coefficient of determination r^2 criterion and Mallow's C_p criterion were used in this work for selecting independent variables. By ex-

amining the models that have the highest r^2 values, one can identify the number and identity of the variables to include in the model. One problem with using r^2 as a criterion is that r^2 increases for each independent variable, even when the new variable has a poor predictive power, and this may result in underspecification and/or overspecification of the predictive model. The C_p statistic seems to balance the problems of overspecification and underspecification. The C_p statistic is defined as *(4):*

$$C_p = \mathrm{SSE}_p/[S_E^2 - (n - 2P)]$$

where

C_p = Mallow's statistic

SSE_p = sum of squares for error from a model with P parameters

S_E^2 = mean square error from the model with largest number of independent variables

P = number of the parameters in the model

n = degrees of freedom (no. of observations).

Theory suggests that the best-fitting model should have $C_p \approx P$. $C_p > P$ indicates a biased model and $C_p < P$ indicates a good model.

The r^2 procedure in SAS was used to perform statistical analyses for variable selection as in Eq. 3 for a_2 as a function of pulping conditions and black liquor composition. This procedure finds subsets of independent variables that best predict a dependent variable by linear regression in the given sample *(5)* and can be set to perform all possible subset regressions.

For a_2 as a function of the cooking variables, the r^2, adjusted r^2, and C_p/P, with respect to the number of parameters in the model, are plotted in **Fig. 11.** As the number of parameters in the model increases, r^2 increases, it reaches a value of 0.9 at P = 10, and then it increases very slightly as P increases to 19. C_p/P with respect to P shows a decrease, reaches a minimum at P = 10, and then increases slowly to 1.0 at P = 19. The adjusted r^2 increases with increasing P, reaches a value of 0.82 at P = 10, and then decreases slowly. Therefore, a ten-parameter model was chosen as the predictive model for a_2.

For a_2 as a function of the liquor composition, the analysis of r^2, adjusted r^2, and C_p/P with respect to the number of parameters in the model *(P)* indicates that, as the number of parameters in the model increases, r^2 increases and reaches a value of 0.85 at P = 10 and then increases very slightly as P increases to 19. C_p/P decreases with respect to P, reaches a minimum at P = 10, and then increases slowly to 1.0 at P = 19. The adjusted r^2 increases with P, reaches a value of 0.8 at P = 10, and then decreases slowly. Therefore, a ten-parameter model was chosen as the predictive model for a_2 as a function of the liquor composition.

There are a number of other procedures that can be used to select the best-fitting regression equation from a set of candidate independent variables. The stepwise procedure is another method that was used in this study. This procedure gives insight into the relationships between the independent variables and the response variable, and differs from the r^2 procedure, which is used for exploratory model analysis and identifies the model with the largest r^2 for each number of variables considered. The stepwise procedure uses forward selection, backward elimination, stepwise, and maximum (or minimum) r^2 improvement strategies in choosing the variables for the models it considers. This requires less computer time than the r^2 procedure. The forward selection technique begins with no variables in the model and adds variables one at a time until a stopping criterion is satisfied. At every stage, the variable that has the largest F statistic to the model is added.

The backward elimination method begins with a model of all independent variables and computes the F statistic for each independent variable as *(4):*

$$F_j = \mathrm{SSdrop}_j/\mathrm{MSE}\ J = 1,2,...$$

where SSdrop_j is the drop in the sum-of-squares error obtained for the complete model, which contains all X's except X_j. MSE is the mean square error for the complete model. The variable with the smallest value of F with respect to a preselected significant level (F_j) will be dropped, and the process is repeated with one variable removed from the model. The maximum r^2 technique, which is nearly the best regression, will find the best one-variable model, the best two-variable model, and so forth, although there is no guarantee that the model with the largest r^2 for each size will be found. In this work, the stepwise procedure with backward elimination and maximum r^2 strategy was used to find the relationship between the response variable and other independent variables. A good predictive model based on the backward elimination technique should have at least nine independent variables. The maximum r^2 strategy indicates that there is no major improvement in r^2 for more than a ten-parameter model. However, a ten-parameter model based on the r^2 *(5)* and two ten-parameter models based on the stepwise *(5)* procedure were used as predictive models for a_2 as a function of the cooking variables, and the regression procedure in SAS was used for residual analysis.