BLACK LIQUORS

Effects of pulping variables on density of slash pine kraft black liquors: predictive models

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ABSTRACT

An empirical model of black-liquor density was developed using data from 25 liquors produced for a statistically designed experiment in a pilot-scale digester. The model can predict the density of slash pine black liquors based on four key pulping conditions (effective alkali, sulfidity, cooking time, and cooking temperature). Density values calculated from the model were within ±2% of measured values over a wide range of liquor temperature (20–90°C) and solids content (up to 70% solids). The discussion includes a detailed review of the model's underlying principles, which are generally applicable to other liquors.

Application:

A model for calculating black-liquor density from pulping conditions.

THE DENSITY OF KRAFT BLACK liquors is an important physical property. Precise knowledge of liquor density is needed to calculate the mass flow rates that are used to develop mass and energy balances for the kraft recovery cycle. These mass and energy balances, in turn, are used to optimize the recovery process and to design new equipment.

OVERVIEW AND BACKGROUND

The literature includes several studies of the density of kraft black liquors. However, most of these are for narrow ranges of temperature and solids content, with no liquor characterization. The variation of liquor density with pulping conditions and/or liquor composition has not been studied systematically prior to this work.

Kobe and McDonald *(1)* reported density data for soda, sulfate, and sulfite black liquors at solids contents below 50% over a temperature range of 96–98°C. Han *(2)* and Lubienska and Graczak *(3)* have reported density as a function of solids and inorganics concentration. Han *(2)* correlated the specific gravities of different liquors (up to 55% solids) at 16°C and 25°C with the inorganics concentration in the liquors. Hunter *et al. (4)*, Volkov and Grigor'ev *(5)*, and Oye *et al. (6)* reported density data for black liquors of different wood species and for various pulping processes. Most of these data are for black liquors containing less than 50% solids.

The most extensive data for density of slash pine kraft black liquors have been reported by Fricke *(7)*, Wight *(8)*, and Zaman *et al. (9)*. In these earlier works, methods were developed to measure density precisely over a wide range of solids contents (up to 100% solids). We observed that black liquors undergo two second-order thermodynamic transitions between 50% and 100% solids *(9)*. Therefore, the liquor-density behavior observed in the lower-solids region cannot be extrapolated to the higher-solids regions above the first transition point.

Figure 1 is a typical plot of black-liquor density as a function of solids content for one of the liquors used in this study at 25°C. It appears that—for this liquor at 25°C—the first and second transitions occur at about 65% solids and 80% solids, respectively. Nevertheless, within each region, there is a linear relation between liquor density and solids content. The density of every liquor at solids contents below the first transition is defined by Eq. 1 (for liquors at 25°C) *(9)*:

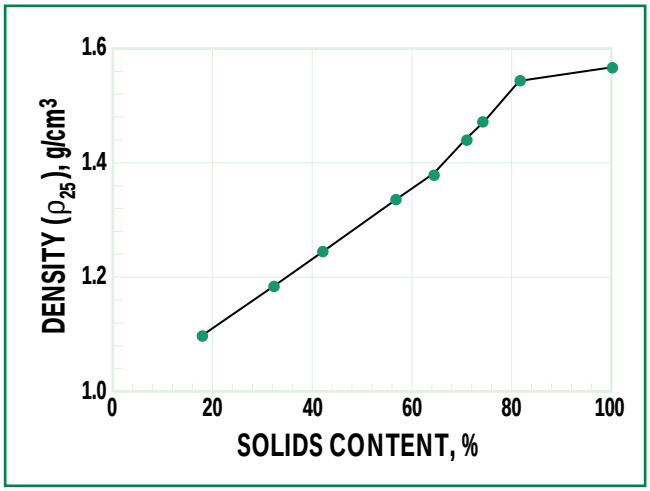
$$\rho_{25} = 0.997 + as \qquad (1)$$

where

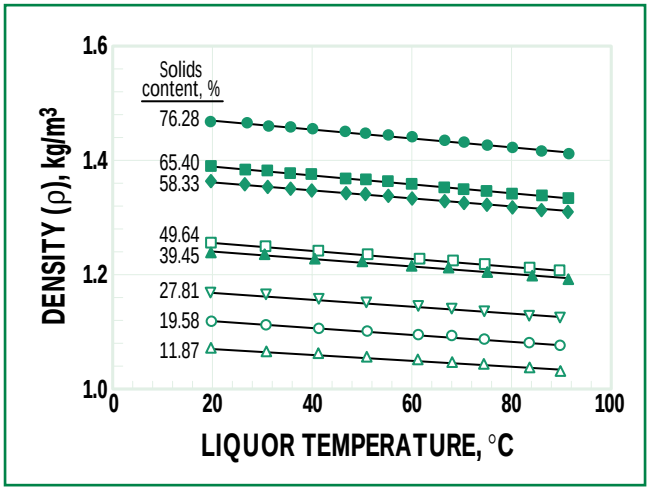
ρ_{25} = liquor density at 25°C, kg/m^3
a = composition-dependent constant that varies from liquor to liquor.
s = solids content, %

The values of a and the cooking conditions for the liquors used in this study are given in **Table I**.

We also determined the thermal expansion for these liquors by dilatometry over wide ranges of temperature and solids content. These data were then used to determine the density of the liquors at temperatures other than 25°C *(9)*. **Figure 2** is a typical plot for density of one of the liquors over wide ranges of temperature and solids content. As can be observed, all densities show a nearly linear relation with temperature at a given solids content. The concept of "corresponding states" *(7–10)* was applied to combine the effects of temperature and solids content and to obtain a reduced plot for density (ρ_R) for a particular black liquor. The reduced density was obtained by dividing the density at any temperature and solids content (ρ) by the corresponding density of the liquor at 25°C and the same solids content (ρ_{25}). The choice of the reference density is arbitrary, and it is possible to use any density in the region where the liquor is in the same physical state. The reduced density curve for each liquor was correlated to temperature using the following empirical equation:



1. Variation of black-liquor density with solids content for a typical kraft black liquor at 25°C



2. Variation of black-liquor density with temperature for liquor ABAFX043,44 at eight levels of solids content

$$\rho_R = 1 + A(T-25) + B(T-25)^2 \qquad (2)$$

where

ρ_R = reduced liquor density, i.e., ρ/ρ_{25}
T = liquor temperature, °C.

A and *B* are constants that vary from liquor to liquor. Differences in *A* and *B* for different liquors are the results only of differences in pulping conditions or of differences in the solids content arising from differences in pulping conditions and wood species. Thus the variations in liquor density resulting from variations in pulping conditions and/or liquor composition can be represented by differences in parameters *A* and *B*. The values of *A* and *B* for the liquors used in this study are shown in Table I.

The liquors used in this study of liquor density were obtained from 25 pulping experiments (i.e., $2^K + 2K + 1$, where K = 4) that were performed in a large pilot-scale digester. The four cooking variables were effective alkali (EA), sulfidity (*S*), cooking temperature (*T*), and cooking time (*t*). In all cases, the white liquor was adjusted to a causticizing efficiency of 85% and a reduction of 93% with Na_2CO_3 and Na_2SO_4. The variable ranges for EA, *S*, *T*, and *t* were 11.5–17.5% (on oven-dry (o.d.) wood), 12.5–42.5% (as active alkali), 433.2–455.4 K, and 20–100 min, respectively. The resulting rotatable composite design—with a total of 25 separate pulping conditions—supplies enough information to study the joint effect of variables on liquor density and to develop statistically based quantitative models that can predict the density of a particular slash pine black liquor at a given set of processing conditions. The center point was not replicated as required to guarantee orthogonality. However, replicates of two earlier factorial experiments on other systems indicated that errors will be small if variation in kappa number is small.

The cooks were made at a liquor-to-wood ratio of 4:1. The pertinent details for the experimental procedure are reported elsewhere *(11)*. Liquors ABAFX011,12 and ABAFX025,26 are extremes, and liquor ABAFX043,44 is the center point of the design. Each liquor is a combination of two individual liquors from duplicate cooks that were mixed together when the kappa numbers agreed to within 10%. A pilot-scale evaporator was used to concentrate the liquors to about 40–45% solids, and a small-scale evaporator was used to concentrate the liquors to higher solids (up to about 85% solids). The details of the design and the operating procedures are given in an earlier paper *(12)*. The solids content of the liquors was determined using a modification of TAPPI method T 625 cm-85 *(13)*.

The objectives of the present study were to

- Study the effect of pulping variables on density by surface-response methods
- Determine empirical correlations for density (at 25°C) and reduced density of slash pine kraft black liquors as a function of the cooking variables.

These correlations will be useful in determining (a) the density of slash pine kraft black liquors at 25°C as a function of solids content and (b) the reduced density of the liquors as a function of the liquor temperature. The density of the liquor can then be determined as a function of temperature and solids content from a knowledge of cooking conditions, as will be described later.

EFFECT OF COOKING VARIABLES ON BLACK-LIQUOR DENSITY

In order to investigate the influence of the pulping variables (effective alkali, sulfidity, cooking temperature, and cooking time) on the density of slash pine black liquors, the values of *a*, *A*, and *B* were determined for slash pine black liquors of different cooking conditions. These values were used to develop different predictive models (for the values of *a*, *A*, and *B*) by em-

Black liquor	PULPING CONDITIONS: Cooking time (*t*), min	Cooking temp. (*T*), °C	Effective alkali (EA), % (on o.d. wood)	Sulfidity (*S*), % (as active alkali)	RESPONSE VARIABLES: *a*, x 10^{-3}	*A*, x 10^{-4}	*B*, x 10^{-6}	*H*-factor
ABAFX011,12 [a]	40	165.6	13	20	6.207	–4.7	–1.565	555
ABAFX013,14	80	176.7	13	20	5.911	–4.9	0.5914	2732
ABAFX015,16	80	165.6	16	20	6.512	–4.6	–0.8610	893
ABAFX017,18	40	176.7	16	20	6.213	–4.6	–1.137	…
ABAFX019,20	80	165.6	13	35	6.117	–4.0	–1.962	838
ABAFX021,22	40	176.7	13	35	5.879	–4.2	–1.917	1499
ABAFX023,24	40	165.6	16	35	6.133	–4.4	–1.279	631
ABAFX025,26 [b]	80	176.7	16	35	5.938	–4.3	–0.8262	2595
ABAFX027,28	80	165.6	13	20	6.027	–4.5	–1.402	982
ABAFX029,30	40	176.7	13	20	6.092	–4.5	–1.343	1401
ABAFX031,32	40	165.6	16	20	6.355	–4.5	–1.361	473
ABAFX033,34	80	176.7	16	20	6.37	–4.7	–0.9270	2606
ABAFX035,36	40	165.6	13	35	5.994	–4.7	–0.8124	575
ABAFX037,38	80	176.7	13	35	6.001	–4.6	–1.050	2422
ABAFX039,40	80	165.6	16	35	6.08	–4.1	–1.245	977
ABAFX041,42	40	176.7	16	35	5.991	–4.5	–0.8742	1433
ABAFX043,44 [c]	60	171.1	14.5	27.5	6.054	–4.7	–1.125	1270
ABAFX051,52	60	182.2	14.5	27.5	5.926	–4.0	–0.7494	3067
ABAFX053,54	60	171.1	11.5	27.5	5.567	–4.7	–1.245	1237
ABAFX055,56	60	171.1	17.5	27.5	5.908	–4.6	–1.005	1234
ABAFX057,58	60	171.1	14.5	12.5	6.249	–4.9	–0.8815	1248
ABAFX059,60	60	171.1	14.5	42.5	5.86	–4.4	–1.368	1179
ABAFX069,70	60	160	14.5	27.5	6.183	–3.9	–1.500	561
ABAFX073	100	171.1	14.5	27.5	6.623	–4.6	–0.8029	1993
ABAFX075,76	20	171.1	14.5	27.5	6.6	–4.7	–1.447	514

[a] Mildest pulping conditions
[b] Harshest pulping conditions
[c] Center point of the experimental design

I. Pulping conditions, parameters a, A, and B (for use in Eqs. 1 and 2), and H-factor for the 25 liquors used in this study

ploying different statistical criteria. The resultant models then were replaced in Eqs. 1 and 2 to define density at 25°C (ρ_{25}) and reduced density (ρ_R), respectively, of the liquors as a function of the pulping conditions. By fixing the liquor temperature and solids content, one can study the joint effect of the input variables of pulping on the density response of black liquor.

Response-surface methods

The empirical study of liquor density as the measured response to the input variables of pulping (effective alkali, sulfidity, cooking time, and cooking temperature) was performed using response-surface methodology *(14)*. To develop plots of the response surface, the following general multiple-regression linear model—consisting of main effects, quadratic terms, and higher-order interactions—was used to develop predictive models for a, A, and B as a function of the pulping variables. The data for the 25 different black liquors provides enough information to develop linear regression models for the response variables (a, A, and B and, as a consequence, liquor density) that consist of 19 model terms (excluding the intercept). The linear regression model can be defined as:

$$Y = ß_0 + \sum_{i=1}^{4} {}^4ß_i X_i + \sum_{i<j}^{4} {}^4ß_{ij} X_i X_j + \sum_{i<j<k}^{4} {}^4ß_{ijk} X_i X_j X_k + \sum_{i<j<k<l}^{4} {}^4ß_{ijkl} X_i X_j X_k X_l + \sum_{i=1}^{4} {}^4ß_{ii} X_i^2 \quad (3)$$

where

Y = estimate for the response variables (a, A, and B)
X_i = main effects (EA, S, T, and t) known for each liquor
$X_i X_j$ = second-order interactions
$X_i X_j X_k$ = third-order interactions
$X_i X_j X_k X_l$ = fourth-order interactions
X_i^2 = quadratic effects.

The constants, $ß_0$, $ß_i$, $ß_{ij}$, $ß_{ijk}$, and $ß_{ijkl}$, are the model parameters. The model contains four linear terms, six second-order interaction terms, four third-order terms, one fourth-order interaction term, and four quadratic terms for a total of 19 model terms (excluding the intercept) in the model.

The regression ("reg") procedure in the SAS (Statistical Analysis System) software package was used to determine the model parameters as in Eq. 3

Variables	PARAMETERS		
	a, kg/m³	*A*, °C⁻¹	*B*, °C⁻²
Intercept	2.193×10^{-1}	3.948×10^{-2}	-2.430×10^{-4}
t	-4.952×10^{-3}	-3.550×10^{-4}	-9.700×10^{-7}
T	-1.211×10^{-3}	-3.430×10^{-4}	1.435×10^{-6}
EA	-1.292×10^{-2}	-1.388×10^{-3}	1.518×10^{-5}
S	-7.347×10^{-3}	-1.129×10^{-3}	1.496×10^{-5}
$t \cdot T$	2.849×10^{-5}	2.095×10^{-6}	7.265×10^{-9}
$t \cdot EA$	3.050×10^{-4}	2.268×10^{-5}	5.540×10^{-8}
$t \cdot S$	1.560×10^{-4}	1.752×10^{-5}	-9.463×10^{-8}
$T \cdot EA$	8.065×10^{-5}	8.473×10^{-6}	-8.397×10^{-8}
$T \cdot S$	4.240×10^{-5}	6.634×10^{-6}	-8.550×10^{-8}
$EA \cdot S$	4.510×10^{-4}	7.255×10^{-5}	-9.800×10^{-7}
t^2	4.760×10^{-7}	5.117×10^{-9}	-1.268×10^{-11}
T^2	-3.460×10^{-7}	6.200×10^{-7}	-5.554×10^{-10}
EA^2	-3.132×10^{-5}	-1.468×10^{-6}	-4.144×10^{-9}
S^2	6.230×10^{-7}	3.668×10^{-8}	1.542×10^{-10}
$t \cdot T \cdot EA$	5.676×10^{-8}	6.550×10^{-9}	-3.280×10^{-11}
$T \cdot EA \cdot S$	-2.614×10^{-6}	-4.280×10^{-7}	5.614×10^{-9}
$t \cdot EA \cdot S$	-9.809×10^{-6}	-1.110×10^{-6}	6.113×10^{-9}
$t \cdot T \cdot EA$	-1.722×10^{-6}	-1.350×10^{-7}	-4.174×10^{-10}
$t \cdot T \cdot S$	-9.050×10^{-7}	-1.030×10^{-7}	5.034×10^{-10}
r^2	0.994	0.999	0.997

II. Complete linear regression model parameters for a, A, and B

and to perform residual analysis *(15)*. The r^2 values for models for *a*, *A*, and *B* were 0.994, 0.999, and 0.997, respectively. The analyses also showed that the responses of *a*, *A*, and *B* (and in consequence density) to pulping variables were nonlinear. This indicates that higher-order interactions should be included in the model-selection process.

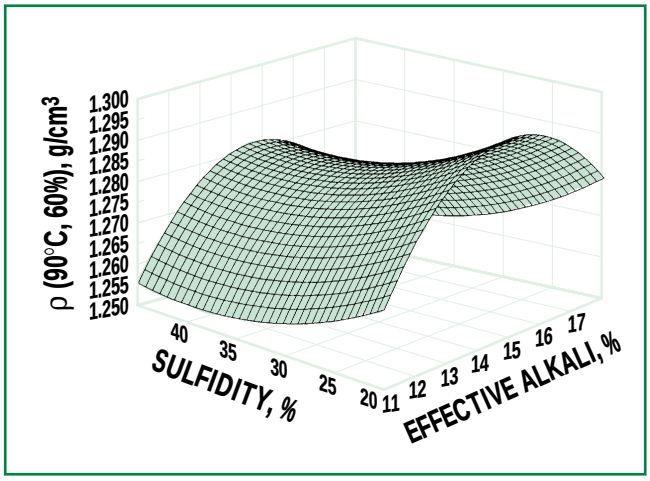
Surface-response plots

As mentioned earlier, Eq. 3 was used to fit the data for *a*, *A*, and *B* by applying the "reg" procedure in SAS. The resultant models can be used to develop geometric representations of the response variable, density, as a function of the input variables of pulping. The estimated model parameters for Eq. 3 for *a*, *A*, and *B* are summarized in **Table II**. By using the models to determine values for *a*, *A*, and *B* to be used in Eqs. 1 and 2, the density at 25°C (ρ_{25}) and the reduced density (ρ_R) were defined as functions of the pulping variables. Equation 1 takes into account the effect of solids content on the density at 25°C, while Eq. 2 defines the reduced density as a function of temperature. For a specific black liquor of known cooking conditions, one can determine (a) the reduced density of the liquor at any desired temperature and (b) the density of the liquor at 25°C at any desired solids content. The density of the liquor at that particular temperature and solids content can then be determined by multiplying the reduced density by the density of the liquor at 25°C.

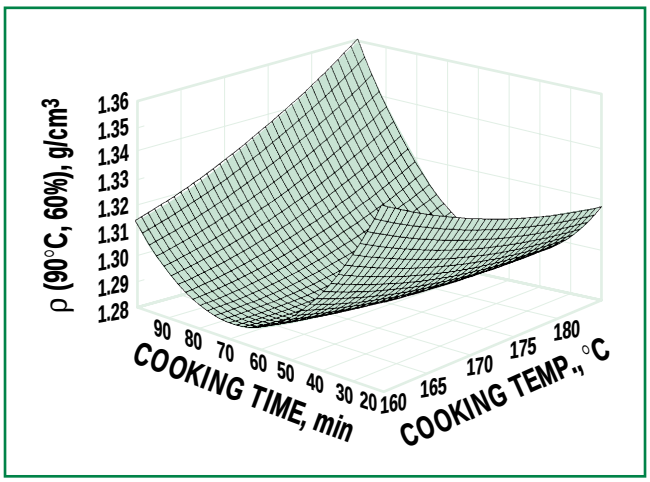
Since there are four independent variables—and since the density for every liquor is a function of temperature and solids content—two of the pulping variables as well as the liquor temperature and solids content must be fixed if a three-dimensional surface response is to be prepared. Different combinations of the input variables can be selected, depending on different needs. In this study, the temperature and solids content of the liquor were fixed at 90°C and 60% solids. Then, densities at 90°C and 60% solids [denoted as ρ(90°C, 60%)] were defined as a function of the cooking variables by using Eqs. 1 and 2 and the regression models for parameters *a*, *A*, and *B*. Three-dimensional plots for ρ(90°C, 60%) were developed by fixing two of the cooking variables at the center point of the design and varying the other two variables. **Figures 3–6** are examples of the response surfaces for density at 90°C and 60% solids as a function of the input variables of pulping (effective alkali, sulfidity, cooking time, and cooking temperature). Since the density is an increasing function of the solids content and a decreasing function of the liquor temperature, the same conclusions can be made at other solids contents and liquor temperatures.

Figure 3 represents the response surface for ρ(90°C, 60%) as a function of effective alkali and sulfidity at a constant cooking temperature of 171.1°C and a constant cooking time of 60 min. At this level of cooking time and cooking temperature, the density response is a rising–falling ridge with respect to effective alkali and a falling–rising ridge with respect to sulfidity at all levels of effective alkali. The variation of density with respect to effective alkali is much larger than its variation with respect to sulfidity. Density increases as the level of effective alkali is increased, reaches a maximum in the middle range, and then decreases with further increase in the level of effective alkali. It seems that the variation of density with sulfidity is more significant at lower levels of sulfidity.

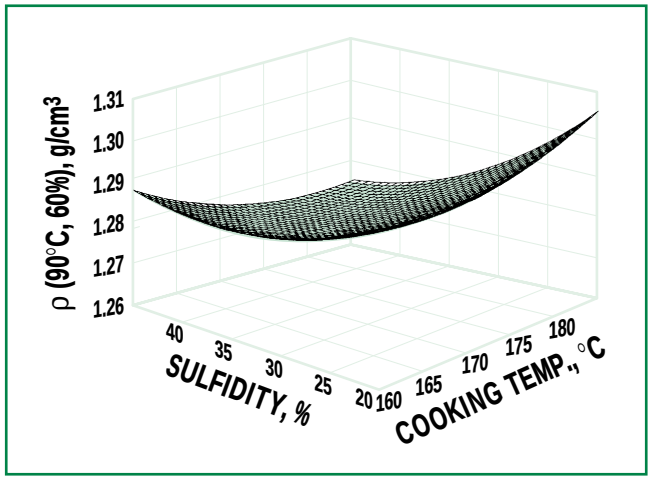
Figure 4 is the response of density with respect to cooking time and cooking temperature at a constant effective alkali of 14.5% and a sulfidity of 27.5%. The response of density to cooking time is a falling–rising ridge at all levels of cooking temperature. At a constant cooking temperature, density decreases as the level of cooking time is increased, reaches a minimum in the middle range, and then increases with further increase in the level of cooking time. With respect to the cooking temperature, the density response of black liquor depends on the level of cooking



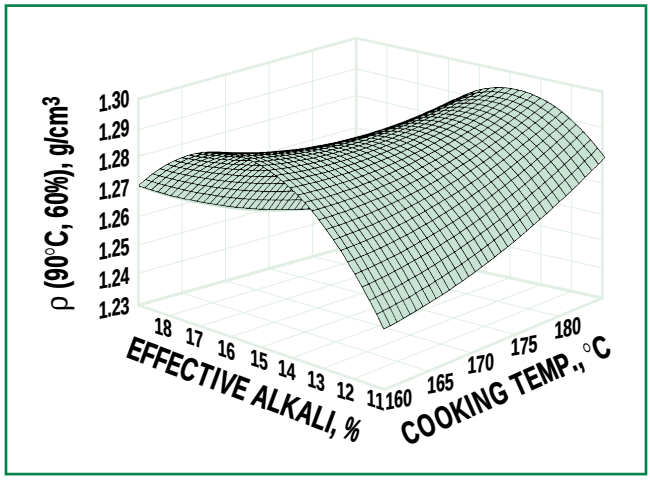
3. Surface-response plot for density of slash pine black liquors (at 90°C and 60% solids) as a function of sulfidity and effective alkali at constant cooking time (60 min) and temperature (171.1°C)



4. Surface-response plot for density of slash pine black liquors (at 90°C and 60% solids) as a function of cooking time and cooking temperature at constant effective alkali (14.5%) and sulfidity (27.5%)



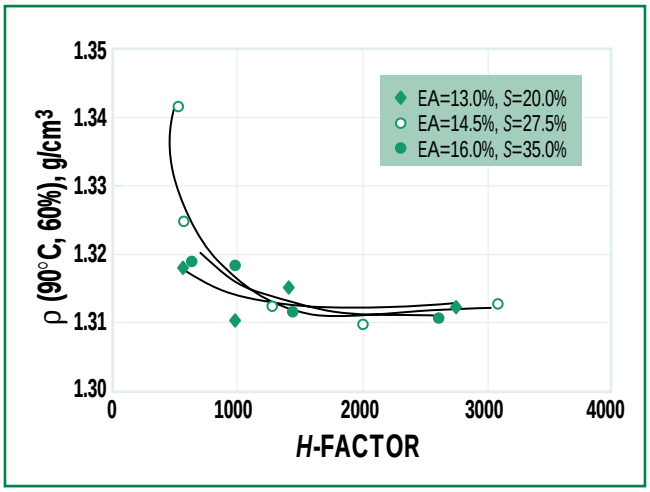
5. Surface-response plot for density of slash pine black liquors (at 90°C and 60% solids) as a function of sulfidity and cooking temperature at constant cooking time (60 min) and effective alkali (14.5%)



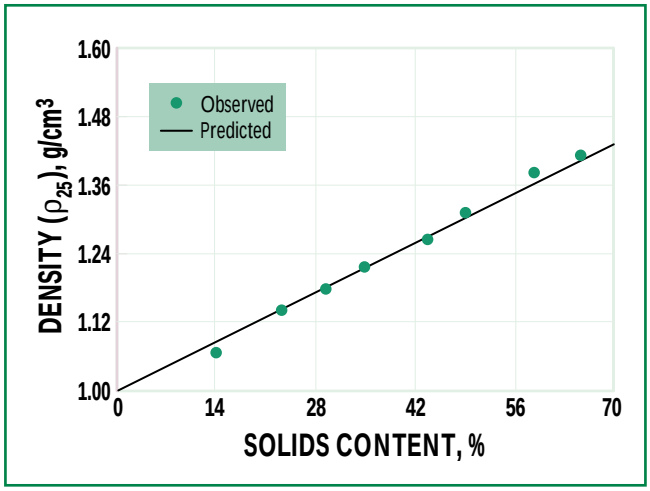
6. Surface-response plot for density of slash pine black liquors (at 90°C and 60% solids) as a function of effective alkali and cooking temperature at constant cooking time (60 min) and sulfidity (27.5%)

time. At low levels of cooking time, the density is a slightly decreasing function of the cooking temperature. At high levels of cooking time, density is an increasing function of the cooking temperature. The dependence of density on cooking temperature is more significant at higher levels of cooking time.

In the pulp and paper industry, the combined effect of cooking time and cooking temperature is known as the *H*-factor, and it is of value to explore the use of *H*-factor *(16, 17)* to study the joint effect of cooking time and cooking temperature on density. In this work, *H*-factors were calculated from the time–temperature profiles recorded for each cook and are reported in Table I. **Figure 7** is a plot of ρ(90°C, 60%) as a function of *H*-factor for cooks at three levels of effective alkali and sulfidity. In general, the density is high at low *H*-factor, decreases to approximately a minimum at intermediate *H*-factor, and is almost constant (or increases slightly) with further increase in *H*-factor. Since *H*-factor is related to lignin content and lignin molecular weight in the liquor during the cooking process *(8, 18, 19)*, the density behavior of black liquor can be described in terms of lignin content and its molecular weight. The sharp decrease in density at lower *H*-factors is due to an increase in the lignin content up to a maximum at intermediate *H*-factors *(8)*. Since, at higher *H*-factors, degradation of lignin is significant and prevents the formation of larger-molecular-weight lignins, further increase in *H*-factor decreases the molecular weight of lignin. There also may be a small decrease in lignin concentration from greater carbohydrate degradation at higher *H*-factors, which dilutes the lignin in the liquor solids.



7. Variation of black-liquor density (at 90°C and 60% solids) with H-factor at different three levels of effective alkali and sulfidity



8. Calculated and observed black-liquor density as a function of solids content for liquor ABAFX017,18 at 25°C

Figure 5 represents the effects of cooking temperature and sulfidity on the density response of black liquor at a constant effective alkali of 14.5% and a cooking time of 60 min. The density is a falling–rising ridge with respect to both cooking temperature and sulfidity. At every level of cooking temperature or sulfidity, the density increases with cooking temperature or sulfidity, reaches a minimum, and then increases with further increase in the level of these variables.

Figure 6 is the response-surface plot for density with respect to cooking temperature and effective alkali at fixed levels of sulfidity of 27.5% and cooking time of 60 min. The response is a rising–falling ridge with respect to effective alkali. At low levels of effective alkali, the density is an increasing function of the cooking temperature, while at high levels of effective alkali, it is a decreasing function of the cooking temperature.

Figures 3–6 present the results for the specific levels of the input variables noted in each case. These response-surface plots serve as examples to illustrate the utility of the regression models. The density response of black liquor to the pulping variables may be different at other levels of the cooking conditions, but the response can be examined by using the correlation to construct the required response surface.

STATISTICAL MODELING

The objective of finding models that can predict black-liquor density at process conditions is more challenging. The models for a, A, and B that were obtained contain 19 terms (excluding the intercept), but the significance levels indicate that several of the variables are not reasonable candidates as independent variables. Increasing the number of parameters in the model would require more experimental data and thus higher costs. Instead, a variety of statistical procedures were used to select the proper independent variables for predictive models with acceptable accuracy and time frame. These procedures are discussed in detail in several references *(14, 20)*.

The first selection procedure was performed using the "rsquare" routine in SAS *(15)* with Mallow's Cp criterion. The "rsquare" procedure finds subsets of independent variables that best predict a dependent variable by linear regression in the given sample. The routine can be set to perform all possible subset regressions. The results indicated that the best model without bias for a could be obtained with 10 independent variables. For A and B, the best model required 11 independent variables. The "rsquare" procedure is used for exploratory model analysis, and it requires running a large number of regression models, which can be very time consuming.

The "stepwise" routine in SAS also was used to select variables for the model. This procedure, which gives insight into the relationships between the dependent and independent variables, provides a variety of strategies for variable selection. The forward selection, backward elimination, and maximum r^2 strategies were used in this work. The forward selection starts with no variable in the model and adds the variable with the largest F-statistic one at a time to the model until a stopping criterion is satisfied. The backward elimination begins with the entire set of independent variables and systematically removes the variable with the smallest value of F-statistic one at a time. The maximum r^2 strategy attempts to ascertain the best model with one parameter, two parameters, and so forth, based on the largest differential increase in r^2 with each new variable.

The predictive models for a, A, and B were chosen using the "rsquare" and "stepwise" procedures. The regression procedure ("reg") in SAS was used for residual analysis. The models for a, A, and B (based on different statistical criteria) are:

$$a = 4.6 \times 10^{-3} - (1.67 \times 10^{-4})t + (8.66 \times 10^{-4})\mathrm{EA} - (1.8 \times 10^{-4})S + (8.51 \times 10^{-6})t\mathrm{EA} + (4.21 \times 10^{-6})tS - (7.99 \times 10^{-7})T\mathrm{EA} + (1.21 \times 10^{-5})\mathrm{EA}S + (3.48 \times 10^{-7})t^2 - (3.52 \times 10^{-5})\mathrm{EA}^2 - (2.85 \times 10^{-7})\mathrm{EA}St \quad (4)$$

Black liquor	*a*		*A*		*B*	
	Calculated, x 10^{-3}	Residual, x 10^{-5}	Calculated, x 10^{-4}	Residual, x 10^{-5}	Calculated, x 10^{-6}	Residual, x 10^{-8}
ABAFX011,12	6.207	3.749	–4.748	1.229	–1.565	–7.620
ABAFX015,16	6.512	–4.617	–4.568	–0.9066	–0.8610	–11.81
ABAFX017,18	6.213	–8.487	–4.635	0.7856	–1.137	–12.15
ABAFX019,20	6.117	–1.341	–4.024	–1.812	–1.962	2.218
ABAFX021,22	5.879	–1.832	–4.180	–0.4164	–1.917	4.792
ABAFX023,24	6.133	–5.827	–4.356	–1.445	–1.279	–1.314
ABAFX025,26	5.938	3.573	–4.277	–3.650	–0.8262	–3.205
ABAFX027,28	6.027	–8.711	–4.529	–0.7714	–1.402	–1.534
ABAFX029,30	6.092	–16.69	–4.450	–0.9856	–1.343	12.23
ABAFX031,32	6.355	–0.3270	–4.530	–0.2872	–1.361	16.85
ABAFX033,34	6.370	–3.877	–4.695	–0.7518	–0.9270	–4.816
ABAFX035,36	5.994	–10.32	–4.738	–1.425	–0.8124	9.335
ABAFX037,38	6.001	–10.30	–4.556	–2.573	–1.050	–2.781
ABAFX039,40	6.080	–11.11	–4.092	–3.003	–1.245	–5.287
ABAFX041,42	5.991	–2.217	–4.504	–2.406	–0.8742	9.339
ABAFX043,44	6.054	–8.720	–4.663	–1.184	–1.125	1.984
ABAFX059,60	5.860	4.055	–4.378	–2.392	–1.368	3.762
ABAFX065,66	5.567	4.343	–4.716	–1.561	–1.245	0.6824
ABAFX067,68	6.249	9.065	–4.948	1.681	–0.8815	7.066
ABAFX051,52	5.926	–1.890	–4.022	–0.5906	–0.7494	–5.674
ABAFX047,48	…	…	–4.592	–0.9682	–0.8029	–13.77
ABAFX075,76	6.600	6.145	–4.733	0.2444	–1.447	13.60

III. Predicted values and residuals for a, A, and B using Eqs. 4–6

with $r^2 = 0.93$ and adjusted $r^2 = 0.85$

$$A = 1.67 \times 10^{-2} - (1.1 \times 10^{-6})t - (2.0 \times 10^{-4})T - (4.11 \times 10^{-4})S + (6.25 \times 10^{-6})tS + (2.4 \times 10^{-6})TS + (2.58 \times 10^{-5})EAS + (5.83 \times 10^{-7})T^2 + (2.26 \times 10^{-9})tTSEA - (1.51 \times 10^{-7})EAST - (3.85 \times 10^{-7})EASt - (3.64 \times 10^{-8})STt \quad (5)$$

with $r^2 = 0.91$ and adjusted $r^2 = 0.81$

$$B = -1.269 \times 10^{-5} - (3.857 \times 10^{-6})t + (8.398 \times 10^{-6})S + (2.41 \times 10^{-8})Tt + (2.59 \times 10^{-7})tEA - (8.316 \times 10^{-9})tS + (3.812 \times 10^{-9})TEA - (4.723 \times 10^{-8})TS - (5.150 \times 10^{-7})EAS + (2.846 \times 10^{-12})tTEAS + (2.906 \times 10^{-9})EAST - (1.604 \times 10^{-9})EATt \quad (6)$$

with $r^2 = 0.96$ and adjusted $r^2 = 0.92$

In Eqs. 4–6, time (t) is in minutes, temperature (T) is in °C, and effective alkali (EA) and sulfidity (S) are in percent. The predicted values of a, A, and B using Eqs. 4–6 are listed in **Table III**, along with residual values. The residual analysis indicates that these models are accurate to within about 10% or better (for a, A, and B).

DETERMINATION OF DENSITY

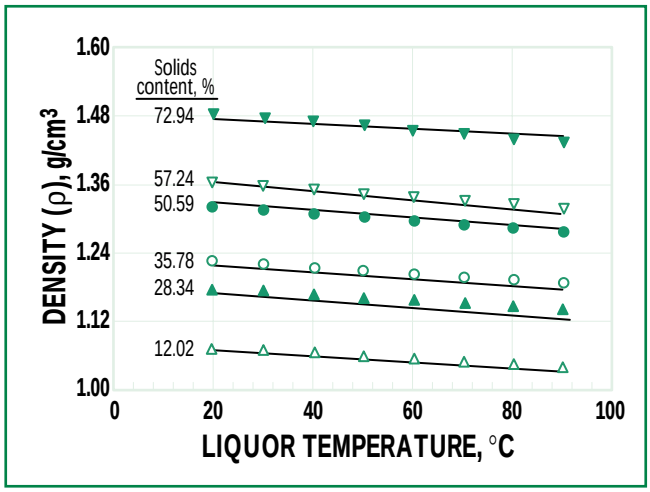
The following procedure can be applied to determine the density of a particular slash pine black liquor of known cooking conditions:

1. Determine parameters a, A, and B from the corresponding model.
2. Determine the reduced density of the liquor as a function of the liquor temperature by replacing the values of A and B in Eq. 2.
3. Determine the density of the liquor at 25°C as a function of solids content by replacing the value of a in Eq. 1.
4. Determine the density of the liquor as a function of the liquor temperature and solids content by multiplying the reduced density by the density of the liquor at 25°C.

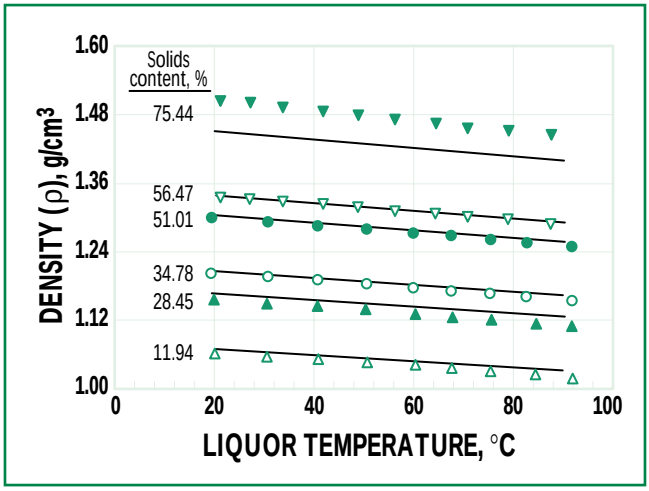
As mentioned earlier, the two second-order thermodynamic transitions that are evident from Fig. 1 occur around 65% solids and 80% solids. Therefore, above 65% solids, one must use the given relations with caution to calculate density. For most of the liquors for which data are available, it appears that these correlations are valid for solids contents up to 70%. These relations are not valid for the upper solids region (>80% solids).

The given procedure was used to determine the density of several of the liquors used in this study as a function of temperature and solids content. To check the accuracy of the models against experimental data, we excluded some of the liquors from statistical modeling. Using this approach, we could make a precise judgment about the predictive accuracy of the models by calculating the density of these liquors and then comparing the predictions with experimental observations.

Figure 8 shows the calculated values of density of black liquor ABAFX017,18 (a liquor that was ex-



9. Calculated and observed black-liquor density as a function of temperature for liquor ABAFX017,18 at six levels of solids content



10. Calculated and observed black-liquor density as a function of temperature for liquor ABAFX039,40 at six levels of solids content

cluded from the statistical modeling) and the experimental values of density at 25°C. There is almost no difference between the predicted and observed values of density at 25°C for this liquor.

Figures 9 and 10 show predicted and observed densities of black liquors ABAFX017,18 and ABAFX039, 40, respectively, at different temperatures and solids contents. (Liquor ABAFX039,40 was included in model selection, while liquor ABAFX017,18 was excluded.) The results are very accurate for solids contents up to 70%. However, the differences between the observed and calculated values (about 3%) of density for liquor ABAFX039,40 at 75.44% solids (Fig. 10) are due to the thermodynamic transition that was discussed earlier. At solids contents above 70%, the calculated values of density are smaller than the observed values, as might be expected.

SUMMARY AND CONCLUSIONS

Density data for slash pine kraft black liquors over wide ranges of temperature (20–90°C) and solids contents (up to 80%) were presented. It was shown that kraft black liquors (at 25°C) undergo two thermodynamic second-order transitions at solids contents of about 65% and 80%. Density shows a linear relation with solids content in all three regions, so three linear equations are required to define the density behavior of the liquor over the entire range of solids (0–100%) at a constant temperature of 25°C. The density data for the lower regions of the graphs for 25 black liquors were correlated to the solids content using a single straight line, with the density of water at 25°C as the intercept of the lines with the *y*-axis (density). Note, however, that the data in the first region of low solids cannot be extrapolated to determine liquor density at higher solids contents.

The concept of "corresponding states" was applied to reduce the density data for these liquors. The liquor density measured at any temperature and solids content was divided by the liquor density at 25°C at the same solids content to obtain a reduced plot for liquor density as a function of temperature over the whole range of solids content. The choice of the reference density is arbitrary; liquor density at another temperature could be used as the reference state. The reduced density data were defined with a single correlation as a function of temperature. The constants of these correlations (every liquor has a different set of constants) were then used to study the effect of pulping variables on the density of black liquors.

The results indicate that there is a small variation in density from liquor to liquor, as indicated in **Fig. 11**, which is a composite plot of the density of three liquors used in this study. Variation in density from liquor to liquor is due to differences in the pulping conditions and/or black liquor composition.

It is interesting to note that the two second-order thermodynamic transitions occur at conditions for which it has been found the liquor exhibits rapid change in thermodynamic and rheological behavior with increase in solids content. We expect that these transitions may shift to higher solids contents as the temperature is increased.

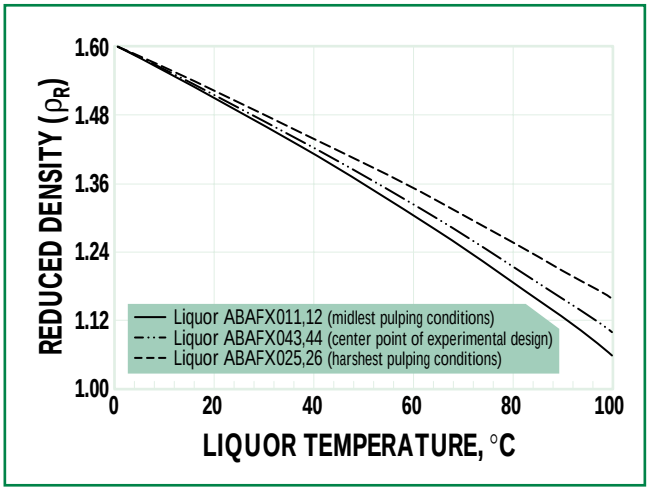
The effects of pulping variables on density response of slash pine black liquors were studied both qualitatively and statistically by surface-response methodology and by different statistical strategies. Accurate empirical models were developed for density at 25°C (ρ_{25}) and reduced density (ρ_R) of slash pine black liquors. The models can be used to predict the density of the liquors at operating conditions. Comparison of the calculated values of density (determined from the correlations that are presented in this paper) with the observed values indicates that the model should be accurate to within ±2% or better over wide ranges of temperature at solids contents less than 70%. At concentrations above

KEYWORDS
Black liquors, density, kraft liquors, models, Pinus elliottii, pulping, solids content, temperature, thermal expansion, variables.

70% solids, higher errors are expected because of the previously noted thermodynamic transitions.

The response surfaces with respect to cooking variables indicate that—at constant levels of cooking time and cooking temperature and at any level of sulfidity—black-liquor density increases with effective alkali, reaches a maximum, and then decreases with further increase in the level of effective alkali. With respect to sulfidity at fixed levels of effective alkali, it seems that there is no significant change in density as the level of sulfidity changes. With respect to cooking time and cooking temperature at fixed levels of effective alkali and sulfidity, variation of density with cooking time is more significant than variation with cooking temperature. At low levels of cooking time, density is a slightly decreasing function of the cooking temperature, while at high levels of cooking time it increases slightly as the cooking temperature is increased. With respect to cooking time at fixed levels of cooking temperature, as the cooking time is increased, density decreases, reaches a minimum, and then increases with further increase in cooking time.

While the results described here are for slash pine kraft black liquors, the principles developed are generally applicable (with few exceptions) to other liquors. The methods permit complete description of the density behavior of a black liquor over a wide range of processing with respect to liquor temperature, solids content, and pulping variables. Liquors from other wood species require less experimental data to describe their density behavior. **TJ**



11. Composite plot for reduced density of three slash pine black liquors as a function of temperature

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