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Studies on the Heat Capacity of Slash Pine Kraft Black Liquors: Effects of Temperature and Solids Concentrations

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Heat capacities of different kraft black liquors from statistically designed experiments for pulping slash pine were measured as a function of solids concentrations over a temperature range of (313.2 to 393.2) K using differential scanning calorimetry. The dependency of heat capacity on temperature and solids concentrations is described in detail. The results indicate that kraft black liquors are nonideal solutions, and their thermal properties cannot be predicted from the properties of pure water and solids. The excess heat capacities were determined using a binary solution assumption and are defined with a single correlation as a function of temperature and solids mass fraction for every single liquor. An empirical method is developed that can be applied to describe the heat capacity behavior of a single liquor as a function of temperature and solids concentrations. The results of this work show that the heat capacities are directly proportional to the organic-to-inorganic ratio in the liquor.

Introduction

The increasing importance of the energy recovery in the recovery unit of the pulp and paper industry has been followed by an increasing demand for the determination of physical properties of black liquors over wide ranges of temperature, solids concentration, and solids composition. Heat capacity data for black liquors are of particular importance in the design and efficient operation of components of kraft recovery systems. Energy balance calculations, estimating heat transfer coefficients, and developing enthalpy−concentration data for black liquors require heat capacity data over wide ranges of temperature and solids concentrations (Stoy and Fricke, 1994a,b). A lack of precise knowledge of black liquor heat capacity introduces an uncertainty in the design of elements of kraft recovery systems, and accurate determination of black liquor heat capacity is essential for a complete thermodynamic description of black liquor. Characterizing the behavior of black liquor, which is very complex in nature and contains many organic and inorganic constituents, will provide a useful tool for understanding the behavior of other compositionally complex materials.

Overview and Background

Although there are many reports in the literature about the physical properties of black liquor, few of them refer specifically to measurements of heat capacities of kraft black liquors. Harvin and Brown (1953) have reported the heat capacity values for sulfate black liquors. Hunter et al. (1953) have presented the heat capacity data as a function of solids concentration and temperature up to 48% solids and (303 to 361) K for sulfite black liquors. Koorse et al. (1977) have reported heat capacity values for bamboo, bagasse, and eucalyptus black liquors for concentrations up to 50% solids and a temperature range of (297 to 353) K. The most extensive studies on thermal properties of black liquors have been reported by Masse (1984), Masse et al. (1987), and Fricke (1987). They were able to develop a thermodynamic model for the heat capacity of black liquors using a pseudobinary solution assumption (a binary solution of organic and inorganic constituents in water) based on studies on the phase behavior of black liquor. Although their model was capable of predicting the heat capacity of black liquor to within (1 to 3)% of the experimental data, their work was limited to only two black liquors. Since the composition of black liquor varies with the cooking conditions and the wood species pulped, it is expected that heat capacities vary from liquor to liquor due to differences in the composition of the liquors. Therefore, more research had to be performed to study these effects on heat capacity and its variation with the cooking conditions and/or liquor composition.

In this paper, the results of the heat capacity of well-characterized slash pine kraft black liquors pulped under carefully controlled conditions are presented. The liquors used in this study were obtained by cooking slash pine in a pilot scale digester (0.111 m^3) with liquor circulation. The cooking variables were effective alkalinity, sulfidity, cooking temperature, and time at the cooking temperature. The liquor-to-wood ratio was held constant at 4/1, and synthetic white liquors with Na_2SO_4 and Na_2CO_3 added equivalent to a causticizing efficiency of 85% and a sulfate reduction efficiency of 93% were used. The cooking conditions for the liquors used in this study along with the pulp yields and lignin content of the liquors are summarized in Table 1.

Since the ultimate goal of this work was to relate physical and thermodynamic properties to black liquor composition, the liquors were analyzed rather completely. Analyses performed can be divided into six categories: (1) inorganic positive ions (Na, K, Ca, Mg); (2) inorganic negative ions (sulfide, sulfite, thiosulfate, sulfate, carbonate, and chloride); (3) organic ions (oxalate, formate, acetate, lactate/glycolate); (4) lignin content; (5) sulfated ash; (6) TAPPI tests (Kappa number, yield, sulfated ash). The analyses that have been performed and the methods used are described elsewhere (Fricke, 1987, 1990; Schmidl et al., 1990; Dong and Fricke, 1990). The chemical analyses for three of the liquors used in this study are shown in Table 2. Black liquor is a very complex solution that contains a myriad of organic compounds in minor amounts that are degradation products of cellulosics and of lignin as well as compounds originating from the extractives in wood. However, it has been found that the analyses described are sufficient to characterize the composition of a black liquor uniquely, and the analytical procedures used yield identical results when analyses are performed in different laboratories.

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Table 1. Pulping Conditions and Heat Capacities (at 65 mass % Solids and 60 °C) for Slash Pine Black Liquors[a]

black liquor	t/min	T/K	EA (%)	SU (%)	yield (%)	lignin content/ (g/g of solids)	C_p/(kJ·kg^{-1}·K^{-1}) at 65% and 333.2 K
ABAFX011,12	40	438.76	13.0	20.0	69.9	0.350	2.97
ABAFX013,14	80	449.86	13.0	20.0	50.6	0.435	2.96
ABAFX015,16	80	438.76	16.0	20.0	54.4	0.380	2.99
ABAFX017,18	40	449.86	16.0	20.0	49.9	0.409	2.87
ABAFX019,20	80	438.76	13.0	35.0	56.0	0.421	2.80
ABAFX021,22	40	449.86	13.0	35.0	55.4	0.417	2.86
ABAFX023,24	40	438.76	16.0	35.0	52.0	0.384	2.95
ABAFX025,26	80	449.86	16.0	35.0	42.7	0.393	3.08
ABAFX027,28	80	438.76	13.0	20.0	59.1	0.408	2.95
ABAFX029,30	40	449.86	13.0	20.0	58.7	0.427	2.95
ABAFX031,32	40	438.76	16.0	20.0	59.7	0.344	3.21
ABAFX033,34	80	449.86	16.0	20.0	41.0	0.440	2.95
ABAFX035,36	40	438.76	13.0	35.0	60.6	0.376	2.94
ABAFX037,38	80	449.86	13.0	35.0	49.5	0.423	2.99
ABAFX039,40	80	438.76	16.0	35.0	52.8	0.406	2.96
ABAFX041,42	40	449.86	16.0	35.0	49.6	0.404	2.92
ABAFX043,44	60	444.26	14.5	27.5	53.2	0.419	2.92
ABAFX045,46	20	444.26	14.5	27.5	68.3	0.365	2.94
ABAFX047,48	100	444.26	14.5	27.5	missing	0.430	2.99
ABAFX049,50	60	433.16	14.5	27.5	65.1	0.339	2.92
ABAFX051,52	60	455.36	14.5	27.5	45.2	0.430	2.91
ABAFX053,54	60	444.26	11.5	27.5	57.9	0.417	2.80
ABAFX055,56	60	444.26	17.5	27.5	50.8	0.406	2.88
ABAFX057,58	60	444.26	14.5	12.5	55.4	0.397	2.96
ABAFX059,60	60	444.26	14.5	42.5	52.5	0.413	2.96

[a] t = cooking time; T = cooking temperature; EA = effective alkali; SU = sulfidity.

Determination of Heat Capacities by Differential Scanning Calorimetry

A Perkin-Elmer differential scanning calorimeter (DSC), model DSC-7, equipped with a PE 7500 professional computer was used to measure the heat capacity of different black liquors over wide ranges of temperature and solids concentration. Differential scanning calorimetry records the differential rate of energy absorbed (or released) by the sample and reference holders to maintain them at the same temperature while changing the temperature of both cells at a controlled rate. Since the cell holders are identical, the differential power provided by the system is due to the rate of energy absorbed by the sample (for an endothermic transition, the power to the sample is increased, while for an exothermic transition, the power to the sample is decreased). The differential power is proportional to the change in enthalpy of the sample (or standard) and is given by (O'Neill, 1966)

$$P = \frac{\mathrm{d}H}{\mathrm{d}t} = mC_p\frac{\mathrm{d}T}{\mathrm{d}t} \qquad (1)$$

where P is the differential power, H is the enthalpy of the sample, m is the mass of the sample, C_p is the heat capacity of the sample, T is temperature, and t is time.

In principle, the heat capacity of the sample can be determined directly using eq 1 and knowing the mass of the sample, heating rate, and the instrument constant. However, in practice, the heat capacities are determined by comparison to a standard sample of known heat capacity. Assuming that P, the differential power, is proportional to the DSC signal and applying eq 1 to both the sample and standard, one can determine the heat capacity of the sample as

$$\mathrm{Cp} = \frac{y}{y_\mathrm{s}}\frac{m_\mathrm{s}}{m}C_{p_\mathrm{s}} \qquad (2)$$

where C_p is the heat capacity, m is the mass of the sample, y is the DSC signal, and s refers to the standard sample (sapphire).

Table 2. Results of Solids Analyses for Selected Liquors

components	component content/(g/g of solids)		
	ABAFX011,12	ABAFX025,26	ABAFX043,44
chloride	2.52×10^{-3}	3.10×10^{-3}	3.47×10^{-3}
sulfite	2.78×10^{-3}	3.15×10^{-3}	2.94×10^{-3}
sulfate	1.42×10^{-2}	2.08×10^{-2}	2.44×10^{-2}
oxalate	6.39×10^{-3}	5.18×10^{-3}	6.22×10^{-3}
thiosulfate	3.28×10^{-2}	6.32×10^{-2}	4.70×10^{-2}
carbonate	2.89×10^{-2}	6.56×10^{-2}	6.02×10^{-2}
lactate/glycolate	6.58×10^{-2}	9.41×10^{-2}	8.06×10^{-2}
formate	6.96×10^{-2}	7.77×10^{-2}	7.08×10^{-2}
acetate	5.19×10^{-2}	4.94×10^{-2}	5.49×10^{-2}
sodium, pre-evap	0.152	0.207	0.153
sodium, post-evap	0.209	0.218	0.21
sulfide, pre-evap	4.85×10^{-3}	2.27×10^{-2}	1.87×10^{-2}
lignin	0.35	0.3928	0.4178
calcium	1.88×10^{-3}	1.81×10^{-3}	2.22×10^{-3}
magnesium	6.73×10^{-4}	6.33×10^{-3}	7.77×10^{-4}
potassium	1.15×10^{-3}	6.85×10^{-4}	7.17×10^{-4}
sulfated ash % NaOH	31.6	36.1	33.2
pH	12.59	12.98	12.83
organic-to-inorganic ratio	2.12	2.051	2.227

Samples of black liquor were prepared by loading 30−35 mg of about 20% solid black liquor into the stainless steel pans and then allowing the water to evaporate to the desired solids content (for a range of concentrations up to 80% solids). The final solids concentrations were determined through material balance, knowing the initial and final masses of the liquor in the pan. When the desired concentration was obtained, the pans were sealed with an O-ring and cap in a press. Liquor samples at 100% solids were prepared by freeze drying samples containing about 20−30% solids (Fricke 1987, 1990). These samples were stored in sealed containers under dry conditions. Transfer and weighings were made in a drybox, since the liquor solids are highly hygroscopic.

The heat capacity of the samples was determined by three consecutive DSC scans: the baseline scan with an empty pan, the standard scan with the standard sample (sapphire), and the sample scan. The scan rate used was 4 K/min, and the heat capacities were determined over a temperature range of (313 to 393) K.

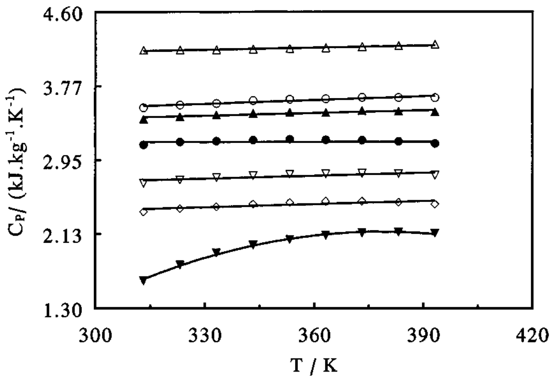

Figure 1. Heat capacity as a function of temperature for black liquor ABAFX011,12 at different solids concentrations: △, water; ○, 35% solids, ▲, 51% solids; ●, 52.5% solids; ▽, 73.3% solids; ◇, 80.4% solids; ▼, 100% solids.

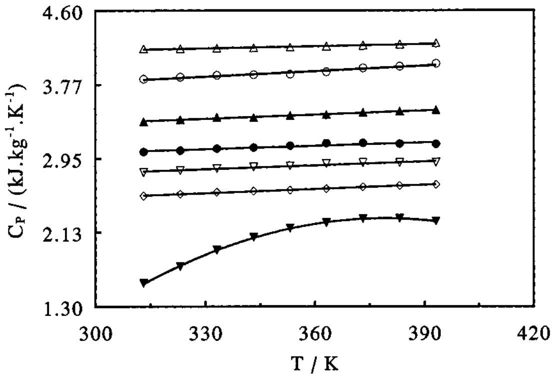

Figure 2. Heat capacity as a function of temperature for black liquor ABAFX015,16 at different solids concentrations: △, water; ○, 12% solids, ▲, 40% solids; ●, 60% solids; ▽, 71% solids; ◇, 80% solids; ▼, 100% solids.

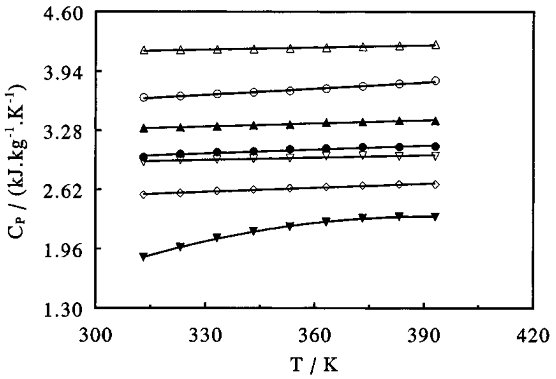

Figure 3. Heat capacity as a function of temperature for black liquor ABAFX043,44 at different solids concentrations: △, water; ○, 20% solids, ▲, 39% solids; ●, 52% solids; ▽, 66% solids; ◇, 80% solids; ▼, 100% solids.

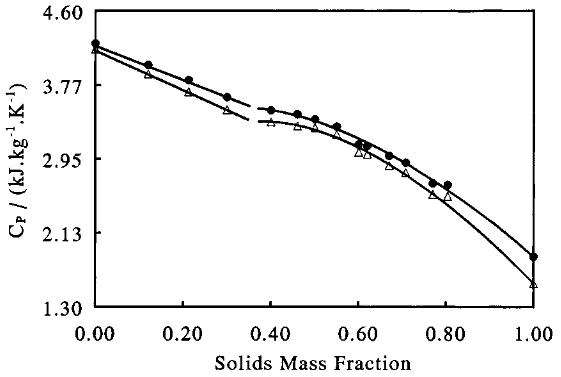

Figure 4. Heat capacity as a function of solids content for black liquor ABAFX015,16 at two different temperatures: △, 313.2 K; ●, 393.2 K.

Table 3. Constants of Eq 3 for Different Black Liquors at Different Solids Concentrations

black liquor	solids, %	a_1/(kJ/(kg K))	b_1/(kJ/(kg K^2))	R^2
ABAFX011,12	35.1	3.119	0.001 396 06	0.93
ABAFX011,12	50.7	3.118	0.000 998 93	0.80
ABAFX011,12	73.3	2.376	0.001 115 73	0.70
ABAFX011,12	80.4	2.036	0.001 181 28	0.64
ABAFX015,16	21.2	3.114	0.001 805 05	0.98
ABAFX015,16	46.0	2.862	0.001 523 32	0.94
ABAFX015,16	67.0	2.464	0.001 379 67	0.89
ABAFX015,16	80.4	2.056	0.001 544 59	0.99
ABAFX043,44	20.2	2.925	0.002 282 02	0.99
ABAFX043,44	52.0	2.555	0.001 427 44	0.93
ABAFX043,44	66.4	2.677	0.000 835 06	0.85
ABAFX043,44	79.9	2.097	0.001 512 86	0.97

Table 4. Constants of Eq 4 for Different Black Liquors

black liquor	a_2/ (kJ/(kg K))	b_2/ (kJ/(kg K^2))	c_2/ (kJ/(kg K^3))	R^2
ABAFX011,12	−15.62	0.093 901 8	-1.24×10^{-4}	0.99
ABAFX015,16	−21.78	0.126 919 7	-1.67×10^{-4}	0.999
ABAFX043,44	−9.24	0.059 251 8	-7.59×10^{-5}	0.999

Results

The heat capacities of three of the liquors as a function of temperature at different solids concentrations are shown in Figures 1−3. Solid lines represent the model predictions that will be discussed later. As can be observed, the heat capacity of black liquor is a decreasing function of the solids concentrations and a slowly increasing function of temperature. The variation of heat capacity with temperature increases as the solids concentration is increased. This is more obvious in the heat capacity of 100% solids black liquors where the heat capacity changes from (1.42 to 2.13), (1.55 to 2.26), and (1.88 to 2.30) kJ·kg^{-1}·K^{-1} for liquors ABAFX011,12, ABAFX015,16, and ABAFX043,44 respectively, over a temperature range of (313.2 to 393.2) K. The data for water (solvent) indicated in these figures are the literature values for the heat capacity of pure water (Weast and Astle, 1979). The heat capacity of black liquors at concentrations lower than 100% solids can be defined with a single straight line as a function of temperature, while at 100% solids, nonlinear behavior is observed and the data cannot be fitted with a single straight line as a function of temperature. The heat capacity of black liquors at concentrations lower than 100% solids is defined as

$$C_p = a_1 + b_1 T \tag{3}$$

where C_p is the heat capacity (kJ·kg^{-1}·K^{-1}). T is temperature (K), and a_1 and b_1 are constants that are concentration dependent. The values of a_1, b_1, and R^2 of the fits are summarized in Table 3 for these liquors at different solids concentrations. The model used to fit the heat capacity data of 100% solids black liquors is

$$C_p = a_2 + b_2 T + c_2 T^2 \tag{4}$$

where a_2, b_2, and c_2 are constants that are composition dependent. These values for liquors A, B, and C are summarized in Table 4. The effect of solids concentration on the heat capacity of liquors ABAFX015,16 and ABAFX043,44 are demonstrated in Figures 4 and 5, which are plots of heat capacity as a function of the solids mass fraction at different temperatures. As can be observed from these figures, the heat capacity of black liquor is a linear function of the solids mass fraction at concentrations lower than (~)0.45 (g of solids)/(g of liquor). At higher concentrations, nonlinear behavior is observed which indicates that

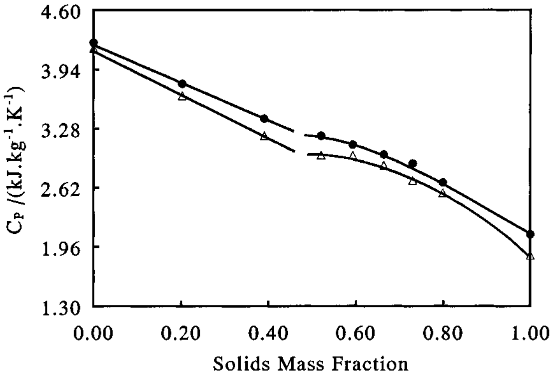

Figure 5. Heat capacity as a function of solids content for black liquor ABAFX043,44 at two different temperatures: △, 313.2 K; ●, 393.2 K.

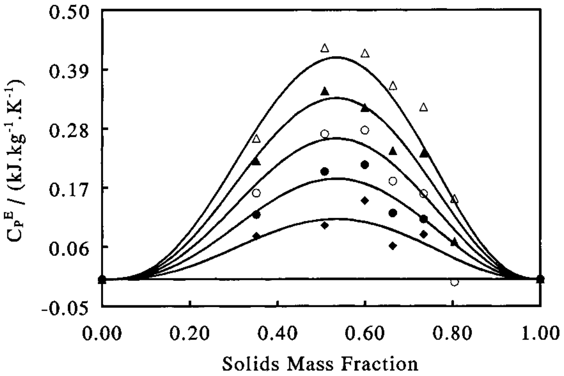

Figure 6. Excess heat capacity as a function of solids mass fraction for black liquor ABAFX011,12: △, 313.2 K; ▲, 333.2 K; ○, 353.2 K; ●, 373.2 K; ◆, 393.2 K.

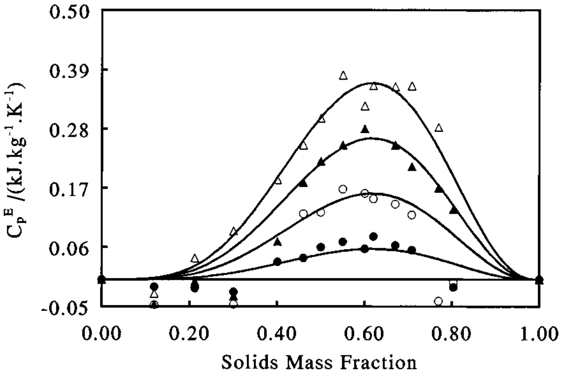

Figure 7. Excess heat capacity as a function of solids mass fraction for black liquor ABAFX015,16: △, 323.2 K; ▲, 343.2 K; ○, 363.2 K; ●, 383.2 K.

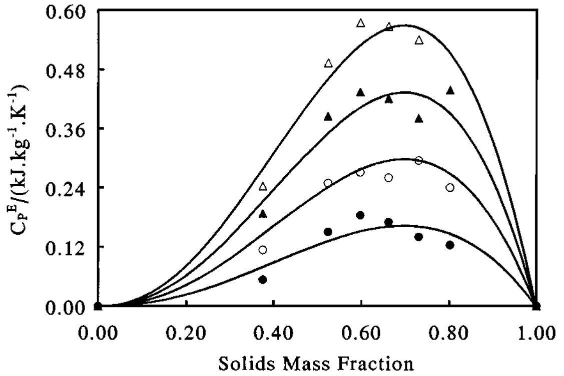

Figure 8. Excess heat capacity as a function of solids mass fraction for black liquor ABAFX053,54: △, 313.2 K; ▲, 333.2 K; ○, 353.2 K; ●, 373.2 K

black liquor is a nonideal solution. The thermal properties of black liquor cannot be predicted from just the properties of pure water and pure constituents (100% solids) due to its nonideal nature. The results indicate that there exists a particular concentration at about 0.43 (g of solids)/(g of liquor) where the liquors begin to exhibit nonlinear behavior. Previous studies (Masse, 1984; Zaman and Fricke, 1994) on the phase behavior of black liquors indicate that, at this concentration, black liquor undergoes a transition which is believed to be a change from a water continuous phase to a polymer continuous phase. The behavior observed for the heat capacity of black liquors appears to confirm the previously observed phase behavior. The heat capacities of all the liquors at 65% solids and 333.2 K are shown in the last column of Table 1. As can be observed, the heat capacity changes from (2.8 to 3.2) kJ·kg^{-1}·K^{-1} over a wide range of pulping conditions.

Excess Heat Capacities

In spite of the multicomponent nature of black liquor and its compositional complexity, earlier studies (Masse, 1984; Masse et al., 1987) indicate that any one black liquor can be treated as a binary solution of organic and inorganic constituents (with polymeric lignin being the main constituent) in water (solvent). Therefore, the excess heat capacity that takes into account the deviation from an ideal solution can be defined as

$$C_p^{\mathrm{E}} = C_p - (wC_p(\mathrm{s}) + (1 - w)C_p(\mathrm{w})) \tag{5}$$

where C_p^{E} is the excess heat capacity, C_p is the heat capacity of black liquor solution, $C_p(\mathrm{s})$ is the heat capacity of 100% solids black liquor, $C_p(\mathrm{w})$ is the heat capacity of water, and w is the mass fraction of solids. The heat capacities in this work are defined as mass-based heat capacities. The excess heat capacities of the liquors at different temperatures were determined by using the experimental values of the heat capacity of black liquor solutions and the literature values for the heat capacity of water at different temperatures. Figures 6–8 are plots of the excess heat capacities as a function of the solids mass fraction at different temperatures. As can be seen, the excess heat capacities are zero for pure components and reach a maximum in the concentration range of (0.7 to 0.8) (g of solids)/(g of liquor). Also, it is observed that, at some of the temperatures, the values of the excess heat capacity are negative over low ranges of concentrations. To the best of our knowledge, such a behavior for black liquors has not been reported in the literature before. Negative values of the excess heat capacity of some materials with strong interactions between different anions and cations (i.e., the presence of hydrogen bonds in the solution) and even mixtures without any specific interactions (Grolier et al., 1984) have been reported in the literature. For black liquor solutions, the observed values of the excess heat capacity at low concentrations are very small, and we think that the negative values are due to experimental error and the range of the accuracy of the instrument used in this work. However, more definite conclusions could be made, if more accurate instruments were used and also if additional properties of these solutions, such as excess enthalpies and excess Gibbs free energies, were available.

Masse et al. (1987) and Fricke (1987), by applying the simple lattice model which was developed by Flory (1953) for polymer solutions, have shown that the excess heat capacity of black liquors at a given temperature can be defined as

$$C_p^{\mathrm{E}} = \gamma(1 - w)^m w^n \tag{6}$$

Table 5. Model Parameters for the Excess Heat Capacity (Eq 8) of Different Black Liquors

black liquor	a_3/(kJ/(kg K))	b_3/(kJ/(kg K^2))	m	n	R^2
ABAFX011,12	78.38	-0.185	2.63	3.01	0.86
ABAFX015,16	203.47	-0.516	2.65	4.28	0.89
ABAFX053,54	21.13	-0.0532	1.02	2.35	0.92

In this equation, the solids mass fractions (w) have been used instead of the volume fraction of the constituents. Since the simple lattice model does not account for the temperature dependence of the component densities and also for the volume fraction of the constituents of black liquor that cannot be determined experimentally, using solids mass fractions is more practical and, especially in the case of a multicomponent solution such as black liquor, offers a reliable means for defining the excess heat capacities as a function of the solids content of black liquor.

The results of earlier work (Masse et al., 1987; Fricke, 1987) indicate that m and n are composition dependent constants (vary with the type of liquor) that are independent of temperature, but the parameter γ is a decreasing function of temperature and also varies from liquor to liquor due to variation in the composition of the solids in the liquor. The parameter γ can be defined as

$$\gamma = a_3 + b_3T \tag{7}$$

where a_3 and b_3 are constants that are composition dependent.

By replacing eq 7 with eq 6, the excess heat capacity can be defined as

$$C_p^{\mathrm{E}} = (a_3 + b_3T)(1 - w)^m w^n \tag{8}$$

In this work, eq 8 was used to fit the data for the excess heat capacity of different black liquors at different temperatures and solids concentrations. The constants of the model along with R^2 of the fits for the liquors used in this study are summarized in Table 5.

The solid lines in Figures 6−8 illustrate the model predictions for the excess heat capacities at different temperatures. The excess heat capacity data and the predicted values agree well over the entire range of concentration. With the model as expressed in eq 8, and using the heat capacity of water, the heat capacity of a liquor can be determined as a function of temperature and solids concentration. The values of a_3 and b_3 listed in Table 5 for different black liquors indicate that the excess heat capacity is a decreasing function of temperature. Therefore, the nonideal behavior of black liquor is decreased as the temperature is increased.

Combined Effects of Temperature and Solids Content on Heat Capacity

As discussed earlier, from the plots of heat capacity as a function of temperature, it can be observed that heat capacity varies linearly with temperature for the different solids concentration levels studied (except for 100% solids liquors which show slightly nonlinear behavior). In this work, extensive efforts were made to combine the effects of temperature and solids concentrations and define the heat capacity of black liquors over the whole range of temperature and solids concentrations with a single correlation. After considerable searching, the following relationship was found to fit the heat capacity data for different black liquors:

$$C_p = (A + BT)S + CT + D \tag{9}$$

where A, B, C, and D are constants and S is the solids mass fraction used instead of w in the rest of the paper for convenience. In this equation a linear dependence for the heat capacity as a function of solids concentration (at a fixed T) is assumed. As discussed earlier, although the variation of the heat capacity with solids content is slightly nonlinear at higher solids concentrations, it does not seem that using a linear assumption reduces the accuracy of the fits significantly.

As the solids concentration approaches zero, eq 9 represents the heat capacity of water as a function of temperature, and the constants C and D can be taken to be the values of these parameters for pure water. Therefore, two constants, A and B, remain that must be determined to define the heat capacity behavior of a particular liquor over the whole range of experimental temperature and solids concentrations. Other methods of correlation for the heat capacity behavior of black liquors as a function of temperature and solids content can be found in the literature, and some are reviewed briefly here.

Koorse et al. (1977) used the following model to define the heat capacity data for bamboo, bagasse, and eucalyptus black liquors:

$$C_p = (a + bT)S + 1 \tag{10}$$

where a and b are the constants of the model and vary from liquor to liquor. As can be seen, this model does not take the temperature dependency of the heat capacity as the solids concentration approaches zero into account. The model predicts a heat capacity of 1 for water at all temperatures.

Harvin and Brown (1953) correlated the heat capacity data of pine black liquors using

$$C_p/(\mathrm{kcal{\cdot}kg^{-1}{\cdot}{}^\circ C^{-1}}) = (0.99 - 0.639S) + (1.44 \times 10^{-4} + 11.52 \times 10^{-4}S)(T/{}^\circ\mathrm{C}) \tag{11}$$

This model predicts a temperature dependent heat capacity as S approaches zero; however, the value of the heat capacity at $S = 0$ differs slightly from the heat capacity of water.

In this work, eq 9 (with values for $C = 6.19 \times 10^{-4}$ $\mathrm{kJ{\cdot}kg^{-1}{\cdot}K^{-1}}$ and $D = 3.98$ $\mathrm{kJ{\cdot}kg^{-1}{\cdot}K^{-1}}$ determined from the heat capacity data for pure water given in the literature) was employed to fit the heat capacity data for many different black liquors. The values of A and B along with R^2 of the fits for some of the liquors are summarized in Table 6. The residual analysis indicates that the experimental and predicted values of the heat capacity agree to within (3 to 4)% or better over a wide temperature range of (313.2 to 393.2) K and a wide concentration range of (0 to 100)% solids. It also appears that the constant A in eq 9 for different liquors is relatively insensitive to the variation in composition of these liquors. The constant B in this equation appears to be strongly dependent upon the solids composition as is indicated in Figure 9, which is a plot of B as a function of the organic-to-inorganic ratio of four of these liquors. It is evident from the figure that B is an increasing function of the organic-to-inorganic ratio. If we ignore the variation of A with the composition of the solids of the black liquor, then it can generally be stated that the heat capacity of black liquor will increase as the concentration of the organic components is increased and/or the concentration of the inorganic components is decreased. The constants A and B can be used to investigate the effects of pulping conditions and black liquor composition on the heat capacity behavior of slash pine black liquors. Also, these constants can be correlated empirically to the pulping conditions and/or black liquor composition to determine predictive models for the heat

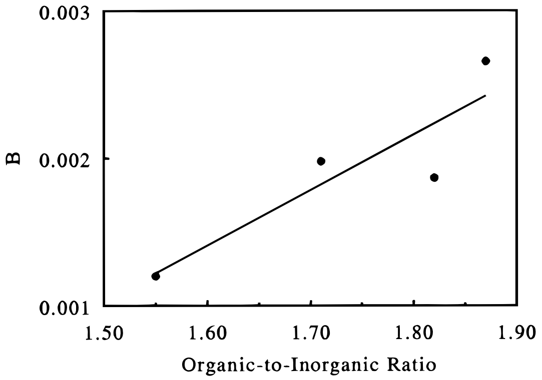

Figure 9. Constant B (as in eq 9) as a function of the organic-to-inorganic ratio in different black liquors.

Table 6. Model Parameters for the Heat Capacity (Eq 9) of Different Black Liquors

black liquor	A/(kJ/(kg K))	B/(kJ/(kg K^2))	R^2
ABAFX011,12	−2.65	0.001 867 2	0.99
ABAFX013,14	−2.66	0.001 898 5	0.99
ABAFX015,16	−2.87	0.002 656 7	0.99
ABAFX017,18	−2.63	0.001 571 3	0.99
ABAFX019,20	−2.67	0.001 632 0	0.99
ABAFX021,22	−2.75	0.001 838 6	0.99
ABAFX023,24	−2.59	0.001 791 1	0.99
ABAFX025,26	−2.41	0.001 202 4	0.99
ABAFX027,28	−2.39	0.001 366 7	0.99
ABAFX029,30	−2.59	0.001 718 0	0.99
ABAFX031,32	−2.71	0.002 124 4	0.99
ABAFX033,34	−2.39	0.001 272 7	0.99
ABAFX035,36	−2.67	0.002 109 9	0.99
ABAFX037,38	−3.26	0.003 210 4	0.99
ABAFX039,40	−2.85	0.002 536 6	0.99
ABAFX041,42	−2.73	0.002 190 5	0.99
ABAFX043,44	−2.68	0.001 977 3	0.99
ABAFX045,46	−2.48	0.001 386 8	0.99
ABAFX047,48	−2.67	0.002 087 3	0.99
ABAFX049,50	−2.28	0.000 938 6	0.99
ABAFX051,52	−2.80	0.002 148 3	0.99
ABAFX053,54	−2.72	0.001 841 8	0.99
ABAFX055,56	−2.52	0.001 498 2	0.99
ABAFX057,58	−2.45	0.001 310 2	0.99
ABAFX059,60	−2.41	0.001 325 5	0.99

capacity behavior of liquors of single species, which is the subject of a future paper.

Summary and Conclusions

Experimental heat capacity measurements of black liquor which is a complex multicomponent solution have shown that kraft black liquors are nonideal solutions, and their thermal properties cannot be predicted by knowing the properties of pure water and solids. As the solids concentration is increased from (0 to 100)% solids, the behavior of the liquors changes from a linear to a nonlinear behavior at concentrations around 43 mass % solids.

Direct measurements of heat capacities of 100% solids slash pine black liquors at 333.2 K are within the range of (1.61 to 3.20) kJ·kg^{-1}·K^{-1}. The heat capacities are a decreasing function of the solids concentrations and a slightly increasing function of temperature. The results indicate that, at a fixed solids content, and concentrations lower than 100% solids, a single straight line can describe the heat capacity behavior of black liquors. At 100% solids, the variation of the heat capacity of the liquors with temperature is nonlinear.

The excess heat capacities of the liquors were determined using a pseudobinary assumption and the model which was developed prior to this work. The excess heat capacity reaches a maximum value at a concentration of nearly (50 to 80)% solids and approaches zero at the concentration extremes corresponding to pure water and pure solutes. The model for the excess heat capacity that was used in this work is such that it takes into account the effects of both temperature and solids concentration on the excess heat capacity of black liquors.

An empirical correlation was defined to describe the heat capacity behavior of black liquors as a function of temperature and solids concentrations. This model was applied to many different slash pine black liquors and shown to correlate the data over a wide range of temperature and solids concentrations accurately. This will reduce the amount of the experimental data that is required to define the heat capacity behavior of a new liquor significantly. The constant B in this model is highly affected by the composition of the liquor solids and is directly proportional to the organic-to-inorganic ratio of solids in the liquor. Variation of B with the organic-to-inorganic ratio indicates that the heat capacity of black liquor is an increasing function of the organic-to-inorganic ratio. These constants, A and B, will be correlated with the pulping conditions and black liquor composition in the future.

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