

Density and thermal expansion of black liquors

Abbas Zaman, Matthew O. Wight, and Arthur L. Fricke

ABSTRACT: *Methods for precise density measurements of black liquors at 10–100% solids and for thermal expansion are available. Black liquors exhibit two second order thermodynamic transitions at 25°C over a range of solids. Linear extrapolation of low solids data does not determine black liquor density. Variation in density for different kraft liquors comes not only from variations in the organic to inorganic ratio. At solids concentrations below 65%, thermal expansion correlates successfully as a reduced variable quantity.*

KEYWORDS: *Black liquors, density, kraft liquors, thermal expansion, thermodynamics, transition temperature.*

The kraft process continues as the dominant wood pulping process worldwide, because it is an economical process for producing high quality pulp from a variety of fiber sources when practiced on a large scale. An essential part of the kraft process is the chemical recovery cycle. Until the mid-1970s, study of the chemical recovery cycle concerned only a minor amount of the total research and development effort devoted to kraft pulping. The sudden increase in energy prices and the threat of energy shortages that occurred then renewed interest in improvements in the recovery cycle.

Although the predicted higher energy prices and energy shortages

have not occurred, the relative cost of energy is much higher today than before 1970. An incentive therefore exists to reduce the capital requirements for chemical recovery and decrease sulfur emissions. Possible techniques involving improvements in the present process or replacement of one or more of the present operations have led a sustained interest in research and development in chemical recovery. Quantitative descriptions of the physical and chemical properties of black liquor are important to improve the present process or to develop replacement operations.

Density of kraft black liquors is an important physical property for

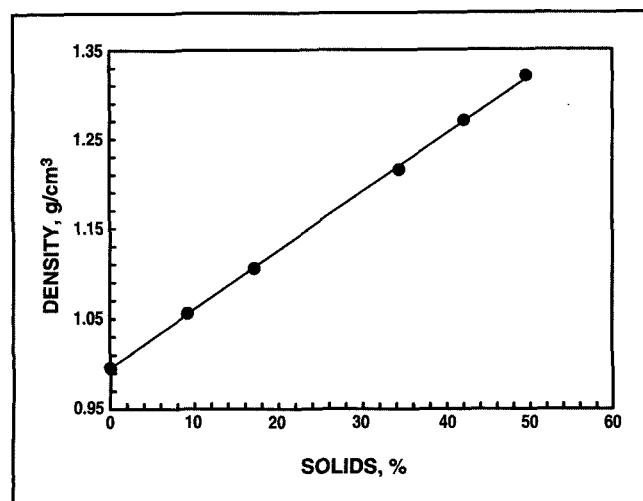
analysis of a plant operation. It is necessary to determine volumetric flow rates and the mass flow rates necessary for mass and energy balances. Density also appears in many engineering relations for design based on similitude. A lack of precise knowledge of black liquor density introduces an uncertainty in applying these relations to the design of process elements for the recovery cycle. Specific volume, the reciprocal of density, is an intensive thermodynamic state property. Precise determination of this quantity is an essential part of a complete thermodynamic description of black liquor.

There are many reports of measurements of the densities of kraft (sulfate), sulfite, and soda liquors. In nearly every case, however, there was no liquor characterization and density values were only at one temperature. Kobe and McDonald (1) reported densities as a function of solids concentration and temperature up to 50% solids and 96–98°C for soda, sulfate, and sulfite liquors. There was no other characterization. Han (2) related specific gravities at 25°C and 16°C for neutral sulfite semichemical (NSSC), kraft, and acid sulfite liquors up to 55% solids with the percentage inorganics for the liquors. Lubienska and Graczak (3) also reported density as a function of solids and percentage of inorganics. Han and Lubienska found that density increases linearly with solids concentration at constant

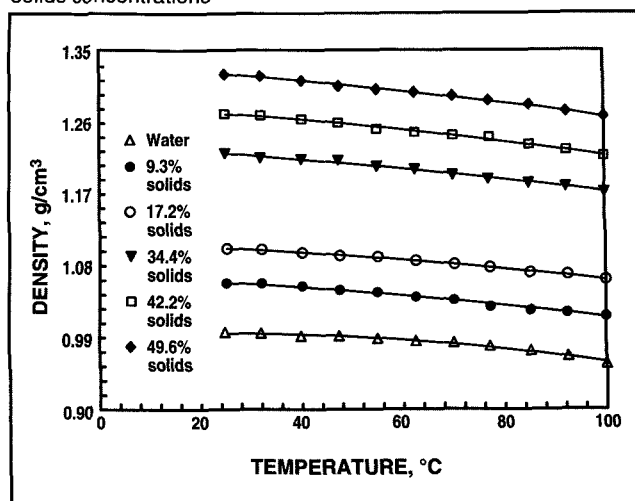
Zaman is post doctoral associate at University of Florida, Chemical Engineering Department, Gainesville, FL 32611, Wight is research engineer at Keyes Fiber Co., Upper College Ave., Waterville, ME 04901, and Fricke is professor at University of Florida, Chemical Engineering Department, Gainesville, FL 32611.

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1. Variation of kraft black liquor density for Liquor T-2823 at 25°C



2. Effect of temperature on density of Liquor T-2823 at various solids concentrations



temperature and solids composition. Hunter *et al.* (4) determined density as a function of solids concentration and temperature for sulfite liquor. Others have also reported density of liquors from various pulping processes used with different fiber sources (5,6). Of these reports, Hultin's has the most details.

Our early work (7,8) has provided the most details for kraft black liquors, and we will critically review some of it later. We found that density at constant temperature is an exact linear function of solids concentration up to 50% for kraft liquors of widely different solids composition. We also developed a correlation for thermal expansion based on principles of corresponding states that correlated Hunter's data with ours. Differences in the density at constant temperature were not totally explainable, however, on the basis of organic to inorganic ratio in the solids. The organic to inorganic ratios of liquors used in the study came from sulfated ash analyses. Extrapolation of the low solids data predicted a density of 1615–1770 kg/m³ for 100% solids at 25°C. Using the densities of the components present in 100% black liquor solids or of substances similar to those present, one can estimate the density of 100% black liquor solids with no solids interaction

I. Kraft black liquor properties

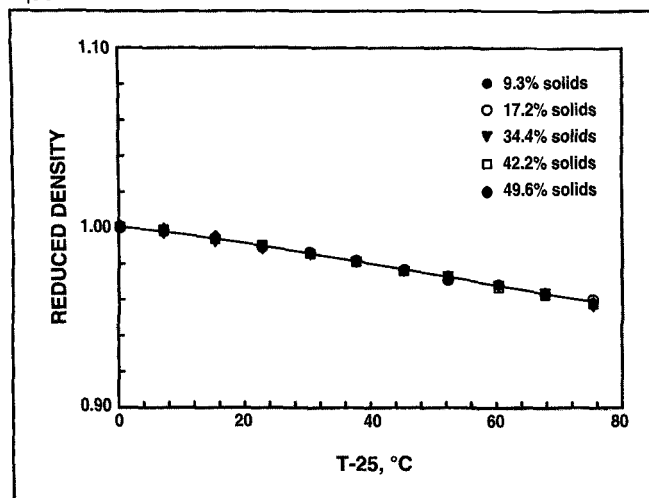
Liquor	Effective alkali, %	Sulfur, %	Time, min	Temp., °F	Kappa no.	Organic to inorganic ratio	$a \times 10^3$ for Eq. 1
T-2810	13	19.9	40	330	129.6	1.630	6.780
T-2816	16	19.9	80	330	58.1	1.960	6.560
T-2820	13	34.7	80	330	65.7	2.391	6.144
T-2823	16	34.7	40	330	82.9	1.516	6.430
T-2825	16	34.7	80	350	18.0	2.253	6.170
T-2880	13	35.0	40	330	96.0	1.587	6.608
T-2881	13	20.6	80	330	85.7	2.140	6.414

as 1540–1580 kg/m³. Since extrapolated values were higher, we concluded that it was not possible to extrapolate low solids concentration data with confidence and that variations in the organic to inorganic ratio could not entirely explain the variations in liquor density (7,8). Adams and Frederick (9) reported results from part of our early work but overlooked the lack of complete correlation of density variations with organic to inorganic ratio and the caveat concerning extrapolation. Precise, direct measurement of density at high solids concentrations and precise measurement of thermal expansion are

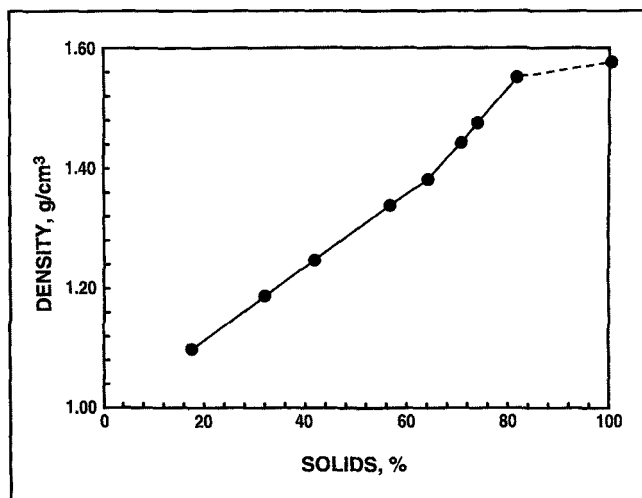
necessary from both practical and thermodynamic standpoints.

In this work, we have developed methods to measure density precisely at all solids concentrations up to 100% and have determined thermal expansion of liquors at solids concentrations up to 85%. Experimental measurements show that extrapolation of low solids density is usually in error and that black liquors apparently undergo two second order thermodynamic transitions between 50% and 100% solids. We also completely describe the methods used and present some results with appropriate discussions.

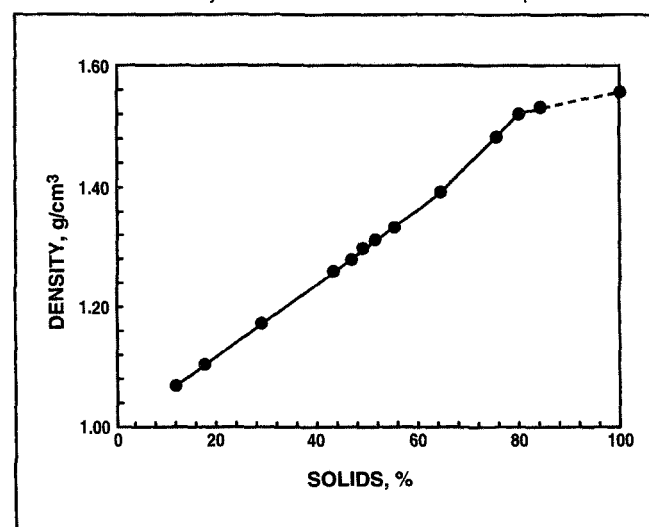
3. Effect of temperature on the reduced density of a kraft black liquor



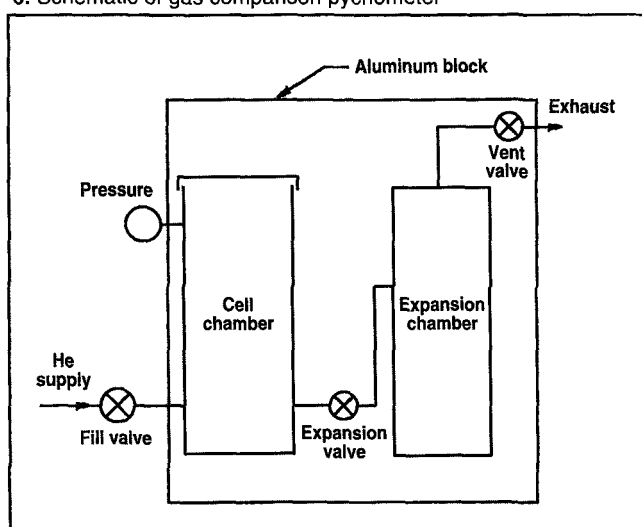
4. Variation of density of a slash pine kraft black liquor at 25°C



5. Variation of density of a mill softwood kraft black liquor at 25°C



6. Schematic of gas comparison pycnometer



Experimental

A variety of different procedures and instruments underwent evaluation. The following combination gave the best results: absolute pycnometry for density at solids below 60%, gas comparison pycnometry at solids above 55%, and dilatometry for thermal expansions. The overlap in ranges for the two methods for density measurements was deliberate to check agreement of the results. We used a 50-mL glass pycnometer that meets American Society for Testing and Materials (ASTM) method ASTM D 153 specifications for low solids den-

sity measurements. We successfully adapted a Micromeritics Model 1330 Accupyc gas comparison pycnometer for high solids density measurements. An American Oil Chemists Society (AOCS) Method Cd 10-57 dilatometer designed for use with fats and oils was a very satisfactory apparatus for thermal expansion measurements. The appendix provides details for the use of these apparatus.

Results and discussion

All densities for kraft black liquors from slash pine showed a linear relation with solids concentration at a constant temperature of 25°C for solids concentrations below 50%. **Figure 1** provides a typical result. We determined densities for a number of kraft black liquors from slash pine pulping. Equation 1 provides an accurate fit for the density values:

$$\rho_{25} = 0.99707 + ax \quad (1)$$

where

ρ_{25} = density at 25°C, g/mL

x = solids concentration, %

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a = constant.

Table I gives the conditions of pulping, values of the constant "a" for Eq. 1, and the organic to inorganic ratio for seven slash pine liquors. There is not a good correlation between the value of "a" for Eq. 1 and the organic to inorganic ratio for these liquors. As noted earlier, one can not linearly extrapolate the density, because extrapolation to 100% solids predicts a density considerably greater than the "ideal" density of about 1.54–1.58 g/mL for 100% solids. We therefore suspected that some changes in character of the liquor might occur. Determina-

tion of the density at high solids concentration had greater interest.

We also determined thermal expansion for these liquors by dilatometry at solids concentrations below 50% solids. **Figure 2** shows typical results. As Adams and Frederick reported (9), we used the concept of corresponding states to reduce this data. We divided the density at any temperature by the corresponding density for equal solids concentration of the liquor at 25°C to yield the reduced density, ρ_R . The choice of reference density for calculating ρ_R is arbitrary. It is possible to use any density in the region where the li-

quor is in the same physical state. We chose the density at 25°C as the reference density for convenience purposes. It is then possible to reduce all thermal expansion data for the liquor to a single curve which the following equation describes:

$$\rho_R = 1.0 - A(T - 25) - B(T - 25)^2 \quad (2)$$

where

T = temperature, °C

A, B = constants.

Figure 3 is a typical result for application of Eq. 2. It shows that the thermal expansion of the liquor com-

Appendix

Description of experimental equipment and methods

Absolute pycnometry using glass pycnometers is satisfactory for density measurements at solids below 60%. A Kimble no. 15123 50 mL Kimax glass pycnometer with ground glass thermometer and capped side arm performs well. The 50 mL pycnometer with 14–37°C thermometer with 0.2°C subdivisions meets ASTM D 153 specifications. Calibration of the pycnometer used water and mercury (12). The pycnometer calibration with mercury used several temperatures between 20–35°C to determine the change of pycnometer volume with temperature. We compared this change with the change predicted by using the correction factor for expansion of glass vessels recommended for such work (12). Since the comparison was excellent, other pycnometer calibration used only one temperature. The calibration correction for temperature differences used the recommended expression (12). One can obtain an accuracy of better than 0.1% with a single density measurement.

All efforts to develop an absolute pycnometry method for measuring liquor density at high solids above 62% failed because of the difficulties in handling and loading liquors. As a result, we selected comparison pycnometry. We successfully adapted a Micromeritics Model 1330 Accupyc (13) comparison pycnometer for these measurements. **Figure 6** shows a schematic of the instrument. The instrument has a cell chamber and an expansion chamber connected by lines containing solenoid valves. A very sensitive pressure transducer connects to the cell chamber. The entire assembly is within an aluminum block to ensure that temperatures of all components are equal. Helium gas at a controlled pressure is the comparison gas. The system operates at greater than ambient pressure during measurement. The sample for density determination is in a metal cylinder that slips into the cell chamber. After placing the sample in the cell chamber, one purges the system with helium and then isolates it to achieve pressure equilibrium. The expansion valve closes and additional helium enters the cell chamber until a preset pressure in the chamber occurs. After opening the expansion valve

and noting the pressure after expansion, density determination derives from the mass of sample, the known chamber volumes, and the pressures before and after expansion. The equipment manufacturer provides a detailed mathematical development for determination of density (13). With sufficient care, one can determine density by a single measurement to an accuracy of 0.07% or better.

There was concern about evolution of water vapor from the sample affecting the comparison measurement. This was not a problem above 50% solids. Density measurements using absolute pycnometry and comparison pycnometry at 25°C for sample concentrations ranging from 50% to 62% solids for a few liquors had excellent agreement.

Liquor preparation to prevent chemical changes and sample loading presents problems. The viscosity of a liquor ranges from about 2×10^{-3} to more than 10^6 Pa·sec (2 to 10^9 cp) as the solids content varies from 10 to 100%. In addition, liquors oxidize and degrade at high solids and moderately high temperatures. Finally, liquor solids at concentrations above 85% solids are hygroscopic. For reproducible re-

pared to water increases proportionally with increase in the liquor density at 25°C due to increase in solids concentration. It also appears that the constants in Eq. 2 are relatively insensitive to the variation in composition of these seven liquors.

A combination of experimental techniques provided density measurements on liquors up to 100% solids. **Figures 4 and 5** show complete density data for a kraft liquor made from slash pine and for a kraft liquor obtained from a commercial mill. The results are somewhat startling at first. There are at least two and possibly three distinct linear re-

gions for the relation of Fig. 4. The third region of 82–100% solids is very likely linear. Figure 5 definitely shows a third linear region at 80–100% solids. In addition, the measured densities for 100% solids for these two liquors fall within the predicted "ideal" density range of 1.54–1.58 g/mL.

The abrupt changes in slope of the density relations are important. The slope of the density relation, $(\partial\rho/\partial C)_{T,P}$ (where C is concentration), is a second order thermodynamic property. A discontinuity of the slope without a corresponding discontinuity in the first order thermodynamic

property, i.e., density indicates a second order transition of some type in the system. At 25°C, these liquors exhibit two second order transitions. One is near 65% solids, and the second is in the region of 80–85% solids. As the temperature increases, the concentrations at which these transitions occur increase. The change is not large, however. At 100°C, the initial second order transition occurs at 68% solids rather than at 65% solids.

The slopes of the lines in the third region of 80–100% solids are much less than the slopes of the lines for the other two regions. The tempera-

sults, one must use special techniques and care in preparing samples and loading instruments.

We prepared samples at concentrations up to 78–84% solids depending upon viscosity by evaporation at reduced pressure (about 0.27 kPa) in a stirred vessel. We stored these in plastic jars at 4°C until use when we heated them to a maximum of 50°C.

If the sample had sufficient fluidity, we poured it into the pycnometer or comparison pycnometer sample cell holder. If the sample was hot, we covered the sample cell with a plastic film, allowed it to cool, removed the film, weighed the cell, and rapidly loaded it into the comparison pycnometer.

If the sample was not fluid enough to pour, we loaded it into a PTFE syringe, compacted it, and allowed it to cool with a force constantly applied to the syringe. After cooling, we extruded the sample as a cylinder from the syringe and loaded a length of the extruded sample cylinder into the instrument.

For very high solids samples that did not allow evaporation at reduced pressure without degrada-

tion, we used different concentration and loading techniques. We froze a sample at 20% solids and freeze dried it to the desired final concentration of up to 100% solids. We placed the dried sample in liquid nitrogen to lower the temperature of the sample below the glass transition temperature, crushed the sample, and loaded the crushed pieces into the sample cell. Crushing and sample loading were in a dry box to eliminate problems with condensation.

We examined various dilatometers and dilatometric instruments of different designs. An excellent apparatus for this work is an AOCS Method Cd 10-57 dilatometer designed for use with fats and oils. The dilatometer has a graduated capillary side arm and a large ground glass stopper at the top of the bulb to permit loading viscous or solid samples. We immersed the dilatometer in an oil bath to make measurements from 5°C to above 100°C $\pm 0.1^\circ\text{C}$ or better. We measured the height of liquid in the sidearm with a cathetometer having a resolution of ± 0.01 mm. We calibrated the dilatometers with mercury.

For measurements, we placed a known mass of mercury in the dilatometer and drew it up into the side arm. Then we poured a sample of liquor into the dilatometer to fill the bulb and closed the dilatometer with the stopper. If the sample was not pourable, we placed a plug of the sample in the dilatometer to displace some mercury and closed the stopper. We collected mercury forced from the dilatometer, weighed it, and corrected for the mass of mercury contained in the dilatometer. We placed the dilatometer in the bath and determined the total volume at temperatures from 10°C to greater than 100°C. The volume of sample is the difference between the total volume and the volume of mercury. One determines the volume of sample in the dilatometer at the temperature of density measurement using pycnometry by interpolation. From the known density and volume of the liquor in the dilatometer, it is possible to calculate the mass of liquor in the dilatometer. Then sample density vs. temperature derives from the sample volume vs. temperature data.

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ture of 25°C is also very close to the glass transition temperature for these two liquors. It may be that these liquors are behaving as plasticized glasses in this region. This would explain the low value for the slope here. Previous work (10,11) has shown that liquors exhibit significant viscoelastic behavior in this region. The maximum deviation in heat capacity from the ideal heat capacity occurs here as well. We have also observed that liquors in this region do not infinitely deform, i.e., the liquors fracture or crumble. Therefore, the region most likely represents a regime in which it is not possible to use the present technology based upon fluid flow and droplet formation for chemical recovery.

As the temperature increases, the concentration at which the upper second order transition occurs should shift to a higher concentration. Unfortunately, we cannot use comparison pycnometry at elevated temperatures. One can theoretically determine the temperature to concentration boundary for this transition by locating the temperatures for abrupt changes in $(\partial\rho/\partial T)_{C,P}$ from dilatometry data, but the dilatometry data must be very precise.

The lower second order transition at 65% solids at 25°C may be the same or similar to the transition from freezing to glass formation observed for other liquors (10). Most of the deviations in flow behavior and heat capacity behavior from that for simpler fluids become distinctly measurable at this condition. It is in the middle region that viscosity increases very rapidly, excess heat capacity increases nearly to the maximum, and the rate of increase of boiling point elevation with increase in solids concentration begins to decrease in many cases. All of these should occur with some change or changes in short range order in a system containing a polymer as a major or significant component.

Thermal expansion data for these two liquors up to 65% solids can reduce to the single curve described by Eq. 2. For data above 65% solids, one must exercise caution. It appears today that Eq. 2 covers data up to 70% and above 70°C, if one defines ρ_{25} as the value obtained by extrapolation from the low solids region. Additional work is in progress to define density in a reduced form up to at least 80% solids.

We are analyzing the data accumulated from almost 30 liquors of widely different compositions. Qualitatively, all exhibit behavior similar that of the two liquors illustrated in Figs. 4 and 5.

Conclusions

Experimental density measurements have shown that kraft black liquors undergo two thermodynamic second order transitions at 25°C as the concentration increases from 0–100% solids. One occurs at 65% solids and another at 85% solids. Thermal expansion measurements show that the concentrations at which these occur increase 3–5% as the temperature increases from 25°C to 100°C.

Direct measurements of densities of 100% solids black liquors at 25°C are within the region of 1540–1580 kg/m³ predicted from calculation. The calculation uses densities of the known components or densities of very similar substances to those known to be present. It assumes no solids interactions. This is the "ideal" density.

In the low solids region below 65% at 25°C, the density at a constant temperature above 25°C increases linearly with solids concentration for every liquor for which data is available. The differences in density for different liquors at fixed concentration and temperature do not relate solely to the organic to inorganic ratio in the liquor solids as determined from sulfated ash or other methods, however.

Thermal expansion of liquors in the low solids region correlates to the reduced density relation developed during this work and reported by Adams and Frederick (9). Variation in the reduced density function for kraft black liquors of very different compositions is slight. This indicates that most, if not all, of the variation in density due to liquor solids composition results from the base density relation (density vs. solids concentration at 25°C) used as a reference.

Above 65% solids, one must use the reduced density relation with caution to calculate density. For most liquors for which data is available, it appears that the reduced density relation developed from low solids thermal expansion data is valid up to 70% solids and above 70°C, if one defines the reference density as the value obtained by extrapolation from the low solids region. The reduced density relation is not valid for the upper solids region greater than 80%.

The two second order thermodynamic transitions that are evident from the density results presented for two kraft liquors occur at conditions for which the liquor exhibits rapid change in thermodynamic and rheological behavior, as one should expect. The second order transition occurring at 80% solids at 25°C may represent an upper bound for the application of present technology based upon fluid flow and droplet formation. The solids concentration at which this upper second order transition occurs will increase slightly with temperature. Data necessary to define this temperature to concentration boundary exactly are not available now.

Variations in density from liquor to liquor are not large. The range is only about 5% at 65% solids. This is a substantial error for determining liquor flows, however. The methods described here allow determination of density at all temperatures and all solids concentrations below 65%

using one precise density measurement and one precise thermal expansion measurement. The relations can probably define precisely the density at 100°C up to 70% solids. Precise density measurements are also important in determining fluid transitions that affect other properties such as rheological characteristics. ■

Literature cited

1. Kobe, K. A. and McDonald, E. J., *I&EC* 41(2): 2847(1949).
2. Han, S. T., *Tappi* 40(11): 921(1957).
3. Lubienska, V. and Graczak, M., *Przeglad Papier* 37(5): 168(1981).
4. Hunter, R. E., Tracy, J., Cutts, R., *et al.*, *Tappi* 36(11): 493(1953).
5. Volkov, A. D. and Grigor'ev, G. P., *Physical Properties of Spent Liquors of the Pulp Industry*, Lesnaya Promyshlennost, Moscow, 1970.
6. Oye, R., Langford, W. G., Phillips, F. H., *et al.*, *APPITA* 31(1): 33(1977).
7. Wight, M. O., *An investigation of black liquor rheology vs. pulping conditions*, Ph.D. thesis, University of Maine, Orono, ME, 1985.
8. Fricke, A. L., *Physical Properties of Kraft Black Liquors: Interim Report—Phase II*, DOE, Washington, 1985.
9. Adams, T. N. and Frederick, N., *Kraft Recovery Boiler Physical and Chemical Processes*, American Paper Institute, New York, 1988.
10. Massee, M. A., Kiran, E. and Fricke, A. L., *Chem. Eng. Comm.* 50: 81(1987).
11. Zaman, A. A., *An Investigation of the Rheological Properties of High Solids Kraft Black Liquors*, Ph.D. thesis, University of Florida, Gainesville, FL, 1993.
12. Wheast, R. C. and Astle, M. J., *CRC Handbook of Chemistry and Physics*, 63rd edn., CRC Press, Boca Raton, 1982.
13. Anon., *Micromeritics Accupyc 1330 Pycnometer Operator's Manual*, Micromeritics Instrument Corp., Norcross, 1990.

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