Development of a method for measuring the heat of dilution of kraft black liquor and water

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ABSTRACT: The authors present an absolute calorimetric method for determining heat of dilution of black liquor as applied to kraft liquors. They evaluate results quantitatively and establish a thermodynamic reference state for black liquor solids that is suitable for enthalpy calculations for black liquors. Heats of dilution for diluting black liquor from 80% to 17% solids are 110–115 kJ/kg solids. Ignoring this can introduce substantial errors in the calculation of sensible heat changes occurring during black liquor concentration processes.

KEYWORDS: Black liquors, dilution, enthalpy, heat of mixing, kraft liquors, measurement, thermodynamics, water.

Heat effects due to mixing arise because the forces of attraction between unlike molecules are quantitatively different from those between like molecules. The solution process requires energy to break attractions between like molecules and releases energy to form attractions between unlike molecules. A heat effect which may be endothermic or exothermic accompanies mixing when there is a net difference between these two processes. The magnitude of the heat effect is small for components with similar chemical characteristics such as nonpolar molecules. It can be as large as 20 kJ/mole, however, for components that interact strongly as in the case of hydrogen bonding. Knowledge of the magnitude of the heat of mixing is important for designing many processes. For example, the heat of mixing will affect the energy needed to concentrate a solution by evaporation.

Solution calorimetry can measure the amount of heat absorbed or released during mixing. For engineering calculations, the important quantity to measure is the enthalpy change on mixing. This is equal to the heat of mixing only at constant temperature and pressure. If two pure components mix at constant temperature and pressure, the heat of mixing is the difference between the enthalpy of the solution and the sum of the enthalpies of the pure components. Alternatively, diluting a concentrated solution with pure solvent at constant temperature and pressure generates a resulting heat effect known as heat of dilution.

There are only two single point measurements *(1)* of the heat of mixing of black liquor solids and water or of the heat of dilution of black liquor solutions reported before this work. Consequently, the heat of mixing has been ignored in performing enthalpy calculations for black liquor. Since a black liquor solution is a nonideal solution, the heat of dilution is undoubtedly not zero. Ignoring it could lead to errors in energy calculations. Jelinek *(2)* reported developing enthalpy tables for black liquor by using the heat capacity results of Harvin and Brown *(3)*. This is not feasible, since it is impossible to generate complete enthalpy data for a solution from sensible heat changes measured at constant concentrations only, unless the heat of mixing is zero. Jelinek claimed to have determined heat of mixing indirectly from fitting sensible heat (heat capacity) data only. Proper conversion of his data to isotherms nevertheless leads to enthalpy vs. concentration curves that are

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straight lines. This shows that the heat of mixing is zero.

This work presents development of a method to determine the heat of dilution of black liquor. Our paper gives a description of the method, presents experimental results for some selected kraft black liquors, and discusses data treatment. The method has successfully determined the heat of solution of black liquors at concentrations as high as 85% solids. The ultimate goal of this work is to develop accurate enthalpy–concentration data for black liquors from heat of dilution and heat capacity data.

Method development

Experimental measurement of the heat of mixing of black liquor solids presents a number of difficulties. Black liquor solids are themselves a mixture—not a pure compound. It is essentially impossible to determine completely and accurately the solids composition. To determine the heat of mixing, one must completely remove all the water, but nothing else, from a black liquor solution without causing chemical or irreversible physical association changes in the black liquor solids. This has proven impossible except when drying the black liquor solids by an unusual method such as freeze drying for extended periods. Even this poses problems. Water appears very strongly bound to some of the components of the solids, and the dry solids are highly hygroscopic. Measuring the heat of dilution rather than the heat of mixing avoids these problems, since one need not begin with completely dried solids but only with a solution at a high concentration of solids. The method developed in this study has had successful use with black liquor solutions at concentrations as high as 85% solids. Normal work was 80% solids, however.

Heats of mixing or dilution are thermodynamic state functions. The precision and accuracy of the measurement depend upon the process used, however. Ideally, the two components for mixing undergo mixing in a system with no introduction of any shaft work while introducing heat into or withdrawing it from the system. This is to maintain a constant temperature within the system. Practically, this is not possible. Some mechanical energy is necessary to complete mixing in a reasonable period. The amount required depends largely on the solution viscosity. Higher viscosity requires more mixing energy. The time to effect solution is also important. The integration of the heat flow into or out of the mixing cell during mixing determines the heat of mixing. If mixing is slow, the rate of heat flow will be low and the sensitivity of the measurement of heat flow becomes a factor. Black liquors at high solids concentrations are quite viscous and dissolve slowly in water near room temperature. One must therefore consider viscosity and rate of solution by means of a punctured membrane or by means of an immiscible fluid that is unreactive with either component. All of these factors affect the experimental results.

Measurement of heat of dilution requires use of an absolute calorimetric method. A number of absolute microcalorimeters of various designs are commercially available. We critically reviewed the possible application of each of these for use with black liquor with representatives of the manufacturers. We selected a Setaram model C–80 calorimeter *(4)* with a "rocking cell" as the best instrument for this development, because use of the cell requires only a minimum of mechanical energy introduced into the sample. It operates easily at constant elevated temperatures. The sample size can be small while still providing for a large dilution of 6 to 1. Since mercury can react with some components of black liquor, it is not possible to use this as a sealing fluid for the cell in this instrument. A major problem was identification of an appropriately inert seal fluid. After considerable work, we identified a perfluoroalkylpolyether *(5)* as a fluid with the proper physical characteristics that did not react with black liquor components.

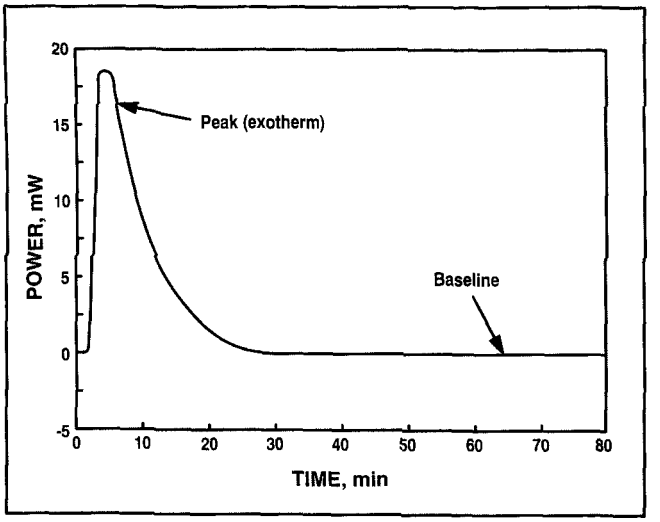
Heat of dilution is a thermodynamic property, but calorimetric measurements are dynamic. It is therefore necessary to reach equilibrium within a reasonable time, if the calorimetric measurement is to be accurate. Black liquor viscosity is quite high at high solids, and black liquor dissolves slowly in water at low temperatures. It is necessary to conduct heat of dilution experiments for black liquor at elevated temperature to complete mixing and establish equilibrium within a reasonable time. Preliminary work suggested an experimental temperature of 80°C, because this temperature gave accurate results with reasonable times for establishing thermal equilibrium. **Figure 1** is a typical instrument response curve for dilution of a sample at 80°C. Thermal equilibrium typically occurred within 1 h with a baseline drift of less than 0.1 mW. The appendix provides complete details of the method and its calibration.

Results

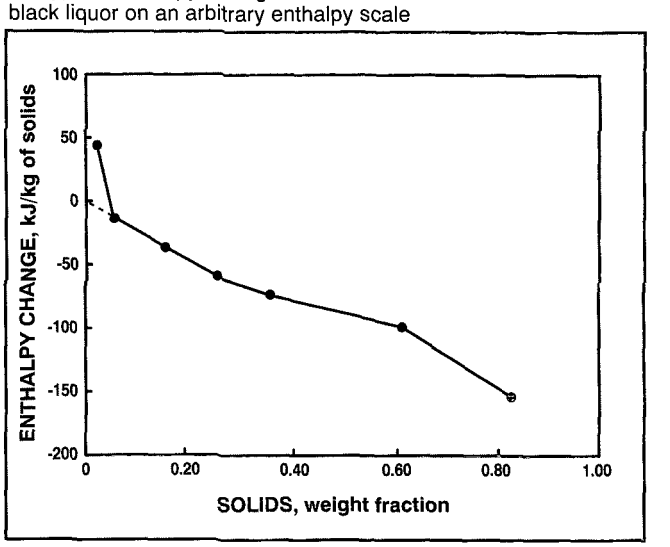
The development of this method for measuring heat of dilution used softwood kraft black liquors made from pulping slash pine in an experimental batch digester. **Table I** gives the pulping conditions for the four liquors used. The conditions represent a wide range of pulping conditions and pulping results. The table also provides the kappa numbers for the four pulps.

For each liquor, there was a series of dilution experiments to cover the range from 80% solids concentration down to 1.67% solids. There were duplicate dilution experiments for two of the four liquors studied. Results agreed within 1% above 25%

1. Typical microcalorimeter power response curve for dilution of black liquor at 80°C



2. Typical enthalpy changes for incremental heats of dilution of black liquor on an arbitrary enthalpy scale



I. Pulping conditions and pulp kappa numbers for slash pine black liquors

Liquor No.	*Time, min*	*Temp., °F*	*Eff. alkali, %*	*Sulfidity, %*	*Kappa No.*
L1	60	340	14.5	12.5	25.8
L23	40	330	13.0	20.0	107
L31	80	330	16.0	20.0	61.1
L51	80	350	16.0	35.0	18.5

solids concentration, within 2% or less from 25% to 5% solids concentration, but to within only 6% below 5% solids concentration. The percentage difference in duplicate runs should not have increased so substantially below 5%, if only mixing (which is not dependent upon thermal history) was occurring. Some reactions or associations depending upon thermal history must therefore occur when diluting black liquor to below 5% solids.

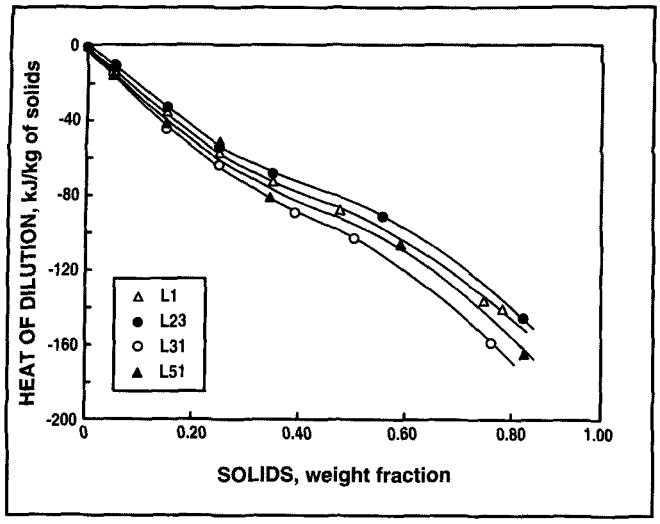
Numerical integration of the area under the power curve generated for a dilution provided calculations to determine the enthalpy change. Dividing this by the mass of solids normalized this change. Each measurement represents an integral enthalpy change resulting from dilution over a finite range of solids. **Figure 2** shows a typical plot of these integral changes vs. weight fraction of solids with an arbitrary zero for the enthalpy scale. The actual enthalpy is unknown, of course. Data points connected by a segmented straight line represent the starting and ending concentrations for a single dilution experiment and the corresponding enthalpy change. Joining of these segments on an arbitrary enthalpy scale illustrates the total change expected from a series of dilutions.

The sharp increase in the enthalpy change per unit mass of solids for dilution at concentrations below 5% is striking. This sharp increase and the decrease in precision discussed earlier strongly suggested that a heat effect other than mixing was occurring in this region. The broader and usually irregular shape of the calorimeter power curve in this region also suggested that a reaction of some sort was occurring. Lignin associates when the pH of black liquor drops below 12. We estimated the pH of these liquors was about 12 at 5% solids. Since the types of lignin association that occur are very likely exothermic, the major contributor to the heat effects observed for dilution below 5% solids concentration is probably lignin association.

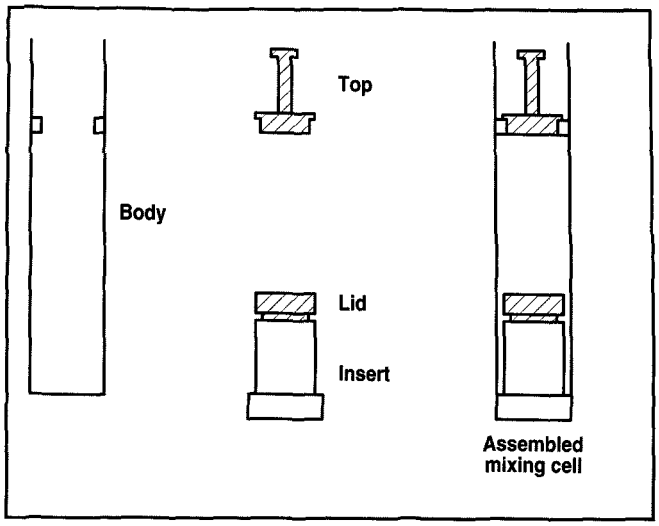
Enthalpy relations require definition of reference states for which the enthalpy has a zero value, since it is only possible to determine enthalpy changes between states. For this work, a reference state for water is liquid water at 0°C. The preferred reference state for solids of 100% solids at 0°C is not usable, since the enthalpy change for dilution of 100% solids is immeasurable. An alternative reference state often used for heat of dilution is infinite dilution. In our work, this would be infinite dilution at 80°C.

Our original objective was to continue experimental dilutions to the sensitivity limit of the instrument to establish experimentally the reference state for infinite dilution. If only mixing were occurring, the enthalpy change per unit change in solids would asymptotically approach zero

3. Heats of dilution for four slash pine black liquors



4. Schematic of mixing cell for Setaram Microcalorimeter



as infinite dilution approached. This is clearly not the case for black liquor. The use of a true, experimentally determined, infinite dilution reference state is therefore not possible.

Instead, we extrapolated dilution data from above 5% solids to infinite dilution (0% solids) to establish a reference state for solids as Fig. 2 shows. There were two reasons for this. If the behavior upon dilution below 5% solids includes heat effects due to reaction, results are not true heats of dilution. If there are reactions occurring below 5% solids, the state of the solids at concentrations below 5% does not represent the state of the solids at any stage of black liquor processing in black liquor recovery. The extrapolated value for enthalpy at infinite dilution therefore properly represents the solids at infinite dilution in the state in which they exist at concentrations above 5% solids. As shown in Fig. 2, we extrapolated data above 5% solids to infinite dilution to define the reference state for solids at 80°C.

After subtracting the heat effect for apparent reaction or association that occurs below 5% solids, the heats of dilution measured in this work are greater than the two values of 102.3 and 87.3 kJ/kg solids determined by Grace and Funk *(1)* for complete dilution of two samples of black liquor solids. Their measurements, however, were intended to determine only if the heat of dilution is significant. The work was not a definitive study for heat of dilution. The values reported are also considerably lower than the values we have measured for dilution from 80% solids. This difference may be due to heat losses that might have occurred during their measurements.

Figure 3 shows heats of dilution at 80°C for the four black liquors. The reference state in this figure is an infinite dilution of solids at 80°C in solution form existing above 5% solids. In all cases, extrapolation of the data as explained previously determined the reference state at infinite dilution. The shapes of the curves are similar, and there is a range of only 10 kJ/kg of solids between the liquors at any solids concentration, even though the liquors represented quite different pulping conditions. Heat of dilution is not negligible, however. It is 110–115 kJ/kg of solids for dilution from 80% to 17% solids. Ignoring the heat of dilution can result in very significant errors in calculating sensible heat changes for concentrating liquors.

Conclusions

We have developed a method to measure the heat of dilution for black liquor and demonstrated its successful use. The method uses an absolute calorimeter which mixes components without external stirring. This overcomes many of the difficulties of working with a very viscous material such as black liquor. During development, we found a new seal fluid that is inert to black liquor. The method can measure heats of dilution of black liquor to within 2% or better for small dilution increments at final solids concentrations above 5%.

At solids concentrations below 5%, behavior changed dramatically suggesting a second heat effect in addition to dilution. This effect most likely comes from lignin association, since the pH in this range falls progressively below 12.

Extrapolation of data above 5% solids concentration to infinite dilution can establish a reference enthalpy for infinite dilution of solids in the state in which they exist at processing conditions.

Heat of dilution is not negligible concerning the enthalpy of the black liquor. The heat of dilution for concentrating liquor from 17% to 80% solids is 110–115 kJ/kg. This can rep-

resent very significant errors in sensible heat calculations, if ignored. Heat of dilution varies from liquor to liquor, but the range with respect to liquor composition is not large. The general behavior for kraft black liquors from slash pine is generally very similar. On the basis of work with other properties, we expect heat of dilution behavior of kraft black liquors from other wood species to be similar.

We are collecting additional heat of dilution data for other liquors to generalize the results and to attempt measurement of heats of dilution in the 80–100% solids concentration range. We are combining heat of dilution data and heat capacity data to calculate enthalpy–concentration relations. Vapor pressure data will enable us to check the thermodynamic consistency of these relations.

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Appendix

Description of equipment and experimental methods

Two reasons prompted selection of the Setaram model C-80 microcalorimeter over a number of commercial instruments. First, the "rocking cell" it incorporates permits measurement with viscous fluids with a minimum of mechanical energy input into the cell. Second, the cell configuration permits dilution over a reasonably wide range. Details of design of the instrument are available from the manufacturer.

The measuring block of the C-80 is cylindrical and mounts vertically on a support stand with a rocking device that rocks the cell through 180° for mixing. The measuring block has excellent insulation and temperature control. Two cells, one for the sample and one for the reference or blank, mount in the measuring block. The measuring block mass is very much greater than the mass of the cells and serves as a constant heat source or sink for the cells. A heat flux meter to measure the thermal exchanges between cells and measuring block during the experiment surrounds each cell. The outputs of the flux meters connect such that a differential flux signal records during an experiment.

Figure 4 shows a schematic of the mixing cells. The insert has a usable volume of 1.35 mL. It holds one of the components for mixing and screws into the bottom of the cell body. A lid, which moves during mixing, fits over the insert but does not form a tight seal. To prevent premature mixing, there is an inert sealing fluid in the annular space between insert and cell body to cover the lid barely. After adding the second component for mixing, one screws on the top. With the minimum volume of seal fluid, the usable volume for the second component is 3 mL.

For measurement, two identical cells are placed in the measuring block. One contains the components for mixing, and the other has an equivalent volume of one of the components. After attaining thermal equilibrium, the measuring cell is rocked to mix the components. Heat of mixing disturbs the thermal balance between the cell and measuring block which causes heat to flow to or from the cell and the block. The heat flux which develops corrected for mechanical stirring from measurement of heat flux for the blank is recorded as a signal that is converted to a power (energy flux) signal. This changes very rapidly to a maximum, and then decays exponentially to zero as thermal equilibrium with the measuring block is reestablished. The area under the power vs. time curve generated is proportional to the enthalpy change.

Mercury is the normal sealing fluid, since its properties make it ideal for most studies. Its density, thermal conductivity, and surface tension are high, but its viscosity is low. It therefore seals well. It tends to move as a consolidated mass in the cell during mixing, and it separates easily from the solution after mixing. Mercury can react with some components in black liquor, however. Another sealing fluid was therefore necessary for black liquor.

After an exhaustive search and many trials, we selected a fluorinated oil. Specifically, it is a perfluoralkylpolyether consisting of a completely saturated polymer chain containing only carbon, oxygen, and fluorine with a density of about 1.88 g/mL (1.88×10^3 kg/m^3). It is available in a wide range of viscosities depending upon molecular weight. Its normal use is as a lubricant, vacuum pump oil, or grease. It is quite inert particularly with respect to the components expected in black liquor. It has a relatively low surface tension.

(appendix continued next page)

After preliminary trials, we selected a relatively low-viscosity version of the oil, even though this oil disperses in black liquor during mixing.

The microcalorimeter used here has yielded extremely accurate results for inorganic salt solutions with mercury as a seal fluid. We checked the particular instrument used in this work by measuring the heat of solution of potassium chloride (KCl) with mercury and with the substitute sealing fluid.

According to the National Institute of Standards and Technology (NIST), the heat of solution of KCl for a 0.111 mole/kg solution at 298.15°K is 235.86± 0.23 kJ/kg. We made multiple measurements of the heat of solution of a very high quality analytical grade of KCl at 25.80°C (298.92°K) using mercury and the fluorinated oil as seal fluids. The mean values and uncertainties at 95% level of confidence for measurements using the fluorinated oil and mercury were 233.3± 0.72 kJ/kg and 234.4± 1.01 kJ/kg, respectively. The mean values differ by 0.47%, but the uncertainty intervals overlap. Both values are lower than the value given by NIST, however, because measurements did not use 25°C. Ambient laboratory temperatures did not permit operation at 25°C conveniently. According to NIST, when performing the experiment within 3°C of 25°C, one can correct results for temperature by the following:

$$\Delta H_{298.15} = \Delta H_{T_m} - (T_m - 298.15)\Delta C_p \quad (1)$$

where

T_m = experiment temperature, °K

$\Delta H_{298.15}$ = heat of solution at 298.15°K, kJ/kg

ΔH_{T_m} = heat of solution at T_m, kJ/kg

ΔC_p = 2.076 kg/kg°K.

Using this relationship, one obtains 234.94± 0.72 kJ/kg and 236.01± 1.01 kJ/kg as the means and uncertainties at the 95% level for measurements using fluorinated oil and mercury, respectively, at 298.15°K. The corrected value using mercury agrees well with the value given by NIST. The mean value using fluorinated oil is 0.39% lower than the value given by NIST. Even though the uncertainty intervals overlap, the difference between using mercury and fluorinated oil for measuring the heat of solution of KCI is statistically significant. This possible bias is quite small, however. We considered it to be acceptable.

It was necessary to conduct heat of solution experiments at an elevated temperature to complete mixing within a reasonable time. We used an experimental temperature of 80°C for all experiments. This temperature of 80°C also substantially reduced the time necessary to reach thermal equilibrium.

Components were weighed into the cells. The insert of the mixing cell was filled to within 2 mm of the lid. Fluorinated oil was then added to a level within 2 mm above the top of the insert lid. The second component was then added on top of the fluorinated oil. The amount added was that necessary to yield the final solution concentration desired. The mixing cell was then closed. The reference cell was filled with fluorinated oil and water to a volume equal to that in the mixing cell as nearly as possible.

The cells were placed in the calorimeter. Time was provided to allow the measuring block temperature and power signals to stabilize. This indicated thermal equilibrium. The experiment then started. The baseline was recorded for at least 2 min. Then the rocking motor was turned on to begin mixing the components. Except for experiments beginning with solids concentrations above 70%, 5 min of mixing or less was sufficient for the power signal to peak. The peak signal returned to the baseline within 40–60 min. For beginning solids concentrations above 70%, mixing was more sluggish. At 80–85% solids, the time for the power signal to peak could be as long as 50 min. Total experimental time was as long as 400 min.

For initial solids concentrations below 60%, black liquor was placed in the insert and water added above the fluorinated oil layer. This is preferred, because the mass of water can be adjusted easily to control the final concentration. Above 60% solids concentration, however, the black liquor was too viscous to flow out of the insert and mix easily or completely. The position of the components therefore had to be reversed in this case. This required a different loading procedure.

The liquor was heated to a moderate temperature of 50–70°C in a closed vessel and then poured into the cell, if possible. Samples too viscous to pour were molded into plugs using a syringe machined from PTFE. The internal diameter of the syringe was slightly smaller than the cell opening, and the syringe was fitted with a plunger to force the sample out as a plug. Heated black liquor was packed into the syringe. After cooling, the liquor was extruded, a sample trimmed to the desired length, and the sample placed in the cell and weighed. The material trimmed from the sample was used to determine the solids concentration of the plug.