Enthalpy concentration relations for black liquor

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ABSTRACT: Considering kraft black liquors as pseudo-binaries, it is possible to combine exact heat capacity data and heat of solution data to develop a relation between enthalpy and concentration. The approximate errors in net energy requirements resulting from ignoring heat of dilution and excess heat capacity in concentrating black liquor from 20% to 65–90% solids by evaporation are 4–6%. Quantitative comparison of the enthalpy results with vapor pressure equilibrium results shows thermodynamic agreement.

KEYWORDS: Black liquors, dilution, enthalpy, heat of solution, kraft liquors, specific heat, vapor pressure.

The kraft recovery cycle is a highly integrated and complex process for disposing of black liquor. It recovers useful energy and inorganic pulping chemicals. Its development over the years has progressed with a very limited knowledge of the principal liquor properties. Investigations have implicitly treated black liquor as an ideal solution with departures from nonideality explained by reference to full-scale systems. This was acceptable in the days of relatively cheap energy. As solids concentrations increased and expectations for energy recovery rose, more exact relations became necessary for proper design. One such essential relation for accurate energy balances is that between enthalpy and concentration.

The relation of enthalpy and concentration for a solution requires quantitative determination of the heat capacity as a function of temperature and concentration. It also requires quantitative determination of the heat of solution (or dilution) at some temperature as a function of concentration. Earlier investigators reported heat capacity for a sulfite liquor *(1)* and for a sulfate (kraft) southern softwood liquor *(2)* in 1953. Han reported heat capacities for sulfite liquors in 1957 *(3)*. Researchers published heat capacities for kraft liquors from bamboo, bagasse, and eucalyptus in 1977 *(4)*. The heat capacity measurements in all cases were for concentrations below 65%. Correlation of the heat capacity used the implicit assumption that the solution was an ideal mixture, i.e., the heat capacity of the solution is a weighted average of the heat capacities of water and of dry solids. There was no case of direct determination of the heat capacity of dry solids. Rather, there was inference from fitting the data.

Massee made the first direct measurements of the heat capacity of 100% liquor solids *(5–7)*. Results demonstrated that the heat capacity of black liquor does not follow an ideal mixing rule as assumed earlier. Instead it exhibits higher values than predicted in the 50–100% solids range. Massee developed an "excess" heat-capacity model based on lattice parameter solution considerations to fit his results to the following:

$$C_p = (1-x)C_{p_w} + xC_{p_s} + Ax^m(1-x) \quad (1)$$

where

C_p = heat capacity at x and T

C_{p_w} = heat capacity of water at T

C_{p_s} = (a + bT) = heat capacity of 100% solids at T

A = (c + dT) = a constant at constant T

T = temperature

x = mass fraction of solids

a, b, c, d, m = constants.

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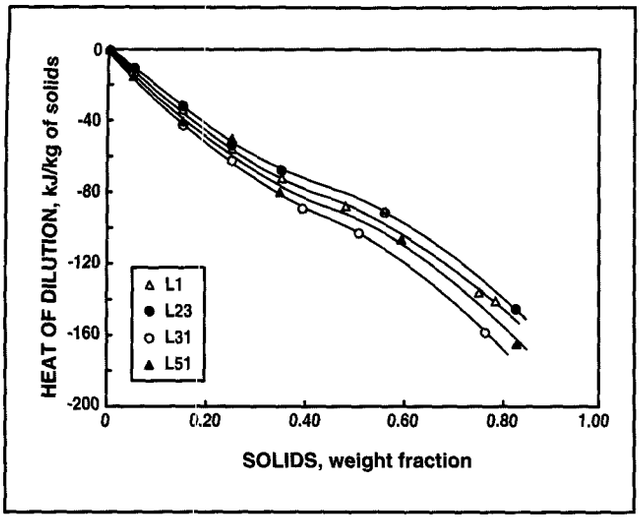
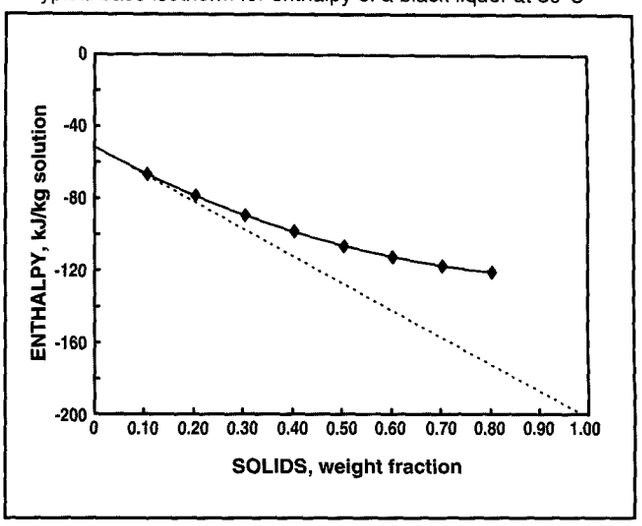
1. Heats of dilution for four black liquors at 80°C



2. Typical base isotherm for enthalpy of a black liquor at 80°C



Further work by Massee *(5, 7)* and others *(8)* showed that this model is valid for all kraft liquors with the appropriate choice of constants. If one ignores the excess heat capacity (the third term in Eq. 1), the error in the heat capacity of the solution can be as much as a 6–12% underestimate.

Jelinek *(9)* claimed to have generated a complete enthalpy table for a black liquor by reanalyzing the data from Harvin *(2)*. This approach has a flaw, since it is impossible to generate an enthalpy table for a solution from heat capacity data alone unless the heat of solution (or dilution) is zero. Jelinek added an expression that he claimed represented the heat of mixing. He reanalyzed Harvin's data to obtain values for the heat capacity of solids and the heat of mixing as he defined it. Careful analysis shows that the heat of mixing term defined by Jelinek is analogous to the excess heat capacity used by Massee to model heat capacity. This is correct, since it should not be a term representing the heat of mixing.

Recent workers have developed a method for measuring the heat of dilution for black liquors *(10, 11)*. This method has successfully measured the heats of dilution of a number of kraft black liquors. The heats of dilution are definitely not zero *(11)*. **Figure 1** shows the heats of dilution of four softwood kraft black liquors at 80°C (353.2°K). The data in the figure use a reference state of infinite dilution of solids at 80°C (353.2°K) in the form existing at concentrations above 5% solids. This comes from our earlier paper *(11)* which contains the reasons for our choice of the reference state. It also includes the details of the method for determining the heat of dilution with respect to the reference state.

Enthalpy relations

The heats of dilution shown in Fig. 1 are for four liquors derived from kraft pulping of slash pine at the pulping conditions given in **Table I**. The table also gives the kappa numbers of the pulps. In addition to the heats of dilution, we have also determined heat capacities for these liquors. We have successfully modeled the heat capacities by using Eq. 1. The data necessary to develop enthalpy relations for liquid black liquor are therefore available for these liquors.

The first step in developing enthalpy relations is to develop a relation for enthalpy as a function of concentration at constant temperature—the "base isotherm." When reference temperatures for both components are the same, this is a trivial problem. It becomes slightly more complicated, however, when reference temperatures are not the same. This is desirable in the present case. The preferred reference temperature for liquid water is 0°C (273.2°K). The reference temperature for solids must be 80°C, because heats of dilution refer to solids at infinite dilution at 80°C (353.2°K). The 0°C (273.2°K) state is an uncorrected, fictitious one.

We next define Q^{∞} as the total heat absorbed in diluting a mass of solution containing a unit mass of solids to infinite dilution at the solids reference temperature of 80°C. It then follows *(10)* that the enthalpy of a unit mass of solution with x mass fraction of solids has the following definition:

$$H_x = (1 - x)H_w - xQ^{\infty} \qquad (2)$$

where

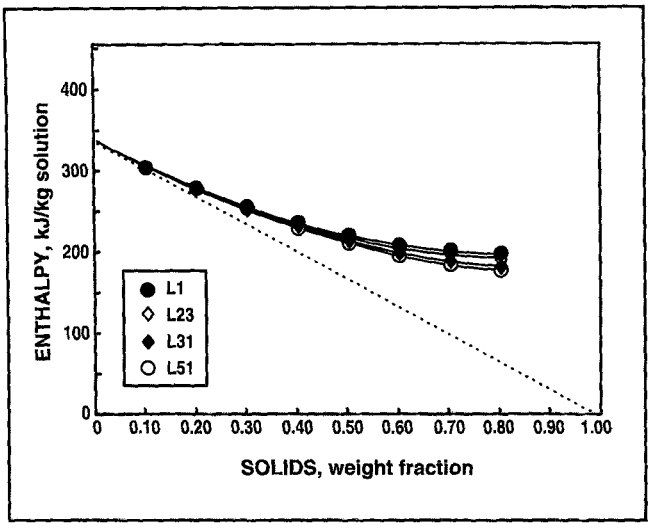
H_w = specific enthalpy of water at 80°C

Q^{∞} = heat of dilution per unit mass of solids at 80°C for solution containing x mass fraction of solids

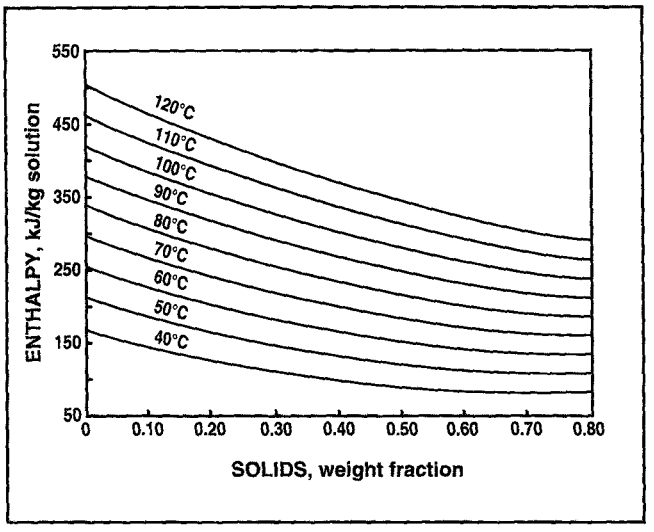
x = mass fraction of solids

H_x = specific enthalpy of the solution containing x mass fraction of solids at 80°C

3. Base isotherms for four slash pine black liquors



4. Enthalpy vs. concentration diagram for slash pine black liquor L1



I. Pulping conditions

Liquor	Time, min	Temp., °F	Effective alkali, %	Sulfidity, %	Pulp 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

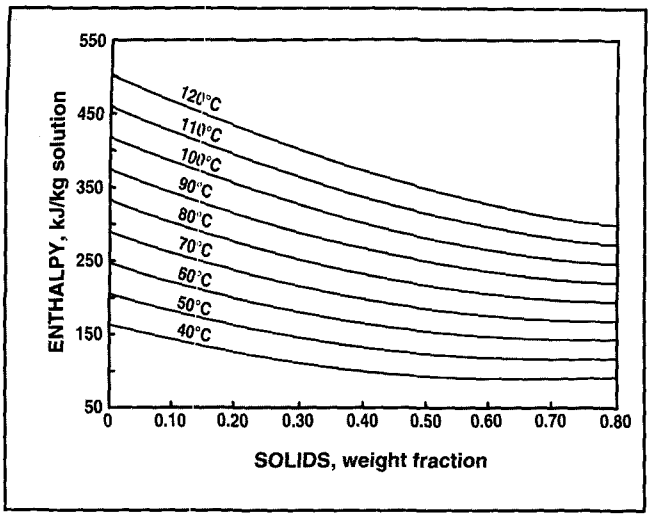
Using Eq. 2, we can construct "base isotherms" for the liquors using the heat of dilution data and the enthalpy for water at 80°C (79.94 cal/g or 334.5 kJ/kg). **Figure 2** shows a typical "base isotherm," i.e., enthalpy vs. concentration at 80°C. The figure uses water at 0°C and black liquor solids at infinite dilution at 80°C as the reference states. The dashed curve would be the base isotherm, if the heat of dilution were zero. The initial value of the base isotherm curve at zero weight fraction should be equal to the value of the specific enthalpy of water at 80°C. This line should extrapolate to zero at 1.00 weight fraction. For comparison, **Fig. 3** shows the base isotherms (T = 80°C, 353.2°K) for the four different softwood kraft liquors studied here. The dashed line would be the base isotherm, if the heat of dilution were zero.

All base isotherms approach a value of 334.5 kJ/kg at infinite dilution as weight fraction approaches zero, as they must. There is very little difference in the base isotherms for these four very different softwood kraft liquors up to 50% solids. Above 50% solids, the difference in base isotherms becomes progressively larger with increase in solids concentration. At 80% solids, the total difference in base isotherms is 20.0 kJ/kg of solution. The median value of the base isotherms is 189.7 kJ/kg of solution. Even for these four diverse softwood kraft liquors, therefore, the maximum difference from the median is ± 5.3% of the median value. One should not conclude, however, that this is the actual range of difference expected for all softwood kraft black liquors, since it comes from results for only four liquors. We can, however, assume a median value for the base isotherm for discussion purposes. The median error in liquor enthalpy at 80°C introduced by ignoring the heat of dilution is 9.07 kJ/kg of solution at 20% solids and 122.8 kJ/kg at 80% solids.

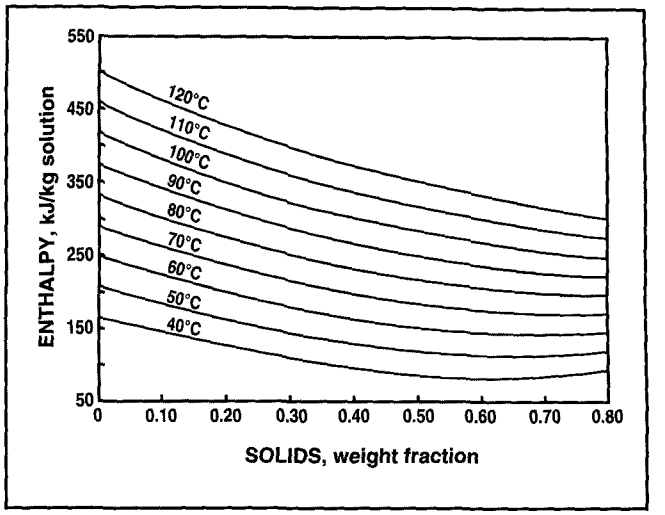
We can use the average values for the heat capacity of solids and for the excess heat capacity for these softwood liquors determined earlier *(5–8, 10)*. This allows a determination of the magnitude of errors in overall energy balances and in liquid stream energy balances resulting from ignoring the heat of dilution, the excess heat capacity, or both.

Consider concentration of liquor from 20% to 65% solids and from 20% to 80% solids. The steam economy would be 4 to 1. Liquid streams would enter and leave at their normal boiling points. These would be 102°C, 113°C, and 122°C for 20%, 65%, and 80% solids, respectively. For concentration to 65% solids, the net energy input ignoring heat of dilution and excess heat capacity corrections adds 71.6 kJ/kg and 7.6 kJ/kg of solids processed, respectively, to the net energy input. The actual net energy input required is 1966 kJ/kg of solids processed. This is a 4.05% increase

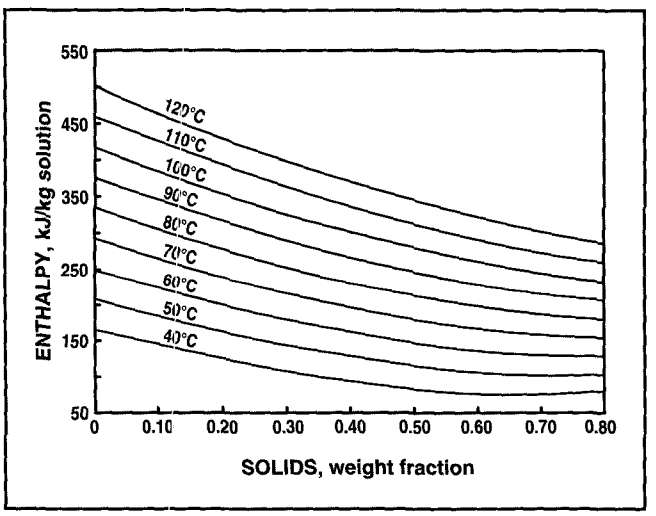
5. Enthalpy vs. concentration diagram for slash pine black liquor L23



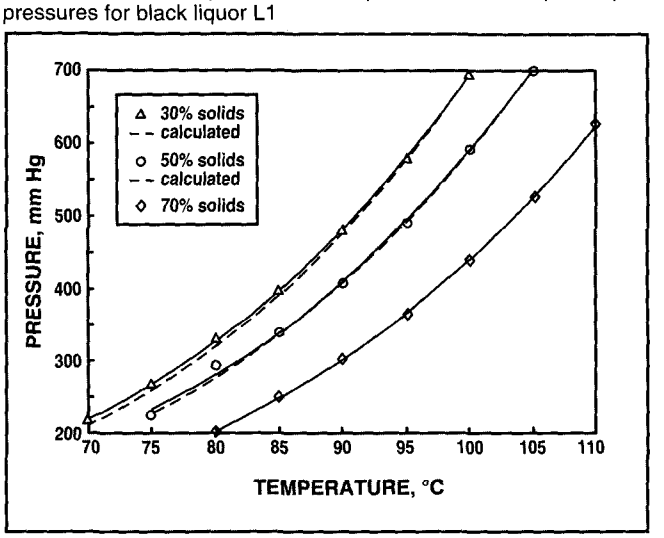
6. Enthalpy vs. concentration diagram for slash pine black liquor L31



7. Enthalpy vs. concentration diagram for slash pine black liquor L51



8. Comparison of experimental and predicted black liquor vapor pressures for black liquor L1



in net energy input. The heat of dilution and excess heat capacity corrections contribute 3.66% and 0.39%, respectively. For concentration to 80% solids, the net energy input ignoring heat of dilution and excess heat capacity is 2146 kJ/kg of solids processed. The heat of dilution and excess heat capacity corrections add 108.4 kJ/kg and 15.8 kJ/kg of solids processed, respectively, to the net energy input. The actual net energy input necessary is 2270 kJ/kg of solids processed. This is a 5.8% increase in net energy input. The heat of dilution and excess heat capacity corrections contribute 5.05% and 0.73%, respectively. Extrapolating the base isotherm data to 90% solids and making the energy input calculation for concentration from 20% to 90% solids with a 4 to 1 steam economy, the net energy input necessary is 2229 kJ/kg of solids processed. This ignores the heat of dilution and excess heat capacity effects. The actual net energy input necessary is 2361 kJ/kg of solids processed, a 5.93% increase in net energy input. The heat of dilution and excess heat capacity corrections contribute 5.69% and 0.24%, respectively.

Errors of 4–6% in the net energy input requirements for concentration do not seem extremely large. They are very significant, however, considering the process scale. Note that the effect of excess heat capacity on the net energy input is slight, even though it represents almost 10% of the heat capacity of a black liquor at 80% solids concentration. This results from the fact that the exit liquor stream is the smallest stream. The excess heat capacity is more important in calculation of sensible heat changes for a liquor at a constant high solids composition.

II. Enthalpy, kJ/kg, for black liquor L1

Temp., °C	Solids, weight fraction								
	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80
40	167.3	143.7	125.3	110.4	98.8	90.0	84.4	82.1	83.9
45	188.1	163.4	143.9	128.1	115.3	105.5	98.8	95.5	96.2
50	209.0	183.4	162.7	145.7	131.8	121.1	113.4	109.0	108.6
55	229.9	203.4	181.5	163.4	148.5	136.7	127.8	122.5	120.9
60	250.8	223.4	200.4	181.1	165.0	152.3	142.5	136.2	133.4
65	271.7	243.4	219.4	199.0	181.8	167.8	157.1	149.7	146.0
70	292.6	263.6	238.5	216.9	198.5	183.4	171.8	163.4	158.5
75	313.5	283.6	257.3	234.5	215.2	199.2	186.4	177.1	171.1
80	334.5	303.8	276.6	252.7	232.0	215.0	201.1	190.8	183.9
85	355.5	324.0	295.7	270.6	249.0	230.6	215.9	204.6	196.7
90	376.5	344.3	314.7	288.5	265.7	246.4	230.8	218.5	209.4
95	397.5	364.5	334.0	306.6	282.7	262.4	245.5	232.2	222.2
100	418.6	384.9	353.3	324.7	299.6	278.2	260.3	246.2	235.2
105	439.6	405.5	372.4	342.9	316.6	294.0	275.5	260.1	248.0
110	460.8	425.6	391.9	361.2	333.8	310.1	290.3	274.1	261.0
115	481.9	446.1	411.2	379.4	350.8	326.1	305.2	288.2	274.1
120	503.1	466.8	430.5	397.7	368.0	342.2	320.3	302.2	287.3

After establishing the base isotherm, it is possible to determine other isotherms from the use of the relation developed for heat capacity. One simply adds or subtracts the sensible heat for heating or cooling the liquor at constant composition to the base isotherm. The full family of isotherms constitute an enthalpy vs. concentration chart or diagram. **Figures 4–7** show examples for the four liquors examined here. **Tables II–V** provide the enthalpy values calculated for the liquors.

Thermodynamic consistency

If treatment of black liquor as a binary system consisting of water and solids were truly valid, one should be able to calculate fugacities (and subsequently vapor pressures) for constant composition by using the enthalpy data and one vapor pressure equilibrium value. Using the experimental, normal boiling point curve and calculated enthalpy data, we did this for liquor L51 at a number of constant compositions. We used standard thermodynamic calculation methods *(12)* and second virial coefficient values for water vapor *(13)*. We calculated the fugacity at atmospheric pressure for a given composition from the equilibrium vapor pressure using the known properties of water *(13, 14)*. Calculation of fugacities for the liquor at a number of temperatures below the normal boiling point followed from use of the enthalpy data for the liquor. Using the known properties of water allowed converting to vapor pressures. This technique provided development of vapor pressure equilibrium curves at a number of constant compositions. We compared these to experimentally determined

III. Enthalpy, kJ/kg, for black liquor L23

Temp., °C	Solids, weight fraction								
	0.00	*0.10*	*0.20*	*0.30*	*0.40*	*0.50*	*0.60*	*0.70*	*0.80*
40	167.3	145.3	125.9	111.8	100.9	92.0	88.0	88.8	92.8
50	209.0	185.6	163.4	147.3	133.2	123.5	117.0	115.0	117.4
60	250.8	224.0	201.0	182.4	167.1	154.2	146.5	142.5	143.3
70	292.6	264.3	240.1	217.1	199.8	185.6	175.5	170.3	167.5
80	334.5	304.7	277.6	254.2	234.9	217.9	205.8	197.7	194.5
90	376.5	345.0	316.8	290.6	269.6	250.2	236.1	225.2	219.1
100	418.6	385.4	356.7	327.3	303.5	282.5	266.3	254.2	246.6
110	460.8	425.7	395.5	363.2	338.6	314.8	296.6	282.5	271.6
120	503.1	466.9	435.0	399.5	373.3	347.1	326.9	310.7	298.6

IV. Enthalpy, kJ/kg, for black liquor L31

Temp., °C	Solids, weight fraction								
	0.00	*0.10*	*0.20*	*0.30*	*0.40*	*0.50*	*0.60*	*0.70*	*0.80*
40	167.3	148.1	128.3	110.9	97.2	88.3	85.5	88.6	97.2
45	188.1	167.4	146.9	128.5	114.1	104.8	100.9	102.7	109.9
50	209.0	186.7	165.3	146.4	131.3	121.1	116.2	116.7	122.5
55	229.9	206.2	183.9	164.1	148.5	137.6	131.6	130.9	135.3
60	250.8	225.7	202.5	182.0	165.7	154.1	147.1	145.3	148.1
65	271.7	245.2	221.1	200.1	183.2	170.6	162.7	159.5	160.9
70	292.6	264.8	239.7	218.0	200.4	187.1	178.3	173.9	173.6
75	313.5	284.3	258.2	236.2	217.8	203.9	193.9	188.3	186.7
80	334.5	304.0	277.1	254.3	235.2	220.4	209.4	202.5	199.7
85	355.5	323.6	295.9	272.4	252.7	237.1	225.2	217.1	212.7
90	376.5	343.3	314.7	290.6	270.3	253.8	240.8	231.5	225.7
95	397.5	363.1	333.6	308.9	287.8	270.6	256.6	245.9	239.0
100	418.6	382.8	352.6	327.1	305.4	287.3	272.2	260.6	252.0
105	439.6	402.6	371.5	345.4	323.1	304.0	288.0	275.2	265.2
110	460.8	422.6	390.5	364.0	340.8	320.8	303.6	289.9	278.5
115	481.9	442.3	409.6	382.4	358.4	337.7	319.4	304.5	291.7
120	503.1	462.3	428.6	401.0	376.1	354.5	335.2	319.2	305.0

V. Enthalpy, kJ/kg, for black liquor L51

Temp., °C	Solids, weight fraction								
	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80
40	167.3	147.4	127.1	110.9	94.1	83.7	77.6	76.2	79.3
45	188.1	166.7	145.5	128.5	111.1	99.7	92.5	90.0	91.6
50	209.0	186.0	163.9	146.4	128.1	115.8	107.6	103.7	103.9
55	229.9	205.5	182.5	164.1	145.0	131.8	122.5	117.6	116.5
60	250.8	225.0	200.8	182.0	162.0	147.8	137.6	131.3	129.0
65	271.7	244.5	219.4	200.1	179.0	163.9	152.7	145.3	141.6
70	292.6	264.3	238.3	218.0	196.0	180.1	167.8	159.2	154.3
75	313.5	283.8	256.9	236.2	212.9	196.2	182.9	173.2	167.1
80	334.5	303.6	275.7	254.3	230.1	212.5	198.0	187.4	179.7
85	355.5	323.3	294.5	272.4	247.3	228.7	213.4	201.3	192.7
90	376.5	343.3	313.6	290.6	264.5	244.8	228.5	215.2	205.5
95	397.5	363.1	332.4	308.9	281.7	261.3	243.8	229.4	218.3
100	418.6	383.1	351.5	327.1	298.9	277.5	258.9	243.6	231.3
105	439.6	402.8	370.5	345.4	316.1	293.8	274.3	257.8	244.1
110	460.8	422.8	389.6	364.0	333.6	310.3	289.6	272.0	257.1
115	481.9	442.8	408.9	382.4	351.0	326.6	305.0	286.1	270.1
120	503.1	462.8	427.9	401.0	368.4	343.1	320.3	300.3	283.1

vapor pressure equilibrium curves at 30%, 50%, and 70% solids for the liquors. **Figure** 8, which is the worst case, shows the comparison for liquor L51. We suspect that the experimental data for 30% solids below 400 mm Hg may be high due to air leakage into the equilibrium still. The agreement of calculated and experimental vapor pressures is nevertheless quite good. We believe these results indicate thermodynamic consistency when treating black liquor of constant solids composition as a binary system. It is also evident that enthalpy and normal boiling point data provide calculation of vapor pressures for temperatures above the normal boiling point.

Conclusions

Black liquor is not an ideal liquid solution as some investigators have implicitly assumed for energy balance calculations involving liquid black liquor. Massee *(5)* showed that heat capacity was nonideal. He developed a model form for heat capacity for kraft black liquor that has generally proven valid to date. Earlier work *(10, 11)* reported heats of dilution measured experimentally for four black liquors at 80°C. It established a suitable thermodynamic reference state for the solids.

Approximate calculations indicate that treating black liquor as an ideal liquid solution can result in a 4–6% underestimate of the energy required to concentrate black liquor from 20% to 65–90% solids at a steam economy of 4 to 1. We have prepared enthalpy vs. concentration charts for the four black liquors by standard thermodynamic methods. These consider black liquor to be a binary system. The enthalpy relations for the black liquors are thermodynamically consistent, as the comparison of experimental and predicted vapor pressure equilibrium curves for black liquor L51 indicates. Accurate enthalpy relations and normal boiling point data can therefore predict vapor pressure equilibria for black liquors.

The liquors investigated represent a wide range. All came from slash pine, but they do not represent the entire range possible even for this source. Other data are neces-

sary. The present work, however, does present the first soundly based enthalpy relations available for black liquors.

Calculations show that energy inputs required for concentration of black liquor by evaporation from 20% to 65–90% solids at a 4 to 1 steam economy are 4–6% greater than presently calculated, since these ignore heat of dilution and excess heat capacity. The major contribution to this difference is the heat of dilution. It is worth noting that ignoring the heat of dilution would lead to even larger differences at steam economies greater than 4 to 1.

Literature cited

1. Hunter, R. E., Tracy, J., Cutts, R., *et al.*, *Tappi* 36(11): 493(1953).
2. Harvin, R. L. and Brown, W. F., *Tappi* 36(6): 270(1953).
3. Han, S. T., *Tappi* 40(11): 921(1957).
4. Koorse, G. M., Mehrota, A. and Veerami, H., *Indian Pulp and Paper* 32(1): 7(1977).
5. Massee, M. A., *Thermal Analysis of Kraft Black Liquor*, M.S. thesis, University of Maine, Orono, ME, 1984.
6. Massee, M. A., Kiran, E. and Fricke, A. L., *Chem. Eng. Comm.* 50: 81(1987).
7. Fricke, A. L., *Physical properties of kraft black liquor: Summary report–phases I and II*, U.S. DOE, Washington, 1987.
8. Fricke, A. L., *Physical properties of kraft black liquor: Interim report no. 2*, U.S. DOE, Washington, 1990.
9. Jelinek, S. F., *Tappi J.* 69(8): 114(1986).
10. Stoy, M. A., *Dependence of the enthalpy and vapor pressure of kraft black liquor on solids content*, Ph.D. thesis, University of Florida, Gainsville, FL, 1992.
11. Stoy, M. A. and Fricke, A.L., *Tappi J.*, in press.
12. Smith, J. M. and Van Ness, H. C., *Introduction to chemical engineering thermodynamics*, 4th edn., McGraw-Hill, New York, 1975, pp. 320-356, 416-470.
13. O'Connell, J. P. and Prausnitz, J. M., *Ind. Eng. Chem. Fund.* 9: 579(1970).
14. Keenan, J. H. and Keyes, F. G., *Thermodynamic properties of steam*, J. Wiley, New York, 1952, pp. 11-33.

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