DOE/CE/40740-T9

A COMPREHENSIVE PROGRAM TO DEVELOP CORRELATIONS FOR PHYSICAL PROPERTIES OF KRAFT BLACK LIQUOR, FINAL REPORT

Part 1: Description of Experimental Methods

A.L. Fricke, A.A. Zaman, M.O. Stoy, G.W. Schmidl,
D.J. Dong, B. Speck

April 1998

Work Performed Under Contract No. DE-FG07-85CE40740

For
U.S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
Washington, DC

By
University of Florida
Gainsville, FL 32611

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Description of Experimental Methods

Arthur L. Fricke, Abbas A. Zaman, Mark O. Stoy, G. Wolfgang Schmidl, D. J. Dong, and B. Speck

1.0 OVERVIEW

A wide variety of experimental techniques have been used in this work, and many of these have been developed completely or improved significantly in the course of the research done during this program. Therefore, it is appropriate to describe these techniques in detail as a reference for future workers so that the techniques can be used in future work with little additional effort or so that results reported from this program can be compared better with future results from other work. In many cases, the techniques described are for specific analytical instruments. It is recognized that these may be superseded by future developments and improvements in instrumentation; however, specific measurements can be more readily adapted to new instrumentation if a complete description of techniques used successfully in the past on other instrumentation is available.

The total pulping and liquor preparation research work performed included chip and white liquor preparation, digestion, pulp washing, liquor and wash recovery, liquor sampling, weak liquor concentration in two steps to about 45-50% solids with an intermediate soap skimming at about 140F and 27-30% solids, determination of pulp yield and Kappa number, determination of total liquor solids, and a check on the total material balance for pulping. All other research was performed either on a sample of the weak black liquor (the combined black liquor and washes from the digester) or on the skimmed

liquor that had been concentrated. Liquor samples were stored in high density polyethylene containers under a nitrogen blanket at 4C. Kraft liquors can be stored in this manner for more than six years without detectable change in properties. Also, softwood kraft liquors stored under these conditions can be diluted reversibly, i.e,. with the same properties as those for an undiluted liquor.

Work with the weak liquor included analysis for total solids, pH, lignin, inorganic anions and cations, sulfated ash, active residual alkali, and some organic compounds of low molecular weight. These low molecular weight organic compounds were formate, acetate, propionate, and glycolate/lactate anions, and these were determined by ion chromatographic methods. Magnesium, potassium, calcium, and iron (occasionally) were determined by analysis by atomic absorption. Sodium and sulfide concentrations were determined by selective ion electrode methods. Sulfite, thiosulfate, sulfate, carbonate, chloride, and oxalate ion concentrations were determined by ion chromatographic methods. Other determinations were performed using TAPPI standard methods.

Work with the concentrated liquor sample was much more extensive. Liquors were stored at no more than 50% solids for our work, because it was determined that liquors at this concentration are reversible; i.e., a liquor at 50% solids diluted to a lower solids concentration had the same properties as it possessed before concentration and dilution. This is not necessarily true for liquors that have been concentrated to above 50% solids. It should also be noted that this limit is specifically applicable only to softwood kraft liquors. Other liquors may have different limits for maintaining reversibility. Limited experience with sulfite, semi-chemical, and carbonate liquors indicate that the limit for reversibility is lower for these. This limit appears to be lowest for semi-chemical liquors at about 28% solids. However, hardwood kraft liquors have been stored at 45% solids for long periods with reversibility, if the carbonate levels are not extremely high.

The concentrated liquor was sampled, diluted to approximately 10% solids concentration, and the same analyses performed by ion chromatography, atomic

absorption, and ion selective electrode methods to determine concentrations of sodium, potassium, calcium, magnesium, chloride, carbonate, bicarbonate, sulfide, thiosulfate, sulfite, sulfate, oxalate, acetate, propionate, glycolate/lactate, and occasionally iron ions in the liquor as were done on the dilute liquors before concentration. This was done for a number of liquors to show that results were identical. The pH was measured at a standard dilution for the concentrated and skimmed liquor and lignin content and sulfated ash were determined by UV-visible and ashing methods.

A sample of the concentrated and skimmed liquor was diluted to 5-7% solids and then titrated with acid to a pH of 1.0 to precipitate lignin. The precipitated lignin was separated, washed a number of times, redissolved in a caustic solution, filtered, retitrated to a pH of 1.0 with acid to reprecipitate the lignin, and the reprecipitated lignin separated by centrifugation. This lignin was washed a number of times, freeze dried, extracted with an organic solvent that did not dissolve lignin, filtered, and freeze dried. This purified lignin was subjected to analyses for contaminating ions by ion chromatography and atomic absorption. The purified lignin was then used for lignin characterization for molecular weight, intrinsic viscosity, and surface effects, as well as for determining thermal characteristics. Number average molecular weight was determined by Vapor Pressure Osmometry (VPO), weight average molecular weight was determined by Low Angle Laser Light Scattering Spectrophotometry (LALLS) with differential refractive index for lignin solutions determined by Differential Laser Refractive Index (DLRI), molecular weight distribution was qualitatively determined by high temperature, high pressure size exclusion chromatography (HTHPLC), intrinsic viscosity by viscosity methods, and transition temperatures, decomposition temperatures, and solubility characteristics by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and rheological methods. These are described in detail later.

A major effort for each liquor was preparing concentrated samples at different concentrations from the skimmed and concentrated base sample for other experimental work. This was done by evaporation in a small scale evaporator under reduced pressure

until the desired solids concentration was attained. During concentration, the boiling point elevation was determined as a function of concentration via a mass balance. The evaporation apparatus involved extensive development to devise an apparatus and a method that would yield results equivalent to equilibrium conditions. This apparatus is described in detail later in this report.

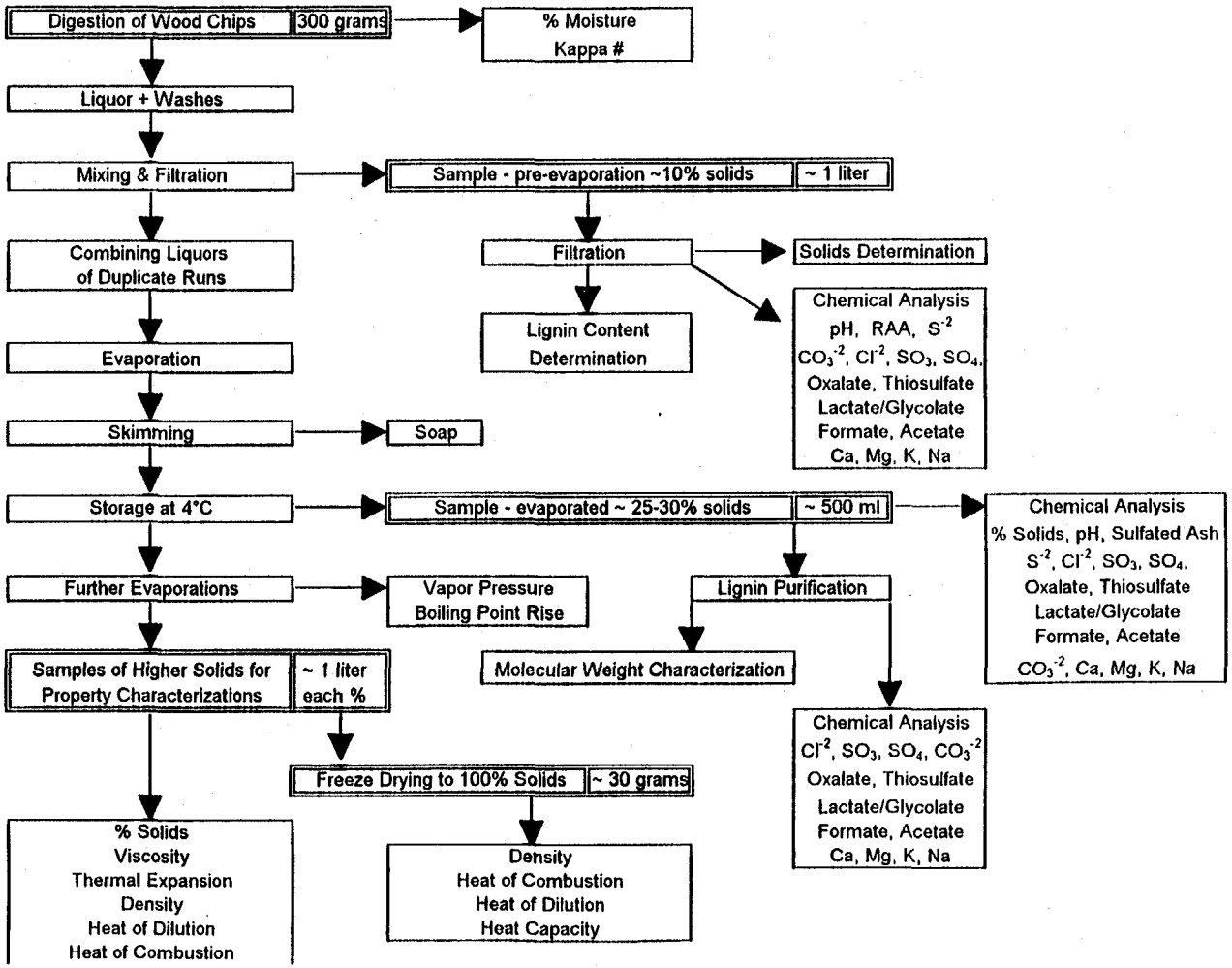
Each concentrated sample produced was stored at 4C in a high density polyethylene bottle until used for experiments. Experiments were run with these concentrated liquor samples only at the one concentration. It should be noted that "concentrated liquor sample" includes samples at concentrations ranging from 10-50% solids as well as at concentrations above 50% solids. Samples at concentrations below 50% solids were prepared simply by dilution of a well mixed sample at 45-50% solids with a weighed amount of hot distilled water. Thus, all data taken for physical properties were for a skimmed liquor containing a minimum amount of soap.

Experiments were run with the concentrated liquor samples to determine rheological properties as function of concentration, temperature, and shear rate (or frequency) by using a wide variety of rheological instruments; to determine density as a function of concentration and temperature; to determine heat capacity as a function of concentration and temperature; to determine heats of dilution as a function of concentration; to determine liquor vapor pressure as a function of concentration and temperature; and to determine liquor transition temperatures as a function of concentration.

Experiments were run with the freeze dried and with the purified lignin samples to determine heat capacity as a function of temperature, to determine transition temperatures, and to determine density as well as the experiments previously cited for the purified lignins.

Experiments were run with freeze dried portions of the concentrated black liquor that were dried to 100% non-volatiles (solids) to determine heat of combustion, density at

FIGURE 1
Black Liquor - Path for Production and Resulting Analyses



room temperature, heat capacity as a function of temperature, and transition temperatures.

The data collected were reduced to normal forms and data reduction schemes developed. In general, we attempted to first correlate data for one liquor as a function of temperature (and shear rate in the case of rheological data) and then combine this with the effect of concentration. Whenever possible, the results were checked for thermodynamic consistency or consistency of behavior as has been observed for other fluids. In every case, final correlations combining the effects of concentration and temperature (and shear rate in the case of rheological data) could be determined for each liquor. Further, these appear to be fairly general, since they have proven to be applicable to all liquors tested, except for certain acid sulfite and thermal mechanical liquors. Finally, generalized correlations for the constants of the correlations for properties of individual kraft liquors from slash pine were empirically determined to relate these to pulping conditions and to liquor solids composition in some cases. While these empirical equations are applicable only for slash pine liquors, the forms of the correlations are applicable to kraft liquors from other species and to liquors derived from other types of pulping in most cases.

The data reduction correlation forms developed in this work for properties of a single liquor will permit properties of a liquor to be determined exactly over a wide range of solids concentration and temperature (and shear rate or pressure for the cases of viscosity and boiling point elevation, respectively) with greatly reduced effort. Furthermore, the forms of the correlations relating properties to pulping conditions or liquor solids composition developed in this work will greatly reduce the work needed to develop similar quantitative correlations for liquors produced from kraft pulping of other species and for liquors produced from most other pulping processes, since it has been demonstrated that behavior is thermodynamically consistent and general and since the general correlations have been reduced to their simplest form. We believe that a generalized correlation for an new liquor system could be developed with data from as few as twelve liquors produced at different pulping conditions that represent the entire range of pulping conditions. These two developments in correlation afford an economically

attractive approach to liquor characterization needed for design and operation of recovery systems. This is very likely as significant a development of this work as the results of the work itself.

Methods and results have been published in many research publications that have appeared in TAPPI Journal, Holzforschung, Industrial & Engineering Chemistry Research, Journal of Pulp & Paper Science, AICHE Symposium Series, AICHE Journal, Journal of Wood Chemistry & Technology, Chemical Engineering Communications, TAPPI International Recovery Conference Proceedings, Journal of Applied Polymer Science, Materials Research Society Symposium Proceedings, Polymer, and the Journal of Chemical & Engineering Data, but description of methods and procedures was necessarily very abbreviated in these research publications. Except for TAPPI International Recovery Conference Proceedings, all of these publications are abstracted by Chemical Abstracts and are available in most research libraries. TAPPI International Recovery Conference Proceedings are available through TAPPI headquarters in Atlanta, GA. However, since description of methods and procedures are abbreviated in the publications, and since some are not reported at all, it is appropriate to document the procedures used in our work in detail for use by future researchers.

2.0 PULPING

2.1 Digester. Pulping was conducted in a digester system designed and built for this work (Fricke, 1990).. It is housed in a two story, isolated building built by the University of Florida specifically to house the digester and large pilot scale evaporator used for liquor concentration. The specific design of the digester system was given in detail in an earlier DOE report (Fricke, 1990) on this program. The system is all stainless steel. The digester itself is a 2.5 cubic foot capacity, 12 inch diameter, jacketed vessel with a conical bottom with reduction to 4 inch diameter and a 300 lb flanged head at the top. The digester is mounted in a frame with axles at its approximate balance point so that it could be operated as a tumbling, end-over-end, autoclave reactor.

Steam is supplied to the jacket and condensate removed through rotary connections mounted in one of the axles. The other axle is connected to a drive system so that the rate of tumbling can be varied and controlled from about 0.2 to 1.5 RPM.

Heating is indirect by steam supplied to the jacket. The steam supply is saturated steam at 245-250 psig. The steam pressure to the jacket can be controlled from 100-250 psig and the rate of steam flow can be controlled and measured.

A chip basket consisting of a 12 inch diameter, thin walled, stainless steel cylinder designed to fit closely , but loosely, into the digester is used to hold the chips. Removable filter screen assemblies are fitted to each end of the basket. The bottom screen assembly is conical with supports for liquor drainage. Screen packs, usually consisting of a 20 mesh, two forty mesh, a 60 mesh, and a 20 mesh , two 40 mesh, a 60 mesh, and a 20 mesh stainless steel screens in series are used in the screen assemblies. The very small space between the interior digester wall and the chip basket are sealed by Teflon oversized gaskets mounted between the screen packs and the chip basket.

The chips are loaded into the basket with a thermocouple assembly in place for measuring chip bed temperatures. This thermocouple assembly consists of a stainless steel tube and Swaglok fitting assembly with five grounded, type J thermocouples spaced about

25 cm apart down the axis of the bed and placed to measure temperatures at about 7 cm from the center of the bed. The thermocouples are connected to a multiple rotary switch and thence to a recorder.

The digester is sealed after the loaded chip basket is in place. The digester is connected to the white liquor supply, wash water supply, black liquor circulation, and vent equipped with vacuum through fittings in the top flange that are connected with flexible armored hoses. The bottom conical end is fitted to a 4 inch, full opening ball valve that is connected by a 4 inch flexible armored hose to the liquor receiver. Black liquor suction for circulation is through a 3/4 inch line mounted below the bottom conical screen. When operated as a tumbling autoclave, the black liquor circulation lines are disconnected and the other fittings disconnected during tumbling. When operated with liquor circulation, all connections are left intact during digestion.

The white liquor supply tank is a 60 gallon, stainless steel, insulated vessel equipped with electrical heaters and temperature control. The white liquor is pumped to the digester by using a two stage centrifugal pump and flow rate is monitored and totalled by means of a turbine flow meter. The water supply tank was a 200 gallon, stainless steel insulated vessel equipped with a steam coil and temperature control. Water was pumped to the digester by using a two stage centrifugal pump and flow rate was monitored and totalled by means of a turbine flow meter in the line.

Black liquor can be circulated through the digester when operated as a circulating digester by directing liquor from below the chip basket to a Lapp diaphragm pump equipped with a speed control and circulated back to the top of the digester where it is distributed over the chip bed by the top screen pack.

The Lapp pump has a double mechanical seal with pressurized water between the seals. A small pressure differential (2-5 psi) was maintained between the water seal fluid and the liquor circulation line to prevent liquor leakage. There is a small water leakage

into the liquor through the seal during digestion, but this amounts to only about 100-150ml during digestion, which is a negligible dilution of the liquor.

The liquor circulation rate can be controlled by controlling the speed of the Lapp diaphragm pump. Liquor circulation also permits temperatures to be measured throughout the bed during digestion, which cannot be done when the digester is operated as a tumbling autoclave.

Thus, the digester can be operated in one of three modes: as a closed autoclave, as a tumbling autoclave, or as a fixed reactor with liquor circulation. The only limitation is that digester heating is indirect only.

The black liquor receiver is a 150 gallon stainless steel vessel equipped with a U-bend, stainless steel heat exchanger for liquor cooling and with a thermocouple for monitoring the liquor temperature. The receiver is connected to a vent equipped with a vacuum pump and with a nitrogen purge system to assist in excluding air. The receiver outlet is connected to a centrifugal pump piped for liquor circulation during cooling and for liquor discharge through an inline filter. Cooled and filtered liquor is discharged into small, portable, high density polyethylene tanks for weighing and for transfer to the pilot evaporation system.

The digester system includes instrumentation for batch control of liquid feeds, pressure measurement and chip bed temperature measurement in the digester during digestion (except when operated as a tumbling autoclave), control of digester tumbling rate, control and recording of white liquor and water temperatures, control and recording of steam pressure, flow rate, and total flow, control of black liquor circulation rate, and measurement of temperature and pressure in the liquor receiver.

The digester could be modified easily to permit direct heating with steam, but this was not done. Also, with the black liquor circulation system and the batch control system,

the digester could be modified in the future with the addition of more tankage to permit simulation of staged digesters and continuous digesters.

Except for the Lapp pump black liquor circulation system and some instrument details, this system was completely described in detail in an earlier report DOE report on this program (Fricke, 1990).

2.2 Chip Preparation. Slash Pine chips were obtained from Georgia-Pacific Corporation, Palatka, Florida for use in this work. Chips were screened at Palatka and delivered to the University of Florida at Gainesville, Florida where the pulping was done. The chips were spread on a concrete floor covered with a large plastic sheet and chips with large amounts of bark were removed by hand. The chips were then thoroughly mixed and quartered with mixing according to ASTM methods to obtain as identical lots as possible, according to recommended sampling practices. Normally, enough chips were sorted and sampled for ten to twelve batch digestions. Chips were normally about 45% moisture and a normal sized batch for a single digestion was about 70 lbs. of wet chips. Chips for each batch were sampled, then weighed and packaged in vinyl plastic bags until used. Chips were used within five weeks or less after delivery. Chip moisture was determined for the chip sample taken before weighing and packaging the chip batch by the method recommended by TAPPI. A description of the exact procedure used to determine chip moisture is given in detail in TABLE 1. As described, these chip moisture determinations were done in triplicate. If differences between determinations were large, the chip batch was unpackaged, remixed, resampled, repackaged, and moisture determination repeated.

Obviously, the digestion experiments were run in blocks with respect to chips. Replicates were run randomly using chips from several lots to evaluate the block variation. The block variation proved to be negligible and was ignored.

TABLE 1

% Moisture of Chips or Pulp

1. Weigh 3 clean, dry pans at least 6 inches in diameter. Record weight.
2. Fill each pan 1/3 to 1/2 full with chips or pulp. Weigh and record weight.
3. Subtract the weight of the pan from the weight of the wood+pan to get the wood weight. Record this weight.
4. Dry in 105°C oven for 24-48 hours or until a constant weight is reached. This means dry the wood until 2 consecutive weighings 3 hours apart result in a variation of less than 0.1% of the original wet weight.
5. Weigh and record weight of dry wood+pan.
6. Subtract pan weight from wood+pan weight. Record this value.

Calculation

$$\% \text{ Moisture} = \frac{\text{weight of wet wood} - \text{weight of dry wood}}{\text{weight of wet wood}} \times 100$$

TAPPI Method T 210 cm-86

2.3 White Liquor Preparation. Synthetic white liquor was prepared by dissolving weighed amounts of 50% NaOH solution and of 50% Na_2S flakes in water and adding weighed amounts of Na_2CO_3 and of Na_2SO_4 crystals to adjust the liquor to a reduction of 93% and a causticizing efficiency of 85%to form a concentrated solution that was poured into the white liquor tank. The tank was then sealed and water was metered to the white liquor tank using a turbine meter and a totalizing batch control to adjust the NaOH and Na_2S concentrations to yield the effective alkali and sulfidity needed for the digestion experiment. Effective alkali, sulfidity, causticizing efficiency, and reduction were calculated using TAPPI methods. After preparation, a sample of the white liquor was taken, and the liquor heated to the desired temperature for loading into the digester. The white liquor sample was analyzed by ion chromatography and ion selective electrodes for sulfide, sulfate, carbonate, and sodium concentrations. White liquor was typically charged into the digester at 180 to 220F.

2.4 Digester Preparation and Chip Loading. The aliquot of chips to be used was reweighed, resampled for moisture determination, and loaded into the chip basket. The chips were loaded with the thermocouple assembly for measuring chip bed temperatures in place. This unit consists of a stainless steel tube and Swaglok fitting assembly with five grounded type J thermocouples spaced about 25 cm apart down the axis of the bed and placed to measure temperatures at about 7 cm from the center of the bed. The top set of filter screens were bolted into place on the top of the chip basket and the loaded basket was lowered into the digester.

After loading the chip basket, the digester was closed, connected with the liquor receiving tank, and the entire system was evacuated by means of the vacuum pump connected to the receiver vent line. The system was then isolated, and the ball valve connecting the digester to the liquor receiving tank was closed. Steam was fed to the digester jacket under pressure control to preheat the chips. At a point during preheating, the gas exhaust valve on the digester was opened to expel gases and then closed. At this point, the digester was ready for batch digestion to begin.

2.5 Digestion. The white liquor was metered into the digester under batch control until the proper amount had been charged. The batch control worked very well; liquor charge could be controlled to within +/- 0.05 gallons for a charge of 15 gallons, more or less. Charging time was 2-5 minutes.

If the digester were to be operated as a tumbling autoclave, all flexible line connections to the digester were disconnected. If the digester were to be operated with liquor circulation, the flexible line connections were left in place and the liquor circulation system was started. The steam to the digester jacket was opened and steam pressure was controlled to raise the bed temperatures to the digestion temperature within the specified heat up time of 15-20 minutes. When the cooking temperature was reached, the thermocouples in the bed were disconnected if the digester were to be operated as a tumbling digester and tumbling was started. digestion began and continued for the required time at constant cooking temperature. During digestion in the circulating liquor mode, temperatures measured by the thermocouples in the chip bed were recorded.

After digestion for the required time in the circulating liquor mode, the liquor circulation was stopped, the steam to the digester jacket was shut off, the ball valve at the bottom of the digester was opened, and the liquor was discharged by the digester pressure into the evacuated liquor receiver. After digestion in the tumbling autoclave mode, the steam to the digester jacket was shut off, the flex hose to the receiver reconnected quickly, and the liquor discharged by the digester pressure into the evacuated liquor receiver.

The digester drain valve was closed and wash water at 165-180F was metered into the digester by using the same batch control and meter used to meter white liquor. About 8 gallons of wash water were added (about half of the white liquor volume). Black liquor discharge and wash water addition normally took less than 5 minutes, which provided a rather rapid quench of the cooking reaction. After addition of wash water was completed, the circulation system was started and the wash water circulated for about 10 minutes. The circulation system was then shut off, the ball valve at the bottom of the digester was

opened, and the wash added to the black liquor in the liquor receiving tank. The ball valve at the bottom of the digester was closed and the wash repeated with a second aliquot of about 8 gallons of water. This was also added to the black liquor in the liquor receiving tank. The digester was then filled with water and the water in the digester was circulated while the black liquor in the receiver was being cooled.

The black liquor in the receiver was cooled to about 90F by means of the heat exchanger contained in the bottom of the receiver. The black liquor was then pumped from the receiver through a 250 mesh polishing filter into a portable plastic tank and weighed. Samples of the liquor were taken for chemical analysis and for solids determination. The cooled and filtered combined black liquor and washes were taken to the pilot evaporator for concentration and soap separation. Preliminary experiments demonstrated that this procedure recovered 92-95% of the solids dissolved in the black liquor without undue dilution of the liquor and that the black liquor contained solids with a composition identical to that for all of the black liquor, i.e., this procedure yielded a truly representative sample of black liquor solids with a minimum of dilution.

The wash water in the digester was then drained into the reciver and 50-70 gallons of additional wash water were run through the chip bed into the receiver. The accumulated final wash contained in the receiver was pumped into a portable plastic tank, weighed, sampled for solids determination, and then pumped to the sewage treatment system.

The digester was opened and the washed pulp was removed and weighed. The pulp was mixed and sampled to determine moisture and Kappa number as is described later.

The solids concentration and total mass of combined liquor, the solids concentration and mass of final wash, the pulp wet and dry masses, the chip moisture and mass, and liquor charge masses and concentrations of solids, permitted a good overall material balance to be made for the digestion process. The cooled and filtered combined

black liquor and washes were taken to the pilot evaporator for concentration and soap separation.

The temperature profile during digestion was recorded from each of the thermocouples in the bed. If the temperatures were not in agreement within about 2F, the digestion was discarded. In the normal case, temperatures agreed within 1F or better. In most cases, the temperatures during cooking agreed within lF or closer and the variation in temperatures during the entire cook was also less than 1F.

Normally, digestion proceeded smoothly with few problems. After the initial learning process, digestions could be run at a rate of about one every two to two and one half working days. A total of more than 120 digestions were made in this system with more than 80 considered successful. Most of the unsuccessful runs were made during the learning process. Only a few failures were due to mechanical or instrument failures experienced during runs. Only twice were there any emissions that were detectable beyond the limits of the digester building.

2.6 Pulp Analysis and H-Factor. Moisture content of the pulp was determined by using the same method as used for determining moisture of chips as described in TABLE 1. The pulp was completely mixed in order to obtain as representative a sample as possible. Measurements were made in triplicate and repeated if variations were more than about 0.1% between replicates. From the pulp moisture, total pulp mass, wet chip mass, and chip moisture, the pulping yield could be calculated.

Kappa Number was also determined for the pulp by a procedure that is identical to, or very close to, TAPPI Standard T236 cm-85. Kappa Number was found to be subject to variations due to procedural variations between testers. Therefore, considerable effort was devoted to minimizing these variations by standardizing procedures even more closely than is described in the TAPPI Standard T236 cm-85.

The exact procedure followed is described in detail in Table 2. Note that the starting material upon which the analysis is based is a small sample of the pulp. It is very important that this sample be taken, not at random, but from mixing and quartering of the total pulp. This is not easy to do, especially at very high Kappa Numbers ; therefore, it is very important that it be done with care in order to get a sample that is representative of the overall average of the pulp.

This small pulp sample was normally about 30 grams. This sample, as discussed in Table 2, was thoroughly washed in deionized water to remove all traces of black liquor. This required extensive washing. The pulp is defibrillated by beating in a Waring blender and is then drained as well as possible. Shives and any particles of knots are removed. This is a very important step that is normally subject to variation between testers, and it may be a source of variation between laboratories. We were very careful in removing all non-uniform appearing material.

The cleaned pulp sample was divided into portions for moisture analysis and portions for Kappa Number determinations as described. the analytical procedure that we used is described in detail in Table 2. We found that standardizing times for addition of chemicals, stirring, and titration was necessary in order to minimize variations. These standards are described in steps 8. through 11. of the procedure given in Table 2. For completeness, details for the blank and for calculation of Kappa Number are given in Table 2. Kappa Numbers were determined in triplicate and the average reported. The deviations from the average for any one determination was a function of the Kappa Number; the deviations were largest at high Kappa Numbers.

The average temperature in the chip bed vs. time, including the time needed to reach cooking temperature after the white liquor was introduced, was used to determine the H-factor for the digestion .

Table 2

Kappa Number

Chemicals needed, made up according to TAPPI Method T 210 om-89:

1. ~0.1N $KMnO_4$ - standardize and record actual normality
2. 4N H_2SO_4
3. 1.0N KI
4. ~0.2N $Na_2S_2O_3$ - standardize and record actual normality
5. Starch Indicator Solution

Equipment needed:

1. Water bath set at 25.0°C ± 0.2°C
2. 2000 ml Erlenmeyer flasks
3. 2 - 100 ml pipets
4. 500 ml graduated cylinder
5. 250 ml Erlenmeyer flasks
6. Long stirring rods
7. Stop watch
8. 25 ml graduated cylinder
9. 50 ml burets
10. Waring blender

Procedure:

1. Wash ~30 grams of pulp with deionized water until residual black liquor is removed. Repeat with second sample.
2. Place cleaned pulp into blender with 300 - 500 ml deionized water. Blend until the pulp is completely separated into individual fibers. Squeeze as much water from the fiber as possible or use a Buchner funnel to drain water from the pulp. Separate the fiber mass and remove any shives or knots. Repeat with second sample.
3. Weigh 3 small aluminum weighing dishes. Record weights. Fill each with damp separated pulp, reserving about 40 grams for Kappa Number analysis. Record weights. Dry overnight in 105°C oven. Record dry weight. Find % moisture-free pulp.
   CALCULATION: (dried pulp mass/wet pulp mass)x100 = % moisture
4. Take sample from reserved portion. As a general guideline use:
   - ~ 5 - 6 g wet weight for Kappa Number = 20 - 35
   - ~ 4 - 5 g wet weight for Kappa Number = 40 - 55
   - ~ 3 - 4 g wet weight for Kappa Number = 55 - 70
   - ~ 2 - 3 g wet weight for Kappa Number = 70 - 1120

   Record weight.
   To calculate an approximate Kappa Number, assume 1/4 wet weight = dry weight. Use this number until your pulp is dry and an accurate dry weight is available for final calculation.
5. Turn on water bath, set to 25°C + 0.2°C and allow to equilibrate.
6. Place sample in 2000 ml Erlenmeyer flask. Add 795 ml deionized water. Set in water bath and allow temperature to equilibrate. Stir to break up pulp mass.
7. Place 20 ml KI into a 25 ml graduated cylinder. Set beside the water bath.
8. Pipet 100 ml each of 0.1N $KMnO_4$ and 4N H_2SO_4 into a 250 ml Erlenmeyer flask. Make sure these solutions are also at 25°C.
9. Start the stopwatch as you add the solution to pulp. Rinse the 250 ml Erlenmeyer flask with 5 ml water. Add this to the sample.
10. Stir pulp suspension ~5 - 10 second every 20 seconds or so with a long stirring rod. Don't incorporate air, but stir to create a small vortex.
11. At exactly 10 minutes, add the KI to stop the reaction.

Table 2 (continued)

Kappa Number

12. Immediately take the 2000 ml flask to a buret and titrate with ~0.2N $Na_2S_2O_3$ (sodium thiosulfate). Either put in a magnetic stir-bar or swirl the flask as you titrate. For these pulp amounts and expected Kappa Numbers, it should take about 22-30 ml to reach the endpoint. Color will go from red or red-brown to orange or gold. At this point, add ~10 ml starch indicator solution. Swirl to mix. Color will be blackish, brownish and lighter as you titrate, then **blue** and very shortly clear. This is the endpoint. Note ml of titrant used and record.
13. Repeat all steps with clean flasks (dry flasks are not required), but omit pulp for a blank run. This will require ~52 - 55 ml titrant.
14. Analysis should be run in duplicate or triplicate and Kappa Numbers averaged.

Calculations:

$$p = (\text{ml used}_{blank} - \text{ml used}_{sample}) \times \frac{N\ Na_2S_2O_3}{N\ KMnO_4}$$

Ex: $(53.40 - 23.40) \times \frac{0.2019}{.1139}$

Note: **p must be between 30 and 70.** If it isn't, repeat with an adjusted amount of pulp.

$$\text{Kappa Num} = \frac{p \times f}{w \text{ (dry weight of pulp)}}$$

Ex: $\frac{53.18 \times 1.007}{1.3963} = 38.4 = \text{Kappa Number}$

The value for f is determined from the $KMnO_4$ consumption table as described in the TAPPI method as follows:

f +	0	1	2	3	4	5	6	7	8	9
30	0.958	0.96	0.962	0.964	0.966	0.968	0.97	0.973	0.975	0.977
40	0.979	0.981	0.983	0.985	0.987	0.989	0.991	0.994	0.996	0.998
50	1	1.002	1.004	1.006	1.009	1.011	1.013	1.015	1.017	1.019
60	1.022	1.024	1.026	1.028	1.03	1.033	1.035	1.037	1.039	1.042
70	1.044									

TAPPI Method T236 cm-85

2.6 Pulping Data Summary and Rationale for Acceptance. The chip load and chip moisture, sulfidity, effective alkali, heat up time, temperature profile during heat up and digestion, digestion temperature, digestion time, white liquor charge, wash charges, combined black liquor and wash quantity recovered and solids content of this combined liquor, pulp mass, pulp moisture, pulp yield, pulp Kappa Number, and H-factor were all determined and recorded. Digestions were run in duplicate. If the Kappa numbers did not agree within suitable limits, the liquors and pulp were discarded and pulping at this condition repeated.

Agreement of Kappa Numbers was reasonably close up to Kappa Numbers of about 60; beyond this level, agreement became progressively worse until a difference of as much as 10 was not uncommon for duplicate runs at Kappa Numbers above 105. Too large a variation in Kappa Number was the primary reason for rejection of cooks. Cooks were occasionally rejected due to temperature variations during cooking that were considered to be too large to be acceptable. If the cooks made at identical conditions gave acceptably close yields and Kappa Numbers for the pulps, the liquors from the two digestions were combined for evaporation on the pilot scale evaporator.

3.0 PILOT SCALE EVAPORATION

The pilot scale evaporator is basically a 1.0 square foot evaporation area jacketed horizontal wiped film evaporator built by Artisan Industries that is equipped with a variable speed wiper sealed with a Crane double mechanical seal (Fricke, 1990). The liquor is fed from portable tanks to the evaporator with a Moyno moving cavity pump equipped with a DC motor and speed control for control of the liquor feed rate. The feed line is equipped with a double pipe steam heated heat exchanger to preheat the feed to, or close to, the boiling point of the liquor. The temperature of the liquor exiting the feed preheater is measured and used to control the steam flow to the exchanger to maintain the final temperature of the feed at the desired value. Steam to the jacket of the evaporator is pressure controlled to maintain a constant outside wall temperature and, thus, a constant delta T in the evaporator.

The vapors pass through a 50 square foot, stainless steel, 1-1 shell and tube exchanger that serves as a condenser. This exchanger is mounted in a vertical position with cooling water in the shell and condensing vapors in the tubes. Condensate from the condenser flows by gravity into a 75 gallon stainless steel condensate receiver equipped with a sight glass for monitoring liquid level.

The pressure in the condensate receiver is measured by a pressure transducer and the vent from the condensate receiver is connected to either a vacuum line or directly to an atmospheric vent. When operating at subatmospheric pressure, the vent line is routed through a trap to a vacuum pump. The pressure in the receiver is used as a control signal to control ballast air flow to the vacuum pump to control the pressure in the receiver. When operating at pressures above atmospheric pressure, the vent is switched to direct venting and the pressure in the receiver is used as a control signal to adjust the vent valve to control the pressure in the receiver.

The concentrated liquor passes from the exit of the evaporator (a 4 inch line) into portable, jacketed, insulated stainless steel tanks of various sizes ranging from 35 to 70

gallons. Two of these are equipped with short lengths of glass pipe and small centrifugal pumps below the bottom outlet valve. These are used to decant liquor for soap skimming. The condensate receiver is equipped with a centrifugal pump for discharging the condensate.

3.1 Normal Concentrating Operation. Normally, the solids concentration of the combined black liquor and washes from the digester ranged from 9 to 14%. This liquor was evaporated at a pressure of 0.4 to 0.5 atmospheres absolute pressure. The liquor was fed at a constant rate of 0.09 to 0.13 GPM, and the jacket steam pressure was maintained at about 30 psig. Under these conditions, the evaporation rate was very constant and the condensate was clear and very nearly water white, although the initial small amount of condensate usually contained mall amounts of organic material. The split of the feed into condensate and concentrated liquor was very constant and could be controlled easily by varying the feed rate, since the evaporation rate was essentially limited by the delta T across the evaporator body. Evaporation was controlled to produce a concentrated liquor with a solids content of 27-30% solids.

When the feed was exhausted, the evaporator was shut down and the concentrated liquor allowed to cool in the receiver to about 140F. This liquor was then pumped back into the evaporator feed tank through the glass decanting section at the bottom of the product receiver to skim the soap from the liquor. The condensate from the condensate receiver was discharged and weighed. A sample of the concentrated liquor was taken and solids concentration determined. The evaporator system was flushed with water and dried.

If the solids concentration of the concentrated liquor were below 26%, the first evaporation step was repeated with adjustment of the liquor feed rate to provide a concentrated liquor with a solids concentration of 27-30% solids for maximum soap separation. After the first few experiments, this was very seldom necessary, because the split of the feed into condensate and product liquor could be predicted very well.

The concentrated and skimmed liquor at 27-30% solids was fed to the evaporator at essentially the same conditions cited previously, except that the liquor feed rate was adjusted to provide a concentrated product at 45-50% solids. The condensate produced during this evaporation was always clear and very nearly water white; there was essentially no entrainment nor evaporation of volatile organics evident.

When the feed was exhausted, the concentrated liquor was discharged into 5 gallon high density polyethylene containers that were capped with nitrogen and sealed. These were placed in a large refrigerator maintained at 40F and preserved for use in our experiments. A sample of the concentrated liquor was taken and the solids concentration determined. The condensate was discharged from the condensate receiver and weighed. Occasionally, the condensate was sampled and analyzed for inorganics and total organic carbon. The condensate was disposed of by discharging it into the sewage disposal system. The evaporator system was flushed with water and dried for its next use.

4.0 LIQUOR ANALYSES

The major analyses of the liquors were performed on the concentrated, skimmed liquors, and these analyses methods are best described in the context of analyses on the skimmed liquors. However, analyses were performed on the liquor from the digester receiver also in most cases. In addition, lignin was acid precipitated from the liquor, purified, and analyzed for molecular weight. The purified lignins were used in other research also to determine their optical properties, surface characteristics, rheological and thermal properties, and to explore some applications. Finally, samples of the liquor were concentrated to 100% solids by freeze drying to provide material for experiments requiring samples of 100% solids. Freeze drying is the only means that we found for preparing such samples with the certainty of no chemical or irreversible physical changes(Massee, 1984).

4.1 Total Solids Determination. A necessary fundamental measurement for our work was determination of the solids concentration. This is necessarily an arbitrary determination. Basically, total solids concentration is the non-volatile content upon drying at about 105C, but this is subject to variations due to drying rates that vary with skimming of surfaces, decompositions from overheating or prolonged heating, etc. A modification of the TAPPI method that was originally proposed by McDonald (1977, 1979) was adapted and improved for our work. Recognizing that skinning and decomposition could probably be minimized or eliminated by increasing the surface area for drying, McDonald proposed substituting a porous, unreactive fibrous pad for the sand bed as recommended by TAPPI and tried accelerated drying by microwave heating.

We worked to improve this method. The method as developed is given in detail in Table 3. The best fibrous pad found was a glass fiber pad, Fisher G2 or equivalent. This was placed in an aluminum pan and the pad and pan dried before weighing for tare. For best results, it was found that the solids content for the measurement should be 25% or less. Thus, liquor at higher concentrations required dilution. A well mixed weighed

TABLE 3

Per Cent Solids

% Solids is performed on samples of less than 25% estimated solids. If the black liquor is estimated to have a higher solids content than that, then the liquor must be diluted before performing the analysis to an estimated solids content of 15 - 20% solids.

estimated solids	dilution w/w	water g	black liquor g
25-35%	1+1	5	5
35-50%	1+2	6	3
50-65%	1+3	7.5	2.5
over 65%	1+4	8	2

Using the analytical balance, tare a clean, dry 13 ml glass vial. Make sure that any labelling necessary is done either prior to the taring of the vial or after dilution is complete. Add the appropriate amount of warmed (to 60 °C), well-mixed black liquor to the vial using a disposable pipet or spatula as necessary. Be accurate with the dilution, and record anydeviation from a precise 1+X dilution so that adjustments can be made. Cap tightly, shake well. Some high solids samples may require time in a warm (60°C) oven in order to dissolve well.

Procedure for % Solids

1. Number aluminum dish and add a thick glass fiber filter pad (Fisher G2).
2. Put in 105°C oven for 1 hour. Remove to dessicator and cool.
3. Weigh dish on Sartorius 1601A MP8-1 analytical gram balance. Record weight of pad+dish.
4. Add ~2 ml of sample (or diluted sample). Record weight of pad+dish+black liquor.
5. Repeat for a duplicate sample. All solids are done in duplicate.
6. Place samples in 105°C oven for 12-24 hours or until a constant weight is reached.
7. Remove from oven to dessicator. Allow to cool for 10 minutes.
8. Weigh and record dry weight of pad+dish+black liquor solids.
9. Subtract the pad+dish weight from the wet pad+dish+sample weight to get g black liquor.
10. Subtract the pad+dish weight from the dry pad+dish+sample weight to get g black liquor solids.

Calculation

% Solids = (g black liquor solids/ g black liquor) x 100 x dilution

Record % solids to 4 significant figures. Report only 3 significant figures.

Example of Layout for Solids Analysis

Liquor xxxxx 10-Oct-95

Sample ID	pan #	pan tare	pan+bl	blk. liq	pan+bls	blk liq solids	% solids	avg %	dilution factor	final %solids	blk liq/ tot wt
~11.5%	1	1.356	2.8252	1.4692	1.5277	0.1717	11.687	11.71	1	11.71	1
	2	1.3658	2.7966	1.4308	1.5336	0.1678	11.728				1
~ 20%	3	1.3715	3.0424	1.6709	1.724	0.3525	21.096	21.07	1	21.07	1
	4	1.3573	3.2168	1.8595	1.7486	0.3913	21.043				1
~ 34.5%	5	1.3582	2.9273	1.5691	1.5948	0.2366	15.079	15.13	2.47	37.31	2.508
	6	1.3664	2.9855	1.6191	1.6121	0.2457	15.175				6.1852

sample of liquor is diluted with a weighed amount of deionized water. A weighed amount of the diluted liquor that is sufficient to wet the entire mat but not sufficient to form a free liquid surface is added to the tared pan and mat. The pan is dried to constant weight in a 105C oven as described in Table 3. This usually required 12 hours or less, but could be as long as 24 hours. Analyses were always run in duplicate.

Surprisingly, samples treated in this manner that dried to constant weight in 12 hours showed very slight, if any, additional weight loss when kept at 105C for up to 24 hours. Table 3 includes sample results for a mill liquor to indicate the precision that can be expected under what might be termed the worst results obtained by using this method. In general, we have found that this method yields results that are precise to within +/- 0.15% or better at solids concentrations of up to 80% solids.

Rapid results can be obtained by microwave heating; however, precision and accuracy suffer. This is most likely due to variations in temperature resulting from the microwave heating. Even so, this method yields better results than the method recommended by TAPPI, and this method has been used throughout our work. It should be noted that this analysis reports total liquor solids, not dissolved solids as are measured by refractive index methods.

4.2 Active Alkali and pH. Active alkali of the black liquor was determined according to TAPPI Method T625 cm-85 with one modification. The details of the procedure that we followed are given in Table 4. This again is a procedure that will yield variable results, unless the procedure is followed exactly. The modification used is in step 8. of the procedure where it is noted that the inflection point is at a pH of 8.3 when an electrode pair is used. As noted at the bottom of Table 4, this gave a very sharp inflection point. The calculation procedure used to calculate active alkali (Na_2O) is given. It is also important to run a blank on the formaldehyde used and to correct for chemical consumption by the formaldehyde.

TABLE 4

Active Alkali

1. Pipet 100 ml of A well-mixed black liquor sample into a clean 500 ml volumetric flask containing about 100 ml of deionized water.
2. Add 100 ml of 0.5M $BaCl_2$. Stir and allow mixture to settle until partially clear.
3. Using a glass rod, transfer a drop of the cleared supernatant liquid to a small vial containing 1ml of 1.0N H_2SO_4. If a white precipitate is seen, go on to #4. If no precipitate occurs, add 20 ml $BaCl_2$ to the flask, stir, allow it to settle and recheck. Repeat this until a white precipitate is observed.
4. Dilute to 500 ml with deionized water. Mix well, and pour into a 1000 ml Erlenmeyer flask. Cap with a rubber stopper. Allow contents to settle until about 200 ml of clear liquid stands above the precipitate, *or* use a 10 ml Oxford pipet to carefully remove the supernatant fluid from the flask.
5. Pipet 100 ml of the decanted liquid into a 250 ml beaker.
6. Calibrate the Corning 250 pH meter to 7.00 and 10.00 pH using a saturated calomel reference electrode with a high pH electrode.
7. Put sample in a beaker and place on a on a stir plate, add a magnetic stir-bar and add 5.0 ml of 40% formaldehyde.
8. Immediately titrate with 0.5N HCl, using the calibrated electrode pair to follow the titration to a pH of 8.3, the inflection point.
9. Record ml of HCl used in the titration and its normality.
10. Check pH of formaldehyde. If it is above 8.3, titrate 5.0 ml of it to 8.3 using the 0.5N HCl. Record the amount of HCl used to adjust for the pH of the formaldehyde.

<u>Calculation</u>

Active Alkali (as Na_2O) (meq HCl used by sample - meq HCl used by formaldehyde) x 1.55

Note: Step 8 differs from the TAPPI method T 625 cm-85 in that we titrate the solution to 8.3 instead of 3.5. Our experience is that the inflection point is very noticeable and can easily be seen by <u>slow</u> titration from a pH ~9.5 to the drop that caused a sharp decrease in pH (to 8.3 or below).

pH was determined using standard ph meters that were carefully calibrated. The procedure is given in Table 5. Measurements were replicated. Often, pH was determined at a standard solids concentration for comparison purposes; this concentration was about 12%. Measurements were always made at 25C+/-2C.

4.3 Sulfated Ash. Sulfated ash was determined for the black liquors by essentially following TAPPI Method T 625 cm-85; however, alumina dishes were used instead of platinum. We found that this introduced no significant error. The exact procedure followed is given in Table 6. Test were replicated and averages reported. Each test was made with about 5 gms of liquor. As noted by the calculation given in Table 6, sulfated ash is reported in terms of NaOH as a per cent of total solids.

4.4 Sulfide and Sodium by Ion Selective Electrode. The methods recommended by TAPPI for determining the concentrations of sodium and sulfide in black liquor are atomic absorption and ion chromatography, respectively. However, these methods have limitations. The dilution required in each case in order to make the analyses is extreme, leading to errors, and the very low concentration of sulfide necessary for analysis leads to problems in protecting the diluted solution from oxidation which leads to even further uncertainty. More reliable and more convenient methods of analyses for these components were sought, which led to development of ion selective electrode methods as the preferred alternatives. Ion selective electrodes operate on the principle of ionic transport of the single ion of interest across a permeable membrane. To be effective, the membrane must be highly selective for the particular ion of interest, transport must be at a sufficiently high enough rate for producing a useable signal, and the membrane material must be stable in the solution undergoing analysis. After considerable trials, ion selective membranes that met these requirements were found.

The basic instrument used was a Corning 250 pH/ion meter. Instructions used in our work for calibration of this instrument are given in Table 7. These are given for

TABLE 5

pH Analysis with Corning 250 pH/ion Meter

Instructions for Calibration of Corning 250 pH/ion meter

Mode - selects measurement mode (pH, mV. temperature, activity)

Exit - returns user to the beginning of selected mode

Read - initiates measurement and can freeze the display

Cal - initiates calibration sequence

Set - reviews or allows changes to variables in each mode

← *or* → located at side of small display, selects option or registers value

the large display shows results or settings

To change measurements variables (range, sig. figures. temperature)

1. Choose mode desired.
2. Press **set.**
3. Enter temperature from the keypad. press →
4. The small display says *read*, press →
5. Choose *auto* or *manual,* press ← or →
6. Instrument then recalls calibration values and slope. These cannot be changed here.
7. Set new values for LO or HI range by entering the desired value, then →
8. Set display for *2* or *3* figures after the 0 by pressing the appropriate arrow.
9. The small display should return to mode selected.
10. Go on to calibration by pressing **cal.**
11. Choose *1* or *2 pt* calibration with arrows.
12. Place electrode in Standard 1, press **read.** When stable, press **read** again to set Cal 1.
13. If a 2 point calibration is chosen, repeat step 12 with Standard 2.
14. Read sample by pressing **read.**

To change calibration variables (standard values, temperature, units, etc)

1. Choose mode desired.
2. Press **cal.**
3. Choose *1* or *2 pt* calibration with arrows.
4. Press **set.**
5. Enter temperature from the keypad. press → Do not press **set.**
6. Choose *auto* or *manual,* press ← or →
7. Choose units, if asked (ppm, %, M, M.eq, activity or none) with arrows.
8. Choose display if asked (integer or exponent) using arrows.
9. Display shows *Cal 1*, enter value from keypad, press →
10. Display shows *Cal 2*, enter value from keypad, press →
11. Place electrodes in Cal 1 (std 1), press **read.** When stable press **read** again to set.
12. Place electrodes in Cal 2 (std 2), press **read.** When stable press **read** again to set.
13. Go on to samples. Press **read.**

pH Analysis

Let samples come to room temperature (25C +/- 2C) before measurement.

Calibrate the pH electrodes with a 2-point range, either 4.0 - 7.0 for acidic samples or 7.0 - 10.0 for basic samples and most liquors. Use fresh Fisher 4, 7, or 10 standards in a small beaker with a magnetic stir bar set on medium slow rotations.

Record date, standard range, electrode slope and initial entry.

Immerse electrodes in sample, turn on magnetic stirrer and let reading stabilize. Record data.

Store electrodes in pH 7 buffer.

TABLE 6

Sulfated Ash

1. Weigh Alumina dish on the Sartorius analytical gram balance. Record mass and dish ID.
2. Add ~5 grams liquor. Record mass and liquor ID.
3. Subtract empty dish mass from dish+liquor mass to get mass of liquor.
4. Dry at 105°C. Record mass of dish+solids and calcullate siids fraction.
5. Heat residue from solids in the muffle furnace until organic matter is mostly, but not completely destroyed. Color will be light gray, maybe mottled gray. Temperature will be about 750°C. Ramp the temperature on the muffle furnace in increments of 150°C/hr to keep the alumina dishes from cracking as they are sensitive to rapid heat change.
6. Cool to nearly room temperature, moisten with water and add 1-2 drops of methyl orange.
7. Add 1:2 H_2SO_4 dropwise until a pink color develops.
8. Evaporate to dryness on a steam bath.
9. For this step, work under the hood with the shield down as far as possible. Hold sample dish with tongs and heat over a screened flame slowly (it will try to spatter) to drive off excess acid. After acid has stopped fuming, heat to a dull red to completely destroy organic matter.
10. Cool on ceramic plate of muffle furnace to near 100°C and place in dessicator until the sample reaches room temperature.
11. Weigh sample and record mass.
12. Moisten with a few drops of water and add 1 drop of methyl orange. If a pink color develops, the excess sulfuric acid has not been driven off, so repeat steps 8-11. The remaining residue is assumed to be sodium sulfate.

Calculation

$$\text{Sulfated Ash, as NaOH (as \% of total solids)} = \frac{\text{sulfated ash residue} \times 0.563}{\text{total solids residue}} \times 100$$

This method varies from TAPPI Method T 625 cm-85 by using Alumina dishes instead of platinum; however, or work shows that results are identical.

completeness of reporting; similar instruments will have specific instructions for the preprogrammed sequences for measurement selection and calibration.

Sulfide analysis was performed with the 250 pH/ion meter using a Model IS-146 Sulfide/Hydrogen Sulfide sensing electrode with a Corning 476370 double junction reference electrode. Complete step by step procedures for the analysis are given in Table 8.

The temperature for conducting the analysis and calibration can be at any temperature between about 20 and 30C, but the temperatures for calibration and analysis must be identical. A standard is prepared by first preparing a buffered antioxidant solution of sodium salicylate, ascorbic acid , and sodium hydroxide. Reagent grade hydrated sodium sulfide crystals are used to make the standard. The standard is composed of 7.5 gms of hydrated crystals, 250 ml of antioxidant solution, and deionized water to dilute to one liter. The standard is stored in a dark sealed bottle to further minimize oxidation.

The electrode was standardized by using this standardized solution diluted to different concentrations and measuring the voltage for each concentration. It was found that this electrode could be standardized as ln(conc.sulfide)=A(mv.)+B with a correlation coefficient of 0.995 or better. Tests showed that this remained true for the sulfide ion concentration even in the presence of sulfate, thiosulfate, sulfite, carbonate, and chloride ions. That is, it is highly selective for sulfide as well as highly accurate for reasonably high sulfide concentrations.

The unknown (black liquor) was diluted with an aliquot of antioxidant solution and deionized water as described in Table 8, and analysis made with the protected and diluted sample. This method permitted us to make sulfide determinations accurately over a very wide range of concentrations without the problems introduced by extreme dilution required for ion chromatography. The electrode was found to be quite stable if kept clean as described in Table 8, and to give reproducible and accurate results for samples if carefully rinsed with deionized water between analyses.

TABLE 8

Sulfide Analysis

Use the Corning ion analyzer 250 with Model IS-146 Sulfide/Hydrogen Sulfide sensing electrode with the Corning 476370 double junction reference electrode.

Use deionized water for all solutions.

Use an antioxidant buffer to dilute all sulfide solutions in order to prevent air oxidation of sulfide and to adjust the pH. To prepare the antioxidant buffer, add 250 g of sodium salicylate. 65 g of ascorbic acid and 85 g of NaOH to approximately 600 ml of deionized water and dissolve in 1 liter volumetric flask. Dilute to 1 liter.

Prepare the stock Sulfide Solution (1000 ppm) by adding 7.5 g of sodium sulfide reagent crystals ($Na_2S\ 9H_2O$) to 250 ml antioxidant buffer and enough deionized water to make 1 liter in a volumetric flask. This standard should be stored in a closed bottle to minimize reaction of oxygen with the sulfide.

Standardization

1. Connect electrodes to Corning 250 ion analyzer.
2. Prepare about 200 ml diluted buffer solution by mixing 50ml buffer with 150ml DI water. Use this to prepare Molar or ppm solutions from the stock solution. Make ~4 solutions covering the range expected by the samples.
3. Soak electrodes in a 10 ppm solution for 30 minutes before beginning calibration curve. Rinse them with deionized water between readings.
4. Immerse electrodes into the most dilute standard to a depth of ~1 inch. Set stirrer for a medium slow rate and allow reading to stabilize. Record millivolt reading. Proceed with the rest of the standards working from low to high ppm.
5. Plot millivolts vs. S/HS concentration on semilog plot. Concentration will be log axis. Fit curve to ln(conc) = A*mV + B ; r^2 must be better than 0.995

Measuring Sulfide Ion in Unknown Sample

1. Make sure standards and samples are at the same temperature.
2. To 50 ml well-mixed unknown sample, add 25 ml antioxidant buffer and 25 ml deionized water.
3. After rinsing electrodes and magnetic stirbar, immerse the electrodes into the sample and stir at the same rate as used for the standards.
4. Monitor electrode potential and record the reading after stabilization.
5. Using standard curve (prepared above), calculate unknown concentration. Keep in mind that the curve will give ln(conc). Also, because the samples were diluted with buffer and water in a 1+ 1 proportion, the actual sample concentration is twice that found on the standard curve.

Electrode Storage

The sulfide electrode can be stored in air after it has been rinsed with deionized water. The reference electrode should be rinsed. the cap refilled with storage solution and

This method is much preferred to the ion chromatographic analysis method recommended by TAPPI (which was developed in an earlier stage of this research, incidentally), and should be adapted for mill use. It requires inexpensive instrumentation, the electrode is quite stable, the analysis is rapid, and calibration is straightforward. Calibration is time consuming, but does not have to be repeated very often if the electrode is kept clean.

Sodium content was also determined by selective ion methods as an alternative to other methods. This was developed and adapted in order to overcome to problems associated with extreme dilution in order to determine sodium by absorption or emission methods. These dilutions always led to substantial variation of replicate analysis that we deemed to be unacceptable. We searched for an ion selective electrode for sodium to meet our needs for black liquor. To be effective, the electrode must be highly selective for sodium, unaffected by the organics in black liquor, and the sodium in black liquor must be totally ionized.

After a number of trials, Fisher Catalog No. 13-639-20 electrode, an inorganic membrane with reasonable permeability, was found to be suitable. It should be noted that there are several equivalent electrodes made by other manufacturers. This electrode, together with a Corning No. 476340 reference electrode was used with the Corning Model 250 pH/ion meter to determine sodium ion concentration. This arrangement has a selectivity for sodium of better that 1000/1 compared to potassium ion and even higher selectivity with respect to divalent or multivalent cations, such as calcium, magnesium, or iron. However, there is some interference from hydrogen ion, but this can be eliminated by amines.

The procedures used for calibration and analysis are given in detail in Table 9. The electrode is calibrated with NaOH solutions stabilized by a small amount of triethanolamine solution as described. Analysis can be performed at any temperature between 20 and 35C; however, calibration and analysis should be performed at the same

TABLE 9	
Sodium Analysis by Ion Selective Electrode	
Standardization	
1	Connect electrodes to Corning 250 ion analyzer. Set analyzer to relative millivolt readings.
	Reference Electrode - Corning No. 476340 or equivalent electrode.
	Sodium Electrode - Fisher Cat. No. 13-639-20 or equivalent electrode.
2	Prepare standard stock solution of 1.0 N NaOH.
3	Use this to prepare Molar or ppm solutions from the stock solution. Make ~4 solutions
	covering the range expected by the samples. Add 1 drop of 1+1 triethanolamine to
	each of the solutions.
4	Soak electrodes in a 10 ppm solution for 30 minutes before beginning calibration curve.
5	Rinse them with deionized water between readings.
6	Immerse electrodes into most dilute standard to a depth of ~1 inch. Set stirrer for a
	medium slow rate and allow reading to stabilize. Record millivolt reading. Proceed
	with the rest of the standards working from low to high ppm concentration.
7	Plot millivolts vs. ln(Na^+concentration). Concentration will be y-axis.
8	Fit curve to ln(Na^+conc) = A*mV + B ; r^2 must be better than 0.995
Measurement of Sodium Ion in Unknown Sample	
1	Make sure samples to be measured are at the same temperature as used to
	standardize the electrode.
2	To 50 ml of a well-mixed unknown sample, add 1 drop of 1+1 triethanolamine.
	This prevents the H^+ ion from eliciting a response.
3	After rinsing electrodes and magnetic stirbar, immerse the electrodes into the
	unknown sample and stir at the same rate as used for the standards.
4	Monitor the electrode potential and record the reading after stabilization.
5	Using the standard curve (prepared above), calculate the unknown concentration.
	concentration of sodium ion in the sample.
Electrode Storage	
	The sodium electrode can be stored in air after it has been rinsed with deionized water.
	The reference electrode should be rinsed, the cap refilled with storage solution and
	fitted to the electrode.

temperature. These can be performed at different temperatures, but then a correction based on Nernst's equation must be applied. This is avoided easily by conducting both calibration and analysis at the same temperature. Calibration with NaOH solutions is fitted by ln(Na ion conc.) = A(mv.)+B with a correlation coefficient of 0.995 or better.

As a check on selectivity, one standard solution was analyzed with varying concentrations of potassium, magnesium, calcium, and ferric ions. The selectivities cited by the manufacturer were verified. It was also necessary to insure that the electrode would analyze for total sodium in black liquor, ie, that all of the sodium in black liquor was ionized. This was checked by comparing results with results from emission or absorption analyses of the same black liquor solution. Diluted samples of black liquor were analyzed directly by both emission analysis and selective ion electrode analysis. Results were identical. Black liquor samples at as high as 15% solids were analyzed by ion selective electrode and by emission analysis. Emission analysis required extreme dilution with concomitant scatter in results due to dilution; however, the average emission results agreed very closely with the ion selective electrode results, which indicated that all of the sodium present was ionized at concentrations up to 15% solids if the solution pH was 11.8 or higher.

Thus, the ion selective electrode method for sodium analysis is preferred and should be adopted, since analysis is easy and the cost for the instrument and electrodes is low. There is one caution. Transport rate through the membrane is low; therefore, time is required to reach a stable reading. We have found that five to eight minutes is required for a stable reading. However, we have obtained much more consistent results with less experimental time required for sodium analysis by using this method as compared to emission analysis.

4.5 Determination of Potassium, Calcium, Magnesium ,and Iron. Flame emission and atomic absorption spectrophotometry were used to determine concentrations of calcium, magnesium, and potassium on a routine basis and concentrations of iron and

sodium ocassionally. A perkin-Elmer Atomic Absorption Spectrophotometer was used in this work. the method used was the EPA CLP modification of EPA Method 3050. Complete details for procedures are given in Table 10.

An important step is sample preparation. The black liquor sample must be digested and thoroughly oxidized. A small sample of the liquor is reacted at 95C with strong nitric acid for ten minutes and cooled. It is then reacted with concentrated nitric acid for 30 minutes with reflux. The residual is reacted with 30% hydrogen peroxide diluted 3:2 by volume with deionized water at an elevated temperature until the oxidation subsides. This is repeated with 30% hydrogen peroxide until the sample appears to be unchanged or until a total of 10 ml of 30% peroxide has been added in aliquots. Hydrochloric acid is then added and the sample heated for approximately 10 minutes. the final product is diluted with deionized water to a total volume of 100 ml. A total of five products are prepared: two duplicates, two blanks, and one blank spiked with the cations to be determined.

Detailed step by step procedures used in these analyses with this instrument are given in the procedure section of Table 10. The fuel used in all cases was purified acetylene with air as an oxidant. Standards were prepared by diluting aliquots of the spiked solution to provide five samples with a range of concentrations of 20/1 to 100/1 in the standards. These were run in the instrument as well as the blanks to provide a calibration curve of emission vs. concentration. This was done for each of the cations of interest.

The specifics for analysis for each cation are given in Table 10. For example, determination of magnesium was made in an oxidizing flame with acetylene as the fuel and air as the oxidant at a wavelength of 285.5 nm. The sample had to contain 0.1% potassium or more as an ionization suppressant. The best range for detection of this ion was 5 to 500 ppm with a detection limit of 0.05 ppm. Normally, a number of black liquors

TABLE 10
Flame Emission Analysis by Atomic Absorption Spectrophotometer

Sample Prep

1. Clean 100 ml beakers and watch glass covers and soak in acid bath (equal parts H_2NO_3 and HCl, diluted 1:3) for at least an hour. Rinse well with deionized water.
2. Mix the sample well. Weigh out ~1 gram portion of sample and place in beaker.
3. Add 10ml 1:1 HNO_3, mix sample, cover with watchglass.
4. Heat to 95°C. Reflux 10 minutes without boiling. Cool sample.
5. Add 5 ml conc HNO_3, reflux 30 minutes. Do not let volume be reduced to <5 ml.
6. Add 2 ml deionized H_2O and 3 ml 30% H_2O_2. Return to hotplate to start peroxide reaction. Remove from hotplate if effervescence is excessive to avoid sample loss. Heat until effervescence subsides and cool beaker.
7. Continue to add 30% H_2O_2 in 1 ml aliquots with warming until effervescence is minimal or until sample appearance is unchanged. Do not add more than 10 ml total H_2O_2.
8. Add 5 ml 1:1 HCl and 10 ml deionized H_2O. Return to hotplate and heat 10 minutes.
9. Dilute to 100 ml with deionized water.
10. Prepare 2 blanks, 1 duplicate and 1 spike.

Ref: EPA CLP modification of EPA Method 3050.

Procedure for Perkin-Elmer AA

1. Install purified acetylene tank for analysis of Ca, Mg, K, and Na.
2. Plug in main power cord.
3. Rotate LAMP and GAIN controls completely counterclockwise.
4. Turn on main power supply by turning the power switch to ON position.
5. Install the proper lamp for analysis.
   a. Open lamp compartment door and disconnect lamp plug at the front of box.
   b. Loosen both hold-down screws on the sides of the lamp holder.
   c. Remove lamp holder from the compartment.
   d. Replace lamp with the desired lamp.
   e. Replace housing, ensuring the forward stops are in contact with the base.
   f. Secure holder with the front and back hold-down.
   g. Connect the lamp plug in the LAMP 1 connector.
6. Rotate SIGNAL switch to LAMP 1.
7. Adjust the LAMP 1 current control to the minimum current settings given on the lamp (use the continuous current setting). The lamp current is shown on the LAMP/ENERGY meter.
8. Allow a warm-up of 10 minutes.
9. Reset SIGNAL switch to ABS.
10. Using the NORMAL setting range on the slit scale, set the slit width to the size required by the sample (start with 0.7).
11. Set the wavelength to the correct value by the wavelength counter.
12. Rotate GAIN control clockwise until LAMP/ENERGY meter reads values in the green band.
13. Using the alignment knobs in the lamp compartment, move lamp back and forth to align lamp. When the lamp is aligned, the LAMP/ENERGY meter will show a maximum needle deflection to the right.
14. Reset the needle of the LAMP/ENERGY meter to the green region by the GAIN control and close the lamp compartment.
15. Lower burner head below the light path.

TABLE 10 (continued)
Flame Emission Analysis by Atomic Absorption Spectrophotometer
16. With the WAVELENGTH setting greater than 280. switch the SIGNAL control to ABS and the MODE control to CONT. Zero the display by pressing the AZ key.
17. Raise the burner head with the vertical adjust until absorbance is indicated on the display.
18. Lower the burner head until the display reads zero absorbance, then lower it exactly 1/4 of a turn further.
19. Turn on the vent and hood.
20. Make sure the waste line is connected properly.
a. Form a trap in the waste line. The loop should be about 4 inches in diameter and 12 inches below the burner. Fill the loop with water.
b. Connect one end of the waste line to the burner and submerge the other end beneath ~4 inches of water in a plastic container.
21. Install burner's safety interlock pin in the back of the burner compartment.
22. With the fuel toggle switch in the shut off position (parallel to panel), set the acetylene and air supply pressures to 12-14 psig for acetylene, 85 psig for air.
23. Rotate OXIDANT selector valve to AIR. Set the oxidant flow rate to ~55.
24. Open the fuel toggle switch and adjust fuel flow to 35.
25. Ignite gases by depressing the IGNITE button until the burner is lit. If nothing results, release button and press again. Hold button down for a few seconds.
26. Adjust flame to blue oxidizing flame rather than a white reducing flame.
27. Aspirate a solution with about 0.2 - 0.6 units of absorption.
28. Maximize the absorbance with the HORIZONTAL and ROTATIONAL adjust while aspirating sample.
29. Aspirate a standard.
30. Adjust the nebulizer by loosening the lock ring and turning the knurled knob counterclockwise until maximum absorption is obtained.
31. Tighten the lock ring.
32. Select an integration time by entering the desired value through the keypad and pressing the "t" key.
33. Set the MODE control to either HOLD or CONT. When HOLD is used the READ button must be pressed for each aspiration to read the solution absorbance. If CONT is selected. the system automatically reads the solution's absorbance.
34. Aspirate a blank solution and press the AZ key to autozero display.
35. Select absorption units by setting the SIGNAL switch to ABS.
36. Aspirate the sample.
37. Shutdown.
a. Aspirate pure water to clean burner head.
b. Turn FUEL toggle switch to OFF to extinguish the flame.
c. Close fuel and air access valves.
d. Open the FUEL toggle switch to clear fuel lines.
e. Turn flowmeter valves off and the FUEL toggle switch off.
f. Turn all controls fully counterclockwise and the power switch to OFF
g. Turn off vent and hood.
h. Remove tank of purified acetylene back to the lab.

TABLE 10 (continued)

Flame Emission Analysis by Atomic Absorption Spectrophotometer

Specifics for Ca, Mg, K, Na Analysis

Analyte	Calcium	Magnesiu	Potassium	Sodium*	
Wavelength	422.7 nm	285.5 nm	766.5 nm	589.0 nm	
Flame Type	Oxidizing	Oxidizing	Oxidizing	Oxidizing	
Oxident	Air	Air	Air	Air	
Fuel	Acetylene	Acetylene	Acetylene	Acetylene	
Head Rotation	90 °	Yes	Yes	Yes	if ext. range needed
Ionization Suppressant	0.1% K	0.1% K	0.1% Na *	0.1% K	
Optimum Range, ppm	0.5 - 50	5 - 500	1.0 - 50	0.5 - 10	
Detection Limit, ppm	0.001	0.05	0.003	0.0001	

* Because of the high sodium content of black liquor, no additive needed for anaylsis.

Make a series of 5 standards with a range of 0.10ppm to 10ppm for all but sodium to decide on best fit curve for analysis.

Make spike the equivalent of a mid-range standard, in most cases, 5ppm.

were analyzed within a short period of time in the interests of economy, since calibration only had to be done once for the series of analyses.

It can be noted that the optimum range for sodium is 1 to 50 ppm. Because of this, sodium analysis required very large dilutions of the sample with accompanying uncertainties in analysis due to the dilution. Therefore, after the ion selective electrode method had been developed and proven for sodium analysis, the ion selective electrode method was used to determine sodium concentrations in black liquor.

Details on analysis for iron ions are not included in Table 10. These were run on only a few liquors. The iron ion concentrations were so small that this analysis was not used routinely.

4.6 Analyses for Anions by Ion Chromatography. Analyses for sulfate, sulfite, thiosulfate, chloride, carbonate, oxalate, formate, acetate, propionate, and glycolate/lactate anions were made by using a Dionex 2000i chromatograph arranged in several configurations. The column combinations, eluents, regenerants, and method are described in detail in Table 11. Basically, the analyses are divided into two groups: strong anions and weak (mostly organic) anions.

For the strong anions (chloride, sulfate, thiosulfate, sulfite, and oxalate), a Dionex AS4A-SC strong anion column was used that was preceded by a AG4A guard column and a NG1 organic guard column. The eluent used was a solution of 1.7 mmolar $NaHCO_3$ and 1.8 mmolar Na_2CO_3. The eluent was passed through the instrument at a rate of about ml/minute. A 25 mmolar solution of H_2SO_4 was used for column regeneration and the column was stored in a 0.1 N solution of NaOH. Standards for each of the anions were prepared from sodium or potassium salts of the anions diluted to 1000 ppm in deionized and degassed water.

The organic anions were run with a Dionex AS1-ICE ion exclusion column and a NG1 guard column. The eluent used was a 1.0 mmolar solution of Hcl. The eluent was

TABLE 11	
Ion Chromatography by Dionex Chromatograph	
Reagents and Column Information:	
For chloride, sulfite, sulfate, oxalate and thiosulfate:	
Columns:	**Dionex AS4A-SC** solvent compatible strong anion column
	Dionex AG4A guard column
	Dionex NG1 organic guard column
Eluent:	**1.7mM $NaHCO_3$, 1.8mM Na_2CO_3:** Dissolve 0.5712 g of sodium bicarbonate
	and 0.7632 g of sodium carbonate in degassed water
	and dilute to 4 liters.
	(Dry chemicals in 105°C oven for 1 hour before using to
	make the solution.)
Storage Sol'n:	**0.1N NaOH:** Dilute 32.008 g 50% NaOH in 4 liters of degassed water.
Regenerant:	**25 mM H_2SO_4:** Dilute 25ml of 4N H_2SO_4 in 4 liters of degassed water.
Standards:	**1000ppm Chloride:** Dry KCl in 105°C oven for 1 hour. Dissolve 2.1023 g
	of KCl in degassed water. Dilute to 1 liter.
	1000ppm Sulfite: Dry Na_2SO_3 in 105°C oven for 1 hour. Dissolve 1.574 g
	of Na_2SO_3 in Formaldehyde Master Solution (1 ml 37%
	Formaldehyde in 1 liter of degassed water). Dilute to 1 liter.
	1000ppm Sulfate: Dry Na_2SO_4 in 105°C oven for 1 hour. Dissolve 1.479 g
	of Na_2SO_4 in degassed water. Dilute to 1 liter.
	1000ppm Oxalate: Dry $Na_2C_2O_4$ in 105°C oven for 1 hour. Dissolve
	1.522 g of $Na_2C_2O_4$ in degassed water. Dilute to 1 liter.
	1000ppm Thiosulfate: Dry $Na_2S_2O_3$ in 105°C oven for 1 hour.
	Dissolve 1.410 g of $Na_2S_2O_3$ in degassed water. Dilute to 1 liter.
For lactate, formate, acetate, and carbonate:	
Columns:	**AS1-ICE** ion exclusion column for organics
	NG1 organic guard column
Eluent:	**1.0 mM HCl:** Dilute 40.2 ml of 0.1N HCl to 4 liters with degassed water.
Storage Sol'n:	**5.0 mM HCl:** Dilute 40.2 ml of 0.5N HCl to 4 liters with degassed water.
Regenerant:	**5.0 mM TBAOH:** Dilute 10 ml of 55% TBAOH to 4 liters with degassed water.
Standards:	**1000ppm Acetate:** Dilute 1 ml of Glacial Acetic Acid in 1 liter of
	degassed water.
	1000ppm Formate: Dilute 1 ml of Formic Acid in 1 liter degassed water.
	1000ppm Lactate: Add 1.176 g of 85% Lactic Acid to degassed water.
	Dilute to 1 liter.
	1000ppm Glycolate: Add 1.000 g of Glycolic Acid to degassed water.
	Dilute to 1 liter.
	1000ppm Carbonate: Dry Na_2CO_3 in 105° oven for 1 hour.
	Dissolve 1.767 g of Na_2CO_3 in degassed water. Dilute to 1 liter.
Carbonate can also be run on the **AS1-ICE** column using **degassed water** as an eluent.	

TABLE 11 (continued)	
Ion Chromatography by Dionex Chromatograph	
Standarization Procedure:	
1	Prepare any solutions that need to be made.
2	Prepare deoxygenated water for sample dilutions.
3	Install columns and load eluent and regenerant solutions in reservoirs.
3	Turn on compressed air tank.
4	Set instrument to run either organics or strong anions.
5	Open valve to pressurize the proper regenerant solution for the analysis.
5	Set instrument to run either organics or strong anions.
6	Allow instrument to run with regenerant solution until a stable baseline
	is reached.
7	Stop regenerant flow. Start eluent flow at the proper elution rate.
	Wait until a stable base line is established.
8	Dilute a portion of the standard solution to about 50 ppm. Use a 22μm
	membrane filter and inject the dilute standard solution. Record the
	elution time for the peak. Repeat for each standard solution.
9	Make a mixed standard of all analytes of interest from the 1000ppm solutions
	by pipetting 10ml of each solution into a clean flask.
10	Prepare serial dilutions of 4 or more mixed working standards from the mixed
	standard solution for establishing a calibration curve for each unknown.
11	Regenerate columns. Start proper eluent flow. Establish base line.
	Use a 0.22mm membrane filter and inject a working standard. Measure the
	peak heights and peak areas. Note the elution times.
12	Calculate regression relations for peak height and peak area as a function of
	of concentration for each ion standard. Regression coefficients should be
	0.998 or better. Use peak height calibration relation for analysis if
	coefficient is greater than 0.998. Otherwise. use peak area
	calibration relation.

TABLE 11 (continued)	
Ion Chromatography by Dionex Chromatograph	
Analysis Procedure:	
1	Prepare any solutions that need to be made.
2	Prepare deoxygenated water for sample dilutions.
3	Turn on compressed air tank.
4	Open valve to pressurize the proper regenerant solution for the analysis.
5	Set instrument to run either organics or strong anions.
6	Allow instrument to run until a stable baseline is reached.
7	Stop regenerant flow. Start eluent flow at the proper elution rate.
	Wait until a stable base line is established.
8	The % solids of the unknown sample must be known accurately. Weigh out
	an aliquot of the unknown sample for which the % solids is known accurately
	and dilute the weighed sample in deionized water so that the estimated
	concentration of ion or ions is within the range of the calibration relations.
9	For sulfite analysis. add 0.5 ml of 37% Formaldehyde to the dilution before
	analysis.
10	Stop regenerant flow. Start eluent flow at the proper elution rate.
	Wait until a stable base line is established.
11	Use a 0.22μm membrane filter and inject sample.
12	Record peak heights and peak areas. Calculate ion concentrations from
	calibration relations.
TAPPI Method T 699 om-87	

through the instrument at about 1 ml/min. A 5 mmolar solution of TBAOH was used for regeneration and the column was stored in a 5 mmolar solution of HCl. Standards were prepared from 1000 ppm solutions of the organic acids in deionized and degassed water.

Carbonate anion concentration was determined with the Dionex 2000i with the set up and eluent used for organic anion analyses described above. However, carbonate anion concentration could also be determined with the AS1-ICE column using deionized degassed water as the diluent. The latter set up is preferred, because it gives a sharper peak, even though a third ion chromatographic run is required for complete analysis.

Specific details for operation are also given in Table 11. All methods are similar. Calibrations for each ion set were performed by preparing a mixed standard from the standard 1000 ppm solutions of each anion volumetrically. This mixed standard was diluted with deionized degassed water to prepare a series of mixed standards at 3 to 5 different concentrations. It should be noted that the sulfite standard contained formaldehyde to prevent oxidation. The unit was set for either strong anion or ICE operation with the appropriate eluent and the unit operated until a stable baseline was established. The standard was then injected through a 0.22 micron membrane filter into the instrument and the chromatogram determined . This was repeated for the other concentrations of the standard solution. The peak heights were correlated as a function of the concentration of the anion in the solutions. It was found that peak heights gave as good an analysis as peak areas and peak heights are easier to use. The regression line was sometimes slightly non-liner, but 5 standardizations were sufficient to yield a calibration curve with a correlation coefficient greater than 0.997.

Black liquors were run to analyze for the anions by diluting the liquor with deionized degassed water gravimetrically to 0.05% solids or less. A single analysis required three separate chromatographic runs as described above. Usually, analyses were run in duplicate or triplicate for each liquor.

Ion chromatography has proven to be a convenient, accurate, and reliable method for determining anion concentrations in our experimental black liquors as well as in many mill liquors from kraft, sulfite, carbonate, and semichemical pulping.

It should be noted that this method described is only a minor variation of the TAPPI standard method. TAPPI Method T 699 cm-87 , that has been widely adopted by the pulping industry for white liquor, green liquor, and black liquor analyses.

4.7 Lignin Analysis in Black Liquor by UV-Visible Analysis. Analysis for lignin by UV-visible spectrophotometry is not new, but the analysis has been studied extensively in this work and the analysis improved (Dong, 1992). The basic instrument used was a Perkin-Elmer Lambda 4C dual beam spectrophotometer with a TAC7 Perkin- Elmer System 7 control system. The instrument was equipped for thermostatting the measurement cell. Details for the method and other facts are given in Table 12.

Extensive studies were performed using lignins isolated from softwood and hardwood kraft lignins that had been purified and characterized for molecular weights by techniques described later in this report. These lignins were used to determine the effects of solution pH, lignin concentration, lignin molecular weight, wood source, measurement temperature, and contaminating ion concentration on the UV-visible spectra of kraft lignins (Dong, 1991). It was found that the intensity of the absorption spectra is sensitive to pH below a pH of 13, but not at a ph of 13 or higher. The effect of temperature on absorption intensity was found to be a weak linear function of temperature; therefore, the measurement temperature was standardized at 25.0C.

The absorption at 280 nm was found to be in a plateau region for softwood kraft lignins and in a region with a slight slope for hardwood kraft lignins. The extinction coefficient was most linear at 280 nm as a function of lignin concentration for both softwood and hardwood. The extinction coefficient at 280-300 nm for softwood kraft lignins at pH 13 is slightly affected by the molecular weights of the lignins, which were

TABLE 12

Lignin Analysis by UV-Visible Spectral Absorption

Lignin Analysis by UV-Visible Using Perkin-Elmer Lambda 4C Dual Beam System 7 Analyzer

1	Use a quantity of liquor or lignin sample that yields about 0.15 grams of solids in the stock solution of 50 ml.
2	Dissolve or dilute the sample with 0.1N NaOH to make the stock solution of 50 ml.
3	For solution #1, pipet 1ml of stock solution into a 50ml volumetric flask, and add 0.1N NaOH to give total volume of 50 ml.
4	For solution #2, pipet 2ml of stock solution into a 50ml volumetric flask, and add 0.1N NaOHto give total volume of 50 ml.
5	Use these two samples for UV-Visible analysis as "dilution #1" and "dilution #2", and use the 0.1N NaOH as the blank reference.
6	Turn on the circulator and allow cell to come to thermal equilibrium.
7	Insure that the sample compartment of the instrument is empty before beginning.
8	In this order, turn on UV-vis (instrument), TAC7 controller (bottom shelf), plotter, then computer.
9	At caret prompt, type: **idris**, hit **enter** key.
10	At **login:** prompt, type: **cuv**, hit **enter** key.
11	At prompt **Ready for Next Command**, press **Shift** and **Instrument** keys simultaneously.
12	After a short time, the **Lambda 4C Spectrophotometer** menu page should appear.
13	If it does not, shutdown system, following protocol, and repeat startup.
14	Select **Enhanced Scan by moving the cursor bar** with arrow key.
15	Press soft key **Wave Cal** to recalibrate the deuterium line.
16	Press soft key **Scan** to set parameters for analysis.
17	Using the cursor bar with arrows, select each parameter with a soft key and set the following:
	Abs
	0.000/ 1.000
	190.0/ 900.0 nm
	60 nm/min
	0.25
	3
18	Press **Shift** key and **Background Corr** key simultaneously to run background correction.
19	Press **Menu** key and select **Wlpg** to set the following parameters:
	Abs
	0.25
	8
	Off
20	Set **Wave 1** to 280nm.
21	Insert dilution #1 into holder. The reference sample loads into the back slot and unknown sample into the front slot.
22	Press **Run**. Each measurement is repeated 3 times, and the results are averaged and reported.
23	Repeat procedure for dilution #2.

Calculation	1.	L1 = (Abs(#1) x 10.54) / g solids in stock
	2.	L2 = (Abs(#2) x 5.27) / g solids in stock
	3.	lignin, g/g = (L1 + L2) / 2

determined by methods to be described later, and by the presence of impurities in the lignins. The impurities in the purified lignins were determined by dissolving the lignin in NaOH solution or KOH solution and determining the concentrations of impurities by the methods described above for analyzing black liquor. Some results of these analyses are given in Table 13.

Typically, the purified lignins used for defining the UV-visible analytical method contained 4.4 to 5.4 wt % of impurities. Solutions of these impurities in a pH 7 media were made and run to determine the absorption at different wave lengths at different total concentrations. These were used to correct the extinction coefficients for lignin. The extinction coefficient for lignin, corrected for impurities, at 25C ranged from 23.5 to 24.2 $(gm\text{-}cm)^{-1}$ for softwood kraft lignins over a weight average molecular weight range of 14,000 to 48,300 with no apparent trend. The average extinction coefficient for lignin at 25C in a pH 13 solution was determined to be 23.7 $(gm\text{-}cm)^{-1}$ for lignin solutions of concentrations below 0.08 wt % lignin. Above a concentration of 0.08 wt %, the absorption became non-linear and total extinction at 280 nm was rapidly approached with increasing concentration.

This method was used to determine the concentration of lignin directly in black liquor by using the extinction coefficient determined as explained above and by measuring the corrected absorption of a black liquor of known solids concentration that had been adjusted to a pH of 13 and diluted to a lignin concentration below 0.05 wt %. As will be explained later, there is every reason to believe that this gives a measurement of the total lignin in the black liquor, even though the extinction coefficient and correction were developed by using purified lignins of high molecular weight.

The method for analysis of lignin in black liquor is given in detail in Table 13. It should be noted that the preferred technique is to perform the analysis using a sample that had been freeze dried to 100 % solids. The freeze drying technique and the reasons for freeze drying are explained later in this report. The dried sample is dissolved in 0.1 N

TABLE 13

Extinction Coefficients for Slash Pine Kraft Lignins of Different Molecular Weights

Using the procedure described in Table12, the extinction coefficients for absorption by lignin were determined for the effects of molecular weight, solution pH, and temperature.

The results for 25C are as follows:

	Lignin	Sample	#2	#4	#16	#9	#1	Average
Molecular	Mw	Dalton	14000	17200	21500	48300	39000	
Weight	Mn	Dalton	2380	4170	6090	4060	2250	
(Dalton)	Mw/Mn		5.9	4.1	3.5	11.9	17.3	
	pH	avelength						
Extinction	13	280	22.6	22.4	22.9	22.5	22.7	22.6
Coefficient	13	290	22.8	22.4	23.2	22.8	22.8	22.8
(1/gm.c	13	300	21.6	21.5	22.3	21.7	21.6	21.7
	12	280		21.7	22.4			
	12	290		21.1	22.4			
	12	300		19	20.8			
Corrected	**13**	**280**	**23.7**	**23.5**	**24.2**	**23.6**	**23.7**	**23.7**
Extinction	13	290	23.9	23.5	24.5	23.9	23.8	23.9
Coefficient	13	300	22.6	22.5	23.6	22.8	22.6	22.8
(1/gm.cm)	12	280		22.8	23.7			
	12	290		22.2	23.7			
	12	300		20	22			

Chemical Analysis of Purified Lignin to Correct the Extinction Coefficient

The lignins used for establishing the extinction coefficient were analyzed for impurities and the extinction coefficient was corrected on a weight basis.

The average corrected lignin extinction coefficient of 23.7 (l/gm.cm) at 280nm was selected for use.

Note that for the corrected extinction coefficient, the pH must be 13 or higher and the lignin concentration must be less than 0.08 g/ml to ensure accuracy of the measurement and calculation.

The analysis results were:

Lignin Sample			#2	#4	#16	#1	#9
		Impurities					
Inorganic		Sulfite	0.32	0.42	0.6	0.35	0.36
Ions		Sulfate	0.25	0.24	0.27	0.15	0.22
(wt%)		% Sulphur	1.13	1.22	1.19	1.52	0.95
	Subtotal		1.7	1.88	2.06	2.02	1.53
Organic	Lactate/glycolate		0.8	0.75	1.03	0.63	0.83
Species		Formate	1.34	1.18	1.26	1.03	1.42
(wt%)		Oxalate	0.07	0.1	0.13	0.04	0.11
		Acetate	0.71	0.66	0.91	0.63	0.86
	Subtotal		2.92	2.69	3.33	2.33	3.22
Metal		Calcium	73.5	68.7	49.8	65.7	68.6
Ions		Potassiu	80	103	49.1	44.2	80.2
(ppm)		Magnesiu	5.1	<5	<5	21.6	<5
		Sodium	260	316	233	136	219
Total Impurities (wt%)			4.64	4.62	5.42	4.38	4.79

NaOH solution and then two solutions at different concentrations are prepared such that the concentration of the more concentrated one is twice that of the other. 0.1 N NaOH is used as a reference in one side of the cell and the unknown solution is placed in the other side. The spectra is scanned from 190 to 900 nm at a scan speed of 60 nm/minute in the absorption mode. The wave is set at 280 nm and the sample is run at a slit width of 0.25. The measurement is repeated three times and results averaged. This is repeated for the other concentration of the solution of the unknown. The lignin content of the black liquor in terms of gms/gm of solids is calculated as outlined in Table 12.

This method appears to be the most reliable and convenient method available for direct quantitative determination of lignin concentration in kraft black liquors, and the studies done as described appear to establish the validity of the method.

4.8 Freeze Drying. Freeze drying was used to obtain samples of black liquor at 100% solids concentration and of lignins at complete dryness as the only method that could be used to obtain such samples for study without decomposition or change of the liquor solids. Other methods, such as vacuum drying, produced non-reproducible samples that were of little use. Some vacuum dried samples were essentially totally insoluble, even in strong caustic solutions, which indicated that these had undergone radical transformation during the drying process.

Massee(1984) discovered that kraft black liquors do not exhibit freezing at solids concentrations above about 42%, but undergo a transformation to a glass. Furthermore, the transition temperatures change drastically with concentration. Massee (1987) demonstrated that this is general behavior for polymer solutions of both polar and nonpolar polymers. Since the diffusion rate through glasses is very slow as compared to the diffusion rate through solutions, and since this rate can be increased substantially only by raising the temperature above the glass transition point, it is clear that any drying process that depends upon continued concentration from the solution can lead to

conditions that promote drastic changes in the material being dried. Freeze drying was attempted as a alternative drying process that could eliminate this problem.

In freeze drying, the solution temperature is lowered and the solvent frozen. Upon freezing, the solvent separates as a crystalline solid from the solute or non-volatile material. The frozen mass is then subjected to very low pressure to remove the crystalline solvent from the material by sublimation. Since the frozen mass is a two phase substance. the solvent does not have to diffuse through the non-volatile material to be removed from the mass, and a completely dry sample of the non-volatile components can be obtained without chemical or irreversible physical changes in the non-volatiles. Black liquors were freeze dried using various starting concentrations and slightly different drying conditions for varying amounts of drying times after freezing. The result was that identical dried samples were obtained and that these did not exhibit the effects of the irreversible changes observed with vacuum or oven drying. Therefore. freeze drying was adopted as the process for obtaining samples of black liquors at 100% solids concentrations and for obtaining dry lignin samples for properties studies.

A Labconco Model 8 freeze drier was used in this work. Details of the procedures and techniques used to produce freeze dried samples of black liquor solids or of lignin are given in Table 14. As noted, it is necessary that the liquor be cooled to below the freezing point of the liquor (about -40C at about 30% solids concentration) and frozen before the vacuum is turned on. This permits the water to be transformed into ice that separates from the liquor solids as finely divided crystals. Vacuum must be applied carefully during the early stages, since sublimation can be quite rapid during the early stages of vacuum drying, causing the frozen mass to swell rapidly and erupt. The vacuum is gradually lowered to an absolute pressure of 40 microns of Hg.

This usually requires about 1-1 1/2 hours. after which the drying is continued for an extended period of time. Usually, drying was continued for several days. The dried sample was removed from the drier, scraped from the containers, ground in a dry box, and

TABLE 14

Procedure for Freeze Drying Samples

A Labconco Model 8 Freeze Drier was used in this work.
To prevent glass formation and to freeze a black liquor at temperatures above -15C. one must begin with <30% solids liquor. Lignins must be dried partially, removed from the drier, ground, and then returned to the drier to complete drying.

1. Place 30-50 gms of <30% solids liquor (or 20-30 gms of wet lignin) into 6-7 in. dia. Petri dishes.
2. Set each dish on a separate platform in the "pot" of the freeze dryer.
3. Replace the glass lid to the pot and make sure all valves are closed.
4. Drain the condenser unit, and turn on the refrigeration switch of the freeze dryer.
5. Let the temperature fall to -40°C. Turn on the vacuum pump.
6. Check to see if the pressure is falling. If it isn't, apply pressure to the Plexiglas door on the freeze dryer until the door seals. The rubber seal will look darker where it is sealed.
7. Next, check the rubber valves on the pot. If you find suction on any valve, gently adjust the valve until the valve seals.
8. Finally, apply pressure to the glass lid on the top of the pot. Watch the surface of the liquor on the top shelf. As the pressure begins to fall, the liquor will degas rapidly, causing spattering and loss of sample if the pressure is lowered too rapidly. Minimize this by lowering the pressure very slowly.
9. The pressure must fall to within the green range of the pressure scale over a period of about an hour. If it does not, release the vacuum slowly, and repeat steps 3 through 8.
10. Continue drying for 2-3 days, checking the system periodically.
11. At the end of the drying period, release the vacuum slowly by opening one of the valves on the pot.
12. Turn off the vacuum pump, then turn off the refrigeration unit, drain the condenser unit.
12. Remove the Petri dishes from the drier and place in a gloved dry box.
13. Clean the freeze dryer and check the vacuum pump oil.
14. Remove the sample from the dish, grind to a fine powder, and place the ground sample in a 30ml vial with a rubber lid.
15. Remove the sample vial from the dry box, remove the lid, quickly cover the top with a Kemwipe secured with a small rubber band, and place the vial in a freeze beaker located on the outside of the drier pot.
16. Repeat steps 3-12.
17. Remove the vial, place in a dessicator and allow to warm to room temperature.
18. Remove the vial, seal, and store for use.

* It requires about 7 days to prepare a freeze dried sample, but the drier can be used easily to dry up to 6 samples simultaneously. Lignin and 100% black liquor solids are highly hydroscopic; therefore, care must be exercised to maintain them in tightly sealed containers.

* The freeze dried black liquor solids and lignins were always free flowing powders that were completely soluble in 0.1N NaOH.

the dried sample reloaded into a freeze drier vial. This was reconnected to the freeze drier and drying continued for another 1-2 days.

The dried sample was the removed from the vial, allowed to warm in a desiccator, and then packaged in a dried, sealed container for storage. The procedure outlined in detail was time consuming, but easily conducted with a little practice, and produced completely dry samples of black liquor and of lignin for use in further studies.

5.0 LIGNIN CHARACTERIZATION

Since lignin is a predominant component of black liquor solids and since it was suspected that lignin affected black liquor behavior substantially, particularly at higher solids concentration, a great deal of effort was devoted to separating lignin from black liquor and in purifying the separated lignin in order to characterize the lignin polymeric nature. Also, the lignins were used in studies to determine the UV-Visible spectra, the solution viscosity behavior, and the thermal behavior of this component of black liquor.

Lignin separation and purification studies by acid precipitation were studied in detail in previous work and results of these studies were reported (Kim, 1987, Dong, 1992). During the current work, we repeated much of the earlier study and extended the work to improve separation and purification. The purified lignins were characterized with respect to weight average molecular weight, number average molecular weight, and molecular weight distribution. A number of the lignins were studied in greater detail. Glass transition behavior, the effects of diluents on glass transition behavior, the rheological properties of very concentrated lignin solutions, the viscosity behavior of dilute lignin solutions, the optical properties of dilute lignin solutions, and the surface characteristics of precipitated lignin were all studied in order to try to understand the nature of kraft lignin.

5.1 Lignin Separation and Purification. Lignin was separated from black liquors that had been soap skimmed to remove soap as previously described in the section on pilot scale evaporation. The lignins were precipitated with acid and the precipitate washed, redissolved in caustic, filtered, reprecipitated, washed, dried, extracted, and dried. The final product was not affected by the type of acid used; sulfuric, nitric, and hydrochloric acids yielded exactly the same results. The treatment necessary to separate and purify lignin is drastic and extensive; about 70-75% of the lignin in black liquor can be precipitated and isolated in a purified form by the procedures that we developed. The procedure that we adopted is described in Table 15.

TABLE 15

Lignin Purification:

1. Dilute enough sample to yield 450 ml of ~10% solids and a pH of ~13.
2. Filter through a glass fiber filter to exclude fibers and particulates.
3. Titrate filtered liquor sample with 1.0N H_2SO_4 at a rate of 2 +/- 0.5 ml/min to a final pH of 2.0 with continuous stirring.
4. Centrifuge the slurry and decant the supernate.
5. Wash the remaining lignin with 700ml deionized water, centrifuge and decant the supernate.
6. Redissolve the precipitated lignin in 0.1N NaOH and adjust the pH to 13 to assure that the lignin is fully dissolved before proceeding.
7. Filter through a filter paper to remove any insoluble substances. A white precipitate that is nearly all sulfur is removed in this step.
8. Titrate filtered lignin sample with 1.0N H_2SO_4 at a rate of 2.5 +/- 0.5 ml/min to a final pH of 2.0 with continuos stirring.
9. Centrifuge slurry and decant the supernate.
10. Wash and centrifuge the re-precipitated lignin with 700ml deionized water once, with 0.01N H_2SO_4 twice, and deionized water three more times using about 700ml of liquid each time and centrifuging sample between washings.
11. Freeze dry the washed lignin sample.
12. Extract the dried lignin with hexane in a Sohxlote apparatus to reduce organic impurities, decant, flush with pentane, and freeze dry.

Note: In analyzing black liquor for lignin content, each of the washings are saved and analyzed to give a total % lignin found. 20 to 30% of the total lignin components in black liquor remain in solution in the acidified liquors and washings.

A sample of the skimmed black liquor of known solids and lignin concentration was diluted to about 10% solids and the pH adjusted to about 13, if necessary. This was filtered through a 2 micron glass fretted filter to remove any fibrous material or particulates. The filtered liquor was titrated with 1.0 N sulfuric acid at a controlled rate of acid addition to a final pH of 2.0. Titration to a lower pH did not increase the amount of lignin precipitated, which was surprising. The rate of acid addition was found to be very important in controlling the particle size of the precipitate and in affecting the content of organic contaminants. The best rate is 0.5 to 2 ml/min of acid addition to about 450 ml of 10% solids concentration liquor.

The precipitate was separated from the slurry by centrifugation. Direct filtration was very difficult, because the particulates were very fine and quite compressible. The centrifuged mass was decanted and the supernate collected and weighed. The lignin content of the supernate was determined by UV-Visible analysis as described previously. The precipitate was mixed thoroughly with 700 ml of deionized water, centrifuged, and the supernate collected and weighed. The lignin content of the supernate was determined by UV-Visible analysis as previously described. In a few cases, this lignin was freeze dried, extracted as will be described, freeze dried, and analyzed. The lignin contained considerable impurities, especially sulfur, even when the lignin had been precipitated with hydrochloric or nitric acid.

The precipitated and washed lignin was redissolved in 0.1 N sodium hydroxide and the pH adjusted to about 13 with stirring. Stirring was continued for a considerable time, 20 minutes or longer. The solution was filtered through a fine filter paper and a finely divided precipitate removed. The precipitate was always white and was primarily sulfur. This precipitate was about 1 to 1.5% of the mass of the lignin precipitated in the first step. One should note that this sulfur was in solution on the original black liquor and precipitated with the lignin, but was not soluble in a solution at a pH of 13 after the lignin was

redissolved. Furthermore, this sulfur precipitate occurred even when the lignin was precipitated with nitric or hydrochloric acid. It appears that it was associated strongly with the lignin.

The redissolved lignin solution of about 500 ml was again titrated with 1.0 N sulfuric acid to a pH of 2.0 at a rate of 0.5 to 2.0 ml/min with stirring. The titrated solution was stirred for an additional 10-15 minutes. The slurry was centrifuged as before and the supernate collected, weighed, and analyzed for lignin concentration by UV-Visible.

The centrifuged lignin was subjected to a number of washes with deionized water and dilute sulfuric acid. The sequence and number of washes, as well as the quantity of wash liquid used, were the result of extensive trails to maximize the lignin recovery and minimize the content of impurities in the final product. Again, the type of strong acid used did not affect the final result, so sulfuric acid was used. The centrifuged lignin was washed with 700 ml of deionized water and recentrifuged. The supernate was collected, weighed and analyzed for lignin as before. The centrifuged lignin was then washed twice with 700 ml of 0.01N sulfuric acid, centrifuging after each wash, and collecting each supernate for weighing and analysis for lignin as before. The centrifuged lignin was then washed three times with 700 ml of deionized water for each wash. The supernates were collected for weighing and lignin analysis as before. This reprecipitated and thoroughly washed lignin was freeze dried by the method described previously. It is important to note the freeze drying <u>is essential</u>. A freeze dried lignin is completely soluble at pH 11.5 or higher. A vacuum dried lignin is not completely soluble, even at pH 13. This is strong evidence that heating produces irreversible association in lignin.

The freeze dried lignin was then extracted for 12-24 hours with hexane in a Sohxlet apparatus to remove as much of the organic impurities as possible. The hexane used was weighed and analyzed for lignin. A number of solvents were tested. Hexane was found to be the best extractant for the organics, and lignin is virtually insoluble in

hexane. The extracted lignin was freeze dried, weighed, sealed in a dark container, and stored for use.

As stated previously, about 70-75% of the lignin in the black liquor solids, as identified by UV-Visible analysis of the black liquor, was recovered as purified precipitated lignin. The recovery depended upon the original liquor composition and the average molecular weights of the lignin. A material balance over the entire purification process, using the UV-Visible analyses results as a basis, typically yielded a very good closure (99.8% or better, overall). This gives one confidence in the UV-Visible analysis results and allows us to determine the route of the lignin during the purification process. Almost all of the unrecovered lignin (more than 95%) does not precipitate at all, even at a pH of 1.0. These species must be very small molecular weight fragments from the pulping process. Almost all of the remainder of the unrecovered lignin is lost in the in the first washing step with some loss after redissolving and reprecipitation. The final six washing steps result in a combined loss of less than 0.5% of the unrecovered lignin with an exponentially decreasing loss with each step, as one would expect. Washing was stopped after three final deionized water washes, because there was virtually no further decrease in impurities.

It appears that polymeric lignin affects the properties of black liquor significantly. Therefore, even though only 70-75% of the material that was identified as lignin in black liquor was recovered as a higher molecular weight material, this material was extensively characterized, since this higher molecular weight material should dominate the effects of lignin on most properties.

The purified lignin was a free flowing, finely divided powder that varied in color from a light tan to a deep brown color. None of the purified lignins were black.

Typically, the purified lignins contained 94.5-96+% lignin with an estimated 1-1.5% additional identified as sulfur toghtly bound to the lignin, and they were completely soluble in sodium hydroxide solution at pH 11.5 or higher at room temperature.

5.2 Weight Average Molecular Weight by Low Angle Laser Light Scattering (LALLS). Weight average molecular weights of the purified lignins were determined by LALLS. Basically, the method used was that developed in earlier work (Kim, 1986). However, improvements (Dong, 1992) were made in the method and studies were performed to demonstrate that the weight average molecular weight determined was a true weight average molecular weight. This was done by determining the molecular weight of the same lignin using very different solvents and comparing the results, which was done for a number of lignins. The solvents used were dimethyl formamide (DMF), pyridine, and 0.1 N sodium hydroxide. In all cases, measurements were made at temperatures above the Flory temperature for the solvent.

The base solution preparation is very important. This procedure for preparing a base solution of lignin in 0.1 N sodium hydroxide , along with other parts of the total procedure used, is described in Table 16. The 0.1 N sodium hydroxide solution was prepared using the best analytical grade of NaOH and HPLC grade water purchased from Optima Corporation. The prepared 0.1 N sodium hydroxide solution was filtered through a 0.45 micron filter. The purified lignin was redried overnight. A weighed portion of the lignin was dissolved in the 0.1 N sodium hydroxide solution to yield 100 ml of solution containing 0.003 gm/ml of lignin. After 24 hours, this solution was filtered through a 0.45 micron filter and stored in a volumetric flask for use. This solution was called the "stock solution".

More dilute solutions for use in analysis were prepared from this stock solution by diluting aliquots of it with the 0.1 N sodium hydroxide solution to produce five solutions with concentrations ranging from 0.0006 to 0.003 gm/ml. Solutions in DMF and pyridine were prepared in exactly the same way, except that ACS analytical grade DMF or pyridine

TABLE 16

Weight Average Molecular Weight of Lignin by Low Angle Laser Light Scattering Spectophotometry, Differential Refractive Index, and Sample Preparation

A Chromatix KMX-6 instrument capable of operation at up to 150C and equipped with a Harvard Syringe pump was used for scattering measurements. a Chromatix KMX-16 instrument capable of operation up to 150C was used for differential refractive index measurements, and the Perkin-Elmer Lambda 4C dual beam UV-Visible analyzer was used for light absorption measurements. Measurements were made using three different solvents: pyridine, dimethylformamide(DMF), and 0.1N NaOH. All measurements were made at temperatures above the Theta Temperature for the particular solvent. M_W determinations of an optically active and asorbing polymer such as lignin require precise measurements of refractive index, absorption, flourescence, polarization, and scattering at the same wave length and temperature. Also, solution preparation is important.

Solvent Descripton and Preparation:

Three different solutions were used for lignin M_W measurements. The solvents used and the solution preparation procedures are as follows:

Solvents and Filtering:

Pyridine - ACS grade, filtered through a 0.45µm Millipore Teflon membrane

DMF - ACS grade, filtered through a 0.45µm Millipore Teflon membrane

0.1 N NaOH solution using HPLC grade Optima water, filtered through a 0.45µm Gelman Nylaflo membrane filter.

Solution Preparation:

1. Place ~2 grams of dried lignin in a glass vial with thin filter paper over top of vial.
2. Freeze dry overnight.
3. For NaOH solution, prepare 0.1N NaOH solution by mixing 16 grams of 50% by weight NaOH solution in 2 liters of Optima water, filter, and seal.
4. Prepare a lignin "stock" solution for each solvent at a concentration of 0.003g/ml (0.300g/100ml) in volumetric flasks. Let the "stock" solution sit overnight.
5. Filter the "stock"solution through a 0.45µm syringe filter, seal, and store.
6. Prepare 25-50 ml of each of five dilute solutions from the "stock" solution accoring to the following Dilution Table:

Dilution Table

Dilution	#1	#2	#3	#4	#5
Stock Solution (ml)	5	10	15	20	50
Pure Solvent (ml)	20	15	10	5	0
Total Volume (ml)	25	25	25	25	50
g Lignin / 25ml sol'n	0.015	0.03	0.045	0.06	0.075
mg Lignin / ml sol'n	0.6	1.2	1.8	2.4	3

7. Seal in Volumetric Flasks and Store for use in a dark place.

These dilute solutions are used for measurements. It is extremely important that dilutions be done carefully and accurately if accurate M_W measurements are to result.

Light Absorbance Measurements:

Lignin is extremely light absorbant. Therefore, measurements of absorbancy as a function of concentration must be made at the same temperature and wave length used for light scattering measurements.

The Lambda 4C dual beam UV-Visible Spectrometer was used for these measurements. Cells for the Lambda 4C were cleaned thoughly. The temperature for the circulating bath used to control the temperature of the cell was allowed to reach a steady state at the desired temperature for measurement, the cell with the solution was inserted and allowed to attain thermal equilibrium, and absorbance measurements were made using the procedure detailed in TABLE 12. This was repeated for a number of concentrations, and the absorbancy correlated to concentration and wave length.

TABLE 16 (continued)

Weight Average Molecular Weight of Lignin by Low Angle Laser Light Scattering Spectophotometry, Differential Refractive Index, and Sample Preparation

Differential Refractive Index Measurements:

The differential refractive index, the rate of change of refractive index of the solution with respect to concentration at constant temperature and wave length, must be very precisely determined, since this quantity enters into the calculation of the Rayleigh factor to the fourth power. The KMX-16 DRI was used for this measurement. This instrument is equipped with a red line laser identical to the one used in the KMX-6 for scattering measurements and it accepts a partitioned cell that can be rotated to vary the path length through solvent and solution to determine refractive index as a function of concentration by making measurements at various cell cell angles using one solution. the differential refractive index can be determined easily to six significant figures with this instrument if the solution concentration is known accurately.

1 The instrument calibration was checked periodically using solvents and certified solutions of known refractive index.

2 The circulating temperature bath was turned on and allowed to reach steady state at the temperature to be used for measurement.

3 The solution and the solvent were loaded into the cell compartments, the cell placed in the instrument, and the cell allowed to reach thermal equilibrium.

4 The laser beam was directed through the cells to the detecter, the cell rotated to a number of set angles, and measurements made at each angle.

5 The measurements were correlated to relate refractive index to solution concentration. The linearity of this relation was checked. The derivative of the relation was determined and used as the differential refractive index relation. Normally, the relation was linear for the solvents used.

6 Because of the importance of this quantity for light scattering analysis, the measurement was replicated 3 to 5 times. All data were used to establish the final value(s) of differential refractive index used for light scattering analysis to determine M_W.

TABLE 16 (continued)

Weight Average Molecular Weight of Lignin by Low Angle Laser Light Scattering Spectophotometry, Differential Refractive Index, and Sample Preparation

KMX-6 - Light Scattering for Molecular Weight Determination:

The Chromatix KMX-6 is a low angle laser light scattering photometer (LALLS) with a 2 mW Helium-Neon laser as a monochromatic light source with a wave length of 632.8 nm. The instrument is equipped with a set of auxiliaries consisting of a 632.8nm narrow band filter, a set in incident beam attenuators, a polarizing analyzer, and a thermostatted sample cell designed for flow of the solution through the cell. Scattered light is measured by a photomultipier that measures light collected in an annulus at a solid angle of 4-6 degrees to the incident beam. Therefore, the effect of the conformation of the solute molecule in solution on scattering intensity is negligible. If accurate measurements of differential refractive index and light absorbance for the solution are available (procedures for measurements of these have been detailed above), this instrument can be used to determine the scattering, polarization, and flourescence of the solution as a function of concentration that are needed to determine M_W of the solute from first principles.

Calibration of the Photomultipier:

1. The effect of the attentuating filter combinations on the incident beam must be checked periodically. This must be done as a first step to relate photomultiplier readings to the incident beam intensity; ie., to determine I_θ/I_0 where I_θ is the scattered beam intensity and I_0 is the inciden beam intensity.

1a. Insure that the P_0 attentuator is in place. All readings must be made with the P_0 in place to prevent damage to the photomultiplier.

NOTE: The measurement of the transmittance of # 4 requires special precautions to avoid damage to the photomultiplier. ALWAYS make sure the other four attenuators are in the beam before removing the # 4 attenuator. An Allen wrench can be used to swing the #4 attenuator out of the beam path via the socket head screw below the annulus wheel. It is spring loaded and will automatically return to its normal position when released.

2a. The attenuators are used in combinations and readings taken. A procedure for combinations and settings for the attenuators with an example of results is as follows:

Attenuator Calibration Procedure:

Attenuator	Combination Set to 1.000	Combination for Reading	Results (example)
1	C, 4	1, C, 4	0.2435
2	1, 4, C	2, 4, C	0.2625
3	1, 2, 4	3, 4	0.255
4	1, 2, 3, 4	4, C	0.2495

Each of the attenuators should be read in triplicate and the results for each averaged. The averaged results for each should be close to 0.250. Next, multiply the results.

3a. The ratio of beam intensities for each attentuator combination is now obtained by multiplying the results as:

#1	1	=	0.2435
#2	1 x (1 x 2)	=	6.392×10^{-2}
#3	1 x (1 x 2) x (1 x 2 x 3)	=	3.969×10^{-3}
#4	1 x (1 x 2) x (1 x 2 x 3) x (1 x 2 x 3 x 4)	=	1.541×10^{-5}

TABLE 16 (continued)

Weight Average Molecular Weight of Lignin by Low Angle Laser Light Scattering Spectophotometry, Differential Refractive Index, and Sample Preparation

KMX-6 - Light Scattering for Molecular Weight Determination: (continued)

Calibration of the Photomultipier: (continued)

4a Now for each attenuator combination, multiply the values for the appropriate attenuator.

Combinations	I_θ/I_o	
# 4	1.541×10^{-5}	These values should
#'s 1, 4	3.7523×10^{-6}	remain fairly constant
#'s 2, 4	9.8499×10^{-7}	over a period of a
#'s 1, 2, 4	2.3984×10^{-7}	month or so.
#'s 3, 4	6.116×10^{-8}	
#'s 1, 3, 4	1.4893×10^{-9}	
#'s 2, 3, 4	3.9093×10^{-9}	
#'s 1, 2, 3, 4	9.5191×10^{-10}	

These values remain constant for up to 6 weeks, but these must be reevaluated periodically.

KMX-6 LALLS Operation:

1. The laser should have been on for more than 24 hours and the attenuators calibrated.
2. Fill the syringe pump with solvent and run at a low rate. Turn on the thermal circulator and allow to reach steady state at the desired measurement temperature.
3. Remove syringe and install new line filter (Nylaflo 13 mmx0.2mm with the shiny side of filter facing downstream). Fill syringe with solvent or solution to be measured. replace syringe in the pump.
4. Run pump at 0.5 ml/min for 5 minutes to flush thoroughly. Stop pump.
5. To determine Rayleigh factor for the solvent, the settings are: field stop at 1.5, coarse gain at 900 viewport down, all attenuators in, P_0 in place.
   Start pump at 0.1 ml/min, open viewport, take reading after stable value is reached.
6. To determine Rayleigh factor for the solution, the settings are: field stop at 0.2, viewport down, coarse gain low, attentuators out appropriately, P_0 out, angle dial at 6-7^0.
   Start pump at 0.1 ml/min, open viewport, take reading after stable value is reached.
7. To determine Flourescense, repeat 6 with flourescense filter in place.
8. To determine polarization correction, repeat 6 with polarizer in place, take readings at several positions for the polarizer.
9. To determine Rayleigh factor as a function of concentration, repeat 6-8 for four or more concentrations.

Weight Average Molecular Weight Determination:

1. Correct all readings for light absorbancy using the absorbance determined by UV-Visible for the light path length through the sample cell in the KMX-6.
2. Correct all readings for flourescence.
3. Calculate the Cabannes factor corrections for polarization.
4. Calculate the fully corrcted Rayleigh factor for each concentration.
5. Calculate the ratio of Rayleigh factor to concentration.
6. Determine a regression relation relating the Rayleigh factor to concentration ratio to concentration
7. Extrapolate this relation to zero concentration. the extrapolated value is M_W.

was used instead of 0.1 N sodium hydroxide. One should note that filtration through the 0.45 micron filter is a precautionary step to remove extraneous material, such as dust particles, that would interfere with the light scattering measurements, not to remove undissolved lignin; the lignin totally dissolved and the filter retained virtually no material, certainly no material with any color. This is a normal procedure that is always followed in light scattering.

Light scattering measurements with transparent, nonchromophoric, nonelectrolytic polymers are quite simple and straightforward, particularly for low angle measurements that eliminate the effects of the shape of the molecule on the results. This is not true for a polymer such as lignin which absorbs, fluoresces,and polarizes light in some solvents. Therefore, auxiliary measurements are required to correct light scattering results for these effects; otherwise, determination of weight average molecular weight can be in error by more than 100%! In every case, one auxiliary measurement is required; the refractive index decrement. This is done by determining the differential refractive index as a function of concentration of the polymer. This must be done for each solvent at the temperature of measurement for light scattering. Preferably, this should be done for each unknown.

The differential refractive index of the solutions (dn/dc) was determined using a Chromatrix KMX-16 Laser Differential Refractive Index Instrument. In this device, a solution is placed in one side of a thermostatted divided cell and the pure solvent is placed in the other side. A laser beam is passed through the solution and solvent and the refractive index measured. By rotating the cell, the ratio of path length through the solution to path length through the solvent can be varied. This yields results equivalent to determining the effect of concentration on the refractive index. The differential refractive index for each unknown lignin solution was determined in this manner at the wave length used for the light scattering measurements (632.8 nm). Accuracy for this measurement is critical, because dn/dc appears to the second power in the equation used to determine the weight average molecular weight. Also, this quantity must be constant over the

concentration range used for measurement for best results (the refractive index should vary linearly with polymer concentration). In all cases in this work, the differential refractive index for each type of solution was constant and varied very slightly with temperature or polymer molecular weight.

Since the scattering of incident light through a volume of the solution is measured, the absorption of light in this volume by the polymer will lead to a low reading with respect to scattering. Since lignin is normally absorbing at 632.8 nm, the scattering intensity had to be determined as a function of polymer concentration to correct for this effect. The absorption was determined by measuring the absorption in a dual beam UV-Visible Analyzer, a Perkin-Elmer 7500 Lambda 4C spectrophotometer. This was done for solutions of each unknown polymer to determine the absorption as a function of concentration for each polymer.

The basic light scattering measurements were made with a Chromatrix KMX-6 Low Angle Laser Light Scattering Spectrophotometer. The device is equipped with a 2 mW He-Ne laser as a light source. The beam is split, part passing though the sample cell and part passing directly to an intensity measuring device. The sample cell is thermostatted and equipped to accept flow though the cell. The instrument is equipped with attenuating, polarizing and fluorescence filters. The sample is pumped through a 0.2 micron filter and then through the sample cell at a very slow, constant rate from a Harvard syringe pump.

The first step is to calibrate the incident beam. This is done by using the attenuating filters; filters that have been carefully calibrated by the manufacturer to transmit various fractions of the incident beam. Measurements are made with various combinations of the attenuating filters in the beam path. These measurements, along with the known factors of transmittance of the attenuating filters, are used to calibrate the incident beam intensity. Since a controlled laser is used, the incident beam intensity remains quite constant for an extended period (up to six weeks).

After the incident beam has been calibrated and the solutions prepared, light scattering measurements can be made. The solution to be measured is placed in the Harvard pump and connected to the light scattering cell. Flow is started and a measurement made without polarizing or fluorescence filters at a 6-7° solid annular angle (the scattered light is collected over an annulus at a 6-7° solid angle). Measurement is continued until a stable reading is obtained (usually a few minutes). After this, the fluorescence filter is placed in the field and the measurement repeated. The fluorescent filter is removed and the polarizing filter placed in the beam path. Measurements are made with the polarizing filter at various angles in the beam path. The measurement made without filters is the base measurement. This is corrected for light absorption on the basis of scattering volume and path length to correct the incident beam intensity. The base measurement of scattering intensity is corrected for fluorescence and polarizing effects from the auxiliary measurements made by using theoretically developed correction equations. This procedure is described in detail elsewhere (Dong, 1992). This entire measurement procedure is repeated for solutions at five or more different concentrations. The Rayleigh factor for scattering, fully corrected for absorption, fluorescence, and polarization at each concentration is calculated and the results plotted in the standard manner as (Rayleigh factor/concentration) vs. concentration. This plot is extrapolated to zero concentration. The intercept is the reciprocal of the weight average molecular weight. In most cases, the relation was a straight line which yielded good extrapolation.

One can be certain that the result is the true weight average molecular weight only if measurements of molecular weight of the polymer made in different solvents yield identical results. Measurements were normally made in DMF at 80C, but measurements in some cases were made in 0.1 N sodium hydroxide at 25C and in pyridine at 40C. For these cases, the weight average molecular weights measured for a given lignin agreed within about 12% or less, which is representative of the accuracies to be expected from

such complex light scattering measurements (Dong, 1992). Therefore, we believe that the measurements of weight average molecular weights made for the lignins in this study are true and accurate values.

5.3 Number Average Molecular Weight by Vapor Pressure Osmometry (VPO).

Number average molecular weights of the lignins in this study were determined by vapor pressure osmometry. A Corona/Wescan 232A Molecular Weight Apparatus was used for this work. Basically, this device is used to determine molecular weight as a colligative property by indirectly measuring the boiling point difference of a solvent due to the presence of a solute. The device consists basically of two sensitive thermistors surrounded by wicks that are contained in a chamber that contains a pool of the solvent and that is very well thermostatted. The thermistors form two legs of a bridge to produce a voltage signal that is proportional to the temperature difference between the two transducers. Pure solvent is fed to one wick by a syringe and a solution of known concentration is fed to the other wick. Since the presence of the solute raises the boiling point of the solution, evaporation is faster from the solvent wick, and the thermistor in the solvent wick will be at a lower temperature than the thermistor in the solution wick. This difference is measured as a voltage signal by the measuring bridge. If one repeats this measurement for solutions at different concentrations of solute, the effect of concentration of dissolved molecules on the depression can be measured. From these data, the number average molecular weight can be determined (Dong, 1992).

The exact procedure used in this study is given in Table 17. Almost all measurements were made in DMF, although some measurements were made in pyridine. VPO measurements require that careful procedures be followed to insure cleanliness; even small amounts of contamination can result in erratic data. Particular care must be exercised in cleaning and preparing the wicks. The solvent must be very pure. The wicks must be thoroughly rinsed in pure solvent a number of times. The chamber and the thermistors must be thoroughly rinsed and dried as described. The chamber is loaded with a small

TABLE 17	
Number Average Molecular Weight of Lignin by Vapor Pressure Osmometry (VPO)	
Instrument Used: **Corona/Wescan 232A**	
	VPO is a secondary measurement method based upon colligative property measurement (measurement of boiling point rise with concentration). A difference in voltage for thermistors immersed in solvent and solution is actually measured. Therefore, measurements for solutions containing a solute of known molecular weight must be made to calibrate the instrument readings. Sucrose octaacetate was used as a standard for this work. Measurements were made using dimetyl formamide (DMF) and pyridine as solvents. Solvent specifications are as given in TABLE 16.
Preparation of Solutions of Sucrose Octaacetate (SOA) for standardization:	
1	Dry SOA overnight at 70°C under vacuum, cool in a dissicator, seal.
2	Weigh 0.3 gms of SOA to nearest 0.01 mg and place in 50 ml volumetric flask.
3	After 24 hours, filter through a 0.45μ filter, return to the 50 ml volumetric, and seal. This is the "stock" solution to be used to made solution standards.
4	Prepare about 20 ml each of five standard solutions by dilution of the "stock" solution to concentrations of 0.07060, 0.1500, 0.3000, 0.4500, and 0.6000 gms/100 ml.
5	Place each in a sealed container and store for use.
Preparation of Solutions of Lignin for Analysis:	
	Prepare lignin sample solution concentrations at 0.07060, 0.1500, 0.3000, 0.4500, and 0.6000 gms/100 ml using the lignin "stock" solutions prepared for LALLS as detailed in TABLE 16.
Instrument Preparation:	
1	Remove cover from the syringe unit and loosen the 2 white knobs.
2	Remove the syringes from their cradles.
3	Remove the screw that holds the bar across the syringe tips, carefully remove the 90^0 bend syringe needles from their holes and placethem in a dessicator for their protection until it is time to clean and replace them in the instrument.
4	Remove the black base plate from the measuring chamber, lift the syringe assembly off of the measuring chamber and set it aside.
5	With a screwdriver, loosen the rods that hold the measuring chamber in place, and lift the measuring chamber out of the instrument.
6	Remove the top part of the measuring chamber, exposing the inside of the chamber and the thermistors. Insure that the small pieces of platinum gauze covering the ends of the thermistors are in place. If not, more them in place very carefully.
7	Using fine tweezers, remove the wicks, place them in a small clean beaker, and rinse them thoroughly several times with pure solvent.
8	Rinse all parts of the chamber and aluminum cylinder with pure solvent, dry in clean air.
9	Soak new wicks in pure solvent, drain, and install in wick holders with holders at 90^0 to each other
10	Reassemble the measuring chamber after adding about 20 ml of pure solvent.
	Note the 3 pipes coming up from the top of the assembly. The 2 in line with the rods are supports for the syringe needles. The third one (a Teflon line) is a drain for the chamber. This one should be on the left as you reinstall the chamber in the cylinder.
11	Put the support rods back in place
12	Reconnect the cable from the chamber to the MEAS connector at rear of the electronics unit.
	Replace the syringe unit, fasten with the screws and replace white knobs.
	Install the syringe needles through the support tubes, replace the bar and fasten it.
	Replace syringes and cover, and place entire unit in plexiglas enclosure.

TABLE 17 (continued)	
Number Average Molecular Weight of Lignin by Vapor Pressure Osmometry (VPO)	
Calibratiion of the VPO:	
1	Complete instrument preparation as described earlier.
2	Fill the syringes with solvent only and install them.
3	Set RANGE to 2 and the CURRENT to the value necessary for the temperature desired.
4	Adjust ZERO to produce a reading between 0 and 10.
	Add solvent to the rear thermistor by turning the knob (outside right, back) 3 turns
	clockwise, and then back 2 turns(to prevent any solvent from dropping due to expansion
	of the solvent as it heats up). Repeat this for the front thermistor.
5	If necessary, readjust the ZERO. Successive readings should be within +/- 0.2 microvolts.
6	Take final readings. Calculate the average of all the final readings taken (3-5).
7	Replace the rear syringe with the most dilute SOA standard and turn the knob until the reading
	goes off scale. Advance it 3 more turns. Wait 30 seconds and repeat. This process cleans out
	the syringe needle and cleans the thermistor of the former solution.
8	Advance both syringe knobs (forward 3, back 2) and record reading after it stabilizes. Repeat 3-5
	times and take the average as the reading for this solution.
9	Repeat steps 7 and 8 for each standard solution.
10	Subtract the reading for pure solvent from the each of the solution readings to obtain values of
	voltage difference, (Δ v), for each concentration.
11	Regress Δ v/c vs. c, where c is the solution concentration, and extrapolate to zero concentration.
12	The intercept value, when multiplied by the molecular weight of the standard solute, is the
	calibration factor for the instrument. The molecular weight of sucrose octaacetate is 678.6.
Measurement of an unknown (lignin) molecular weight:	
1	Complete steps 1-11 as described for Calibration of the VPO using the same solvent used
	for calibration.
2	Divide the calibration facor by the intercept value to determine the uncorrected number average
	molecular weight, Mn.
3	The value of M_n determined is the average for the lignin and impurities in the lignin. The identities
	and quantities of the impurities are known from analysis. Use a mass balance to obtain a
	corrected value of M_n.

amount of solvent, the wicks put in place, the chamber closed, and the syringes attached. Measurements can then be made.

The VPO must be calibrated by using a solute of known molecular weight, since the voltage signal produced is an indirect measurement of a colligative property. The standard used must be in pure form, of a reasonably high and exactly known molecular weight, and soluble in the solvent to be used. Sucrose octaacetate was used as a standard for our work, as recommended by the instrument manufacturer. Concentrations of sucrose octaacetate in DMF ranging from 0.706 to 6.00 mg/ml were commonly used as standards. These were prepared by preparing a "stock solution" that was then diluted to other concentrations to prepare a series of five or more standards. A description of preparation of a typical set of standards is given in Table 17. These standard solutions of sucrose octaacetate were used to determine the effect of concentration on the instrument reading. This reading, divided by the concentration, when plotted against the concentration yields a line that can be extrapolated to zero concentration to give an intercept that is inversely proportional to the number average molecular weight. Since the molecular weight of the standard is known, this intercept for the standard can be used to calibrate the instrument. Calibrations with sucrose octaacetate proved to be very reproducible and with instrument readings not far removed from those observed with lignin solutions.

As stated earlier, most measurements with lignin were made using DMF as the solvent. DMF is very stable, it can be obtained in very high purity, it does not form oligimers, and it is a reasonably good solvent for lignin. Measurements were made over a range of temperatures to identify the Flory or Theta temperature of lignin/DMF solutions. At the Theta temperature, the solvent and polymer exhibit neutral interaction. This is exhibited by a zero slope of the line for the instrument reading divided by concentration vs. the concentration, ie, the viral coefficient is zero. This was determined to be about 80C for lignin in DMF. Therefore, measurements were made at 80C or slightly above, in DMF.

At these temperatures slightly above the Theta temperature, one can be assured that the polymer is completely dissociated and extrapolation of the data to zero concentration to determine the number average molecular weight is accurate, because the slope of the line is nearly zero.

Even though the VPO measurements gave very reproducible results and calibration of the instrument with sucrose octaaacetate was very accurate, the direct result is still questionable due to the impurities in the lignin. A correction had be to applied to account for these. It was assumed that the impurities that could ionize were fully ionized in the solution, and the total number of impurity particles in the lignin was calculated from the analysis of impurities made by methods described earlier. This was used to correct the molecular weight reading to determine a corrected value for the number average molecular weight of lignin. This correction was not small; often the correction was as much as 40%. There is some uncertainty in the correction itself; however, this uncertainty was estimated to amount to 2% or less of the corrected molecular weight for lignin. A complete discussion of this method, comparison to past results of other studies, and complete details on procedures can be found elsewhere (Dong, 1992).

5.4 Molecular Weight by High Pressure Liquid Chromatography (HPLC). The molecular weight distribution of the lignins was characterized by means of high pressure liquid chromatography operated at high temperature with size exclusion chromatographic columns. The instrument used was a Waters 150C ALP/GPC high pressure liquid chromatograph equipped with a differential refractive index analyzer and a UV-Visible analyzer, interfaced with a NEC APC IV workstation running Maxima 820 software supplied by Waters. GBR gel columns at 1000A and 10,000A supplied by Jordi were used for this work. Complete details can be found elsewhere (Schmidl, 1992), but an outline of the procedure is given in Table 18.

TABLE 18	
High Pressure High Temperature Liquid Chromatography (HPHTLC)	
The HPHTLC Unit Used was a Waters 150C ALP/GPC	
Instrument Description:	
	Instrument used is the Waters 150C ALC/GPC high-pressure liquid chromatograph with an outboard Waters 486 UV/Vis tunable absorbance detector, interfaced with a NEC APC IV computer workstation running Maxima 820 software. Mobile phase is supplied by a KONTES integrated HPLC mobile phase handling system with a 5 liter capacity and capable of solvent filtration, degassing by sparging with helium and mobile phase storage. The UV/Visible and DRI detectors are connected in series. The lignin displays UV absorbance and is monitored by the UV/Vis detector. The standards used do not show UV absorbance and are monitored by the DRI. The 0.15 minute time lag between detectors is accounted for in the standard retention times. Because of the greater sensitivity of the UV/Visible detector, the injection volume for lignin is 50 µl instead of 100 µl.
Instrument Conditions:	
1	Jordi Gel GBR columns 10^3 Å and 10^4 Å were used. (More than fivecombinations of others were tried).
2	Mobile phase used was dimethyl sulfoxide (DMSO) + 0.1M LiBr. (more than ten others were tried).
3	The flow rate was nominally 1.1 ml/min, but the actual flow rate was 1.03 ml/min.
4	The analysis temperature varied for different solvents and mobile phases, but was 85°C for DMSO +0.1M LiBr.
5	The run time was 30 minutes for the mobile phase used.
6	The injection volume was 100 µl for standards and 50 µl for lignin solutions.
Instrument Operation:	
	1. Select the parameter to be programmed by pressing the round pushbutton adjacent to the parameter. The LED above the pushbutton lights and the current value in memory is displayed.
	2. Enter the new value via the numerical keypad. As the numbers are entered, they are displayed in the SYSTEM MESSAGE display panel for visual verification.
	3. Press ENTER. The new value is transferred from the SYSTEM MESSAGE display panel to the selected parameter display panel.
	4. To lock in the new value (i.e. turn off the LED) press ENTER a second time, depress the same round pushbutton or address another parameter.
Calculation Results:	
1	Lignin molecular weights were calculated from chromatograms using 3rd order calibration curves relating log(M) to elution volume that were established by using narrow molecular weight distribution standards of various structures. The correlation coefficients for the calibration curves were 0.995 or better.
2	Due to the configurational differences between the standard polymers and lignin, values of M_W/M_n determined by HTPHLC and LALLS and VPO differed by 250 to 1500%!
3	Eight chromatograms were used to establish a calibration curve by resolution by moments using values of MW and Mn determined from LALLS and VPO measurements. A 4th order calibration curve relating Log(M) to elution volume was developed.
4	Using the calibration curve developed in step 3, all other values of M_W and M_n calculated from chromatograms agreed with values determined by LALLS and VPO within 12%, except for two cases.

A very large number of trials involving various solvents, temperatures, column types and combinations, and detectors were run. A total of more than 70 combinations were investigated. Of these, only a very few gave reproducible results. In most cases, the lignin apparently absorbed on the column and required inordinately long periods of time to elute from the column. In a few cases, the absorption was non reversible, and the column was ruined. There were also problems in establishing a good baseline, which is an essential requirement for good results. Eventually, three combinations of column, temperature, and mobile phase solvent were identified that gave reproducible results with good baselines. The best combination was DMSO containing lithium bromide with the Jordi 1000A and 10,000A columns in series.

A major problem with GPC is calibration, since this is a secondary method based upon the hydrodynamic radius of the solute in solution. No appropriate standards for lignin exist. A number of monomeric polymer standards were examined, including polyglycols, polyethers, and polysaccharides. None were satisfactory, but the polysaccharide standards were used to calibrate the GPC so that molecular weight distributions could be calculated as well as number average and weight average molecular weights. The results did not compare well with the results from the weight average and number average values from LALLS and VPO. Values from the GPC were consistently lower with weight average molecular weights exhibiting the greater difference. As the weight average molecular weight by LALLS became higher, the difference became greater. Also, the value of M_w/M_n determined from GPC measurements was always smaller than the ratio determined from LALLS and VPO measurements.

This is consistent with the supposition that lignin is a compact, nearly spherical molecule rather than a random coil or flexible rod. A compact, nearly spherical molecule would be partitioned on the basis of size much less than molecules of other shapes; therefore, values of weight average molecular weights determined from chromatographs using molecules of other shapes as standards would be less than the values determined by light

scattering, and the difference would become greater as the molecular weight increased. Surprisingly, even though the values from GPC are not correct, the trend is correct, and values can be used to quantify the effect of molecular weight on most properties, including viscosity. However, the work with GPC was quantitatively disappointing to this stage, even though the values determined from the chromatograms could be used for correlations and the chromatograms themselves showed differences in the lignin molecular weight distributions for different pulping conditions.

A great deal of time was spent in using the chromatographic results to develop a standard by the method of moment resolution. The number average molecular weight is the first moment of the distribution about the origin and the weight average distribution is related to the second moment of the distribution about the origin. These values are known from LALLS and VPO measurements for a large number of lignins for which chromatograms are available.

Since the lignins have been recovered from kraft black liquors from pulping the same species, the lignins should be very similar, if not exactly alike, chemically and should exhibit the same interactions with the solvent. Eight lignins were selected to represent a wide range of weight average molecular weights and molecular weight distributions. Data for these lignins were used to establish a calibration curve for lignin with the columns by moment resolution using the Hooke and Jeeves method to determine a relation between molecular weight and chromatographic elution volume that would bring the weight average and number average molecular weights determined from the chromatographs into agreement with the values determined from LALLS and VPO. This was done successfully, even though it proved to be a most difficult task.

The calibration curve developed was then used to calculate weight average and number average molecular weights form the chromatographs for the other lignins studied and these were compared with the values determined from LALLS and VPO. The agreement

was good to very good; the maximum difference between values was less than 20%, except for two lignins that had very marked bimodal distributions.

The successful calibration by the method of moments has three consequences. Firstly, a reasonably reliable molecular weight distribution can be calculated for the lignins for which the chromatograms are available as well as higher molecular weight averages, such as the z-average molecular weight. Secondly, the calibrated column can be used to determine the molecular weights of new lignins of the same type without the need for LALLS or VPO measurements. Thirdly, a lignin for which a chromatogram is available from this work can be used to calibrate a new column of solvent-column system. This is a significant advance in lignin characterization.

In the future, the success of the moment resolution method of calibration could lead to use of GPC methods to follow pulping as a depolymerization reaction. It is known from our work and the work of others that chromatograms of lignin can be run in NaOH solutions at pH levels of 12 or more. A calibrated lignin could be used to establish a calibration curve in simulated black liquor, assuming that the unidentified constituents did not interfere, which is very likely true at least for soft wood kraft liquors. Samples taken during pulping could be used to determine the concentration and molecular weight distribution of lignin in the pulping liquor as the pulping process proceeds. This information would be invaluable in interpreting the kinetics of pulping as a true depolymerization process.

5.5 Other Lignin Studies. In addition to the studies described in the earlier sections, we also performed studies to further characterize lignin as a polymer. These studies included determination of the glass transition temperatures, the heat capacity, and the density of lignin at room temperature by methods described in later sections, the rheological behavior of lignin solutions, the effect of diluents on the glass transition of lignin, the intrinsic viscosity of lignin in NaOH solution and in DMF, and the effects of different acid precipitations on the surface properties of lignin. Since the methods used are described in

other sections of this report and since experimental results of these other studies have been published in theses and in reviewed research publications, they will not be described here in detail.

6.0 SMALL SCALE BLACK LIQUOR CONCENTRATION AND VAPOR-LIQUID EQUILIBRIA

Black liquors made in our pulping experiments and many mill liquors included in the study had to be concentrated to various higher solids concentrations for measurement of properties. A small scale evaporator was developed for this work. The evaporator was designed to permit operation at constant pressure from 100 to 760 mm He with a controlled rate of evaporation. The unit was developed to permit operation under conditions of total reflux of the vapors or with removal of the vapors as a condensate with provisions for determining a material balance on the system continuously. This system required over two years of development. but was very successfully used, not only to concentrate the experimental liquors. but also to determine the boiling point elevation as a function of solids concentration at constant pressure and the vapor- liquid equilibrium temperatures as a function of pressure at constant solids.

6.1 Description of the Small Scale Evaporator. The evaporator developed was a four liter vessel. The bottom portion of this vessel was an Ace Glass 316 stainless steel two liter flask with a hemispherical bottom and a conical flange at the top. The top portion of the vessel was a length of four inch diameter glass pipe with conical flanges at each end. The top of the glass portion was flanged to a flat 316 stainless steel flange and this assembly was suspended from a metal frame. Four baffles, each 1/2-inch wide, were welded 90 degrees apart to the stainless steel bottom vessel and these extended up into the glass portion of the vessel to within two inches of the top of the vessel. The bottom of the vessel was tapped by a 3/8-inch line with a valve for sampling or draining the vessel. The vessel was equipped with a stirring shaft stepped into a steady block in the bottom of the vessel and with two turbine mixers 2 3/4- inches in diameter that were arranged in opposing pumping positions. The shaft passed out of the vessel through a stuffing box seal in the top metal flange. The stuffing box was filled with Teflon fiber packing that was compressed with a seal ring. The stirrer was driven by a reversible DC motor with SCR

speed control. The shaft was steadied by passing through two pillow block bearings above the vessel that were carefully aligned and was connected to the stirring motor by means of a flexible coupling. The vessel and stirring system were rigidly mounted on a stand with the stirring assembly carefully aligned and locked into place.

The vapors passed though a vertical glass condenser above the vessel and then through a line into a vertically mounted shell and tube condenser with a heat transfer area of about 0.9 square feet. The condensate from this second condenser flowed though a flexible tube to a three liter receiver mounted on a load cell. Non-condensible vapors flowed from the receiver through a cold trap to a vacuum pump system to maintain system pressure.

Heating was provided by an electrical heating mantle surrounding the stainless steel portion of the vessel. The heating rate was controlled by controlling the voltage to the mantle by means of a variable transformer. The upper portion of the vessel and the top flange were insulated with one inch of magnesite or glass foam insulation to minimize heat loss. A small slit was left open in this insulation so that boiling behavior in the vessel could be observed.

The temperature of the liquid in the vessel was measured by a resistance thermometer connected to a Rosemount 414L linear bridge to produce a signal of 1 mv/C. The temperature could be continuously recorded. The pressure in the system was measured by a pressure transducer mounted in the top flange. The signal from the transducer was fed as a control signal to the pressure controller. The output from the pressure controller operated a voltage/pressure transducer that fed a controlled air signal to the control valve. The control valve was connected to the exhaust line downstream of the cold trap and fed air into the exhaust line system. The exhaust line was connected to a vacuum pump that ran at full load constantly with gas provided by the air bleed valve to maintain the constant pressure in the evaporation vessel constant. The load cell upon which the condensate receiver was mounted was connected to a specially designed stepping system to permit

measurement of mass with a signal of about 0.179 mv/gm from 0 to 4000 gms with a maximum signal output for any one step in change in mass of 100 mv. The mass of condensate was continuously recorded during concentration or boiling point elevation studies. The rate of evaporation was very constant and could be controlled easily by varying the voltage to the heating mantle.

For vapor-liquid equilibrium studies, the vertical glass condenser was operated and the condensate was returned totally to the vessel. During these measurements, the boiling rate was limited to about 4 gm/minute or less. For concentration experiments, the vertical glass condenser was drained and the condensate was collected in the receiver. If boiling point elevation was being determined as a function of solids concentration during concentration, the evaporation rate was limited to 6 gm/ minute or less. The rate of evaporation to concentrate liquors was limited by foaming in the vessel during boiling, but could normally be conducted at rates as high as 12 gm/minute.

6.2 System Calibration and Testing. The calibration and testing of the evaporator system are very important and some details on the procedures used are given in Table 19. These procedures were repeated numerous times during the course of the work to insure that data collected were valid.

The temperature measurement is very important. The RTD and linear bridge were calibrated as a unit by measuring the output when immersed in an ice-water mixture saturated with air and when immersed in boiling water with the boiling temperature corrected to the exact barometric pressure. The RTD and linear bridge were also calibrated at increments of about 15C from 25 to 130C when immersed in an oil bath and adjacent to a mercury thermometer calibrated by NIST. A number of RTDs where tested and the ones with the minimum deviations were selected. The RTD systems used were accurate to within 0.02C or better and had a very rapid response (less than an estimated 0.5 seconds for a 15C step change in temperature. The calibrations of the RTDs used

TABLE 19

Small Scale Evaporator Calibration and Operation

Calibration of Components:

Resistance Thermometers:

1. Place resistance thermometer bulb and NIST standard thermometer close together in a temperature bath capable of maintaining a steady temperature within better than 0.1C.
2. Take readings of both at 10C increments from 30 to 140C. If differences are more than 0.05C, reject resistance thermometer.

Pressure Controller Unit:

1. Connect pressure transducer to controller.
2. Read Barometer. At the bottom of the barometer is a knurled knob. Adjust this so that the needle visible through the mercury pool glass just touches the surface of the mercury. Raiseor lower the brass shield so that the bottom of the shield is level with the top of the mercury column. Read the Vernier scale and record the pressure. Read the thermometer and correct for temperature, if necessary.
3. Set pressure controller to the corrected barometric pressure.
   a. Note pressure on Omega controller. Subtract the pressure from the barometer to get the nearest whole degree of difference. either higher or lower that the Omega needs to be adjusted. Ex: barometer 757.25
      Omega 753
      4.25 or an even 4 adjustment
   b. Simultaneously push the TUNE/RETURN. LAST. and the black space to the left of the YES button to put the Omega into **calibration** mode.
   c. Push the PARAMETER/DISPLAY button to cycle to HI VAL screen. Change this number by pushing the YES for increase if Omega value < barometer or NO for decrease (if Omega value > barometer)
   d. Push PARAMETER/DISPLAY button to get calibration complete message.
   e. Push TUNE/RETURN once more to return to normal mode.
   f. Check Omega pressure to be sure it matches barometer. If not, repeat a - f.

Vacuum Check:

1. Drain and dry the evaporator, the collection flask, and the cold trap, and reassemble.
2. Turn on pressure controller and vacuum pump: set pressure to 0 mm Hg.
3. Establish steady pressure of <30 mm Hg. Close valve to vacuum pump.
4. Record pressure at various times. If pressure rises more than 10 mmHg/min, release vacuum, check all connections for leaks and repeat steps 1-3.

Pressure controller Calibration:

1. Drain and dry the evaporator, the collection flask, and the cold trap, and reassemble, greasing all appropnate joints and repacking stirrer bearing.
2. Connect a manometer to the evaporator pot and set the pressure controller as given in Pressure Controller Unit.
3. Connect the multimeter probes to the rear of the Pressure Controller at ports F and H. Set the multimeter to read DC Volts in the 20 volt range.
4. Open the air bleed to the vacuum pump, set the controller to atmospheric pressure.
5. Read the manometer level difference with a cathetometer, read the voltage and pressure controller indicator. Record all three values. Set pressure controller to a new pressure lower than atmospheric, turn on the vacuum pump, establish a steady state (2-5 minutes). read the manometer level difference, read the voltage and pressure controller indicator.
6. Repeat step 5 for at least five pressures between 75 mm Hg and atmospheric pressure.
7. Calculate actual pressures as differences between barometric pressure and manometer readings.
8. Compare actual pressures to pressure controller indicator readings.
9. Regress Pressure (y) vs.Voltage (x) to get the slope (m) and y-intercept (b). (R^2>0.999).
10. Low Val = b (y-intercept), High Val = b + 5m (pressure at 5 volts).
11. Enter these values into the controller.
12. Check two pressures to insure that controller is calibrated well.

TABLE 19 (continued)

Small Scale Evaporator Calibration and Operation

Calibration of Components (continued):

Load Cell Calibration:

The condensate receiver was connected to the condensers by a flexible line and was mounted on the platform of a load cell with a total capacity of about 6kg. Custom circuiry was designed and built that permitted: (1) the tare voltage to be adjusted to zero. (2) the voltage to be adjusted to about 0.25 mv/gm., (3) the voltage to be "stepped" in increments of 100 mv (representing about 400 gms of collected mass), and (4) the number of "steps" counted. The output was connected to a recorder.

1. Turn on circuitry and zero output.
2. Place empty receiver on platform and connect into system.
3. Adjust tare to zero voltage, set "step" to zero.
4. Add weights to platform in 20 gm increments to 100 gms, adjust "step".
5. Remove 10-20 gms. add weights in 100 gm increments to 400 gms, recording voltages at each addition.
6. Regress mass vs. voltage linearly; check for linearity; use slope if R^2>0.999.
7. With the weights removed, turn on vacuum, set pressure at new level, read zero, add 2000 gms, read voltage, remove weights, set new pressure, read zero, add 2000 gms, read voltage.
8. Use data from 7 to develop correction for air displacement.

Normal Operation

Normal operation involved a number of steps in series.

Preparation:

1. Repack stirrer stuffing box, grease and assemble joints, connect receiver, drain cold trap on vacuum line, fill cold trap thermos with ice, turn on circuits, turn on instrument air, turn on hood.
2. Adjust pressure controller following steps 1-3 in procedure given as"Pressure controller Unit".
3. Adjust load cell voltage to zero, add 100 gms, adjust "step", add 1000 gms, check calibration.
4. Turn on vacuum, set pressure controller to zero. When pressure reaches <30 mmHg, close vacuum line and check for leak rate. If leak rate is >10 mmHg/ min, repeat steps 1 and 4.
5. Weigh 2500-4000 gms liquor in container.
6. Open Vacuum line, set pressure controller to about 200 mmHg, draw liquor from container into evaporator pot through bottom line in pot, close bottom line valve, weigh container; liquor charge is difference in weight.

Operation:

Normally, vapor pressure equilibrium data and boiling point rise data were taken sequentially as concentration proceeded.

1. After preparation is completed, set pressure controller to lowest level desired (usually about125 mmHg), turn on water to reflux condenser, turn on stirrer motor and adjust speed, turn on heating mantle and adjust voltage, bring liquor to a boil carefully.
2. When boiling commences, adjust heating mantle voltage to give 2-4 drops/min of condensate.
3. When temperature is constant (about 3-5 min), record pressure and temperature.
4. Set pressure controller to higher desired pressure, adjust heating mantle voltage, bring liquor to a boil carefully.
5. Repeat steps 2 and 3.
6. Repeat steps 4 and 5 to give at least five data for boiling points between 125 mmHg and atmospheric pressure.
7. Turn off heating mantle, cool liquor to below boiing point at the lowest pressure.
8. Drain reflux condenser, turn on water to concentration condenser. Set pressure controller to lowest pressure desired.
9. Turn on heating mantle and adjust to give a condensate rate of 2-5 gms/min when boiling commences.
10. Record temperature and condensate mass as a function of time as concentration proceeds to desired new concentration.
11. When new desired concentration is attained, turn on water to reflux condenser, repeat steps 2-8.
12. Repeat steps 9 -11. When final desired concentration is attained, stop.
13. Release vacuum, turn off heating mantle, turn off vacuum pump, allow liquor to cool.
14. Remove receiver, determine mass of condensate and check vis-a-vis load cell reading.
15. Remove cold trap, weigh mass of condensate collected.

TABLE 19 (continued)	
Small Scale Evaporator Calibration and Operation	
Normal Operation (cotinued)	
Operation (continued):	
16	Turn off hood, air, water to condensers, and stirrer motor.
17	When liquor has cooled appropriately, drain the liquor into weighed plastic bottles, and determine mass and % solids of the liquor collected, seal containers, save liquor for use.
18	Add weighed mass of hot water to the evaporator, mix, and drain into a weighed container. Determine mass and % solids of washings.
19	Check material balance form initial charge and data from steps 13, 15, 17, and 18.
20	Adjust concentration data for small amount of cold trap condensate collected (usually <5 gms), assuming that cold trap condensate has been collected linearly with time during concentration.
21	Thoroughly flush the evaporator components and drain. Clean and dry the condensate receiver.
22	Regress vapor pressure equilibrium data at each concentration as $Log(p) = A/T + B/T^2$.
23	Combine concentration data to give a continuous boiling point vs. concentration curve for the liquor at one pressure at concentrations from the initial to final concentration.

were checked periodically in ice-water saturated with air and in boiling water. The units exhibited no drift with time.

Pressure measurement and control are equally important, if not more important. This required three procedures. The tightness of the system had to be determined, since air leakage into the vessel or condensers could lead to erroneous results. The system was completely dried and closed. A mercury manometer was connected to the vessel as well as the pressure controller. The system was evacuated as described in Table 18 to an absolute pressure of 30 mm Hg or less, and the vacuum line closed. The increase in pressure of the system was recorded. If the rate of increase was more than about 1 mm Hg/min, the vacuum was released and the seals, flanges, and stuffing box packing checked and replaced, if necessary. This was repeated until air leakage was reduced to the acceptable limit.

The pressure transducer and controller were calibrated as one unit. With the system open, the pressure controller was set to the barometric pressure read on a barometer located adjacent to the evaporator unit. A manometer was connected to the vessel and the system was closed. The controller was set to a pressure and allowed to come to equilibrium at that pressure. The pressure was determined from cathetometer measurements on the manometer and the barometric pressure and the controller output was recorded as a voltage and as a controller reading. This was repeated for at least four additional pressures in the range from 150 to 600 mm He. The readings were regressed to develop a linear relationship between system pressure and controller output voltage. If the regression coefficient were not equal to or greater than 0.9999, the calibration was repeated.

The load cell for measuring the mass of the condensate was also carefully calibrated as a single unit. The output of the load cell was set to zero with the empty condensate receiver in place and connected to the system. The load cell was then calibrated over the entire range needed (about 3400 grams) by adding weights to the load cell platform and

recording the output voltage for each mass. The system sensitivity was about 0.2 grams. In fact, the system was so sensitive that, when it was zeroed at atmospheric pressure and then the system evacuated to 100 mm Hg, the mass of air removed from the receiver could be detected by the load cell measuring system. In normal operation, the load cell was zeroed at the lowest pressure to be run and a very small correction made to the reading as the pressure was changed for other conditions.

The system was tested by using NaCl, NaOH, and sucrose solutions for which very accurate vapor pressure-concentration data are available. NaOH solutions up to 50 wt%, NaCl solutions up to almost the solubility limit, and sucrose solutions up to about 83 wt % were used. A solution of known concentration was placed in the vessel, the solution brought to boiling at constant pressure under conditions of total reflux and the temperature determined. This was repeated for a number of pressures from 75 to 760 mm Hg at a given concentration. The same experiment was run at different heating rates to determine the maximum rate at which equilibrium conditions could be maintained. Results were compared with literature values. For all three solutions at all conditions, the agreement was within 0.1C or better. These tests were also used to determine the best conditions for stirrer speed and condenser operation. The tests with sucrose were used to determine the effect of higher viscosities on the operation, and indicated that reliable data could be collected for fluids with viscosities as high as about 900 cp.

The system was also tested for use in determining boiling point elevation as a function of concentration at constant pressure using NaCl and NaOH solutions. The system was shown to produce results equivalent to equilibrium results under controlled conditions of boiling rate. If the boiling rate were restricted to less than about 6 gm/minute with a solution volume in the vessel of about 500 ml or more with good stirring, the results agreed with values determined from literature data to within 0.1C or better at pressures above about 150 mm He. At lower pressures, air leakage introduced an error that increased with decreasing system pressure, but results were still comparable to results derived from literature data to within about 0.3C or better.

The weak point of the system was shown to be air leakage through the stuffing box for the stirrer shaft. This was given particular attention, and the stuffing box was normally reset after every run. If the stuffing box were to be replaced with a magnetic coupling to yield a completely closed system, this apparatus could be operate successfully at pressures as low as 50 mm Hg. However, data taken at pressures ranging from 150 to 760 mm Hg proved to be sufficient for our work, and the revisions of the system necessary to install a magnetic coupling for the stirrer drive were not made.

6.3 Loading and Mass Balance Procedures. The normal liquor loading procedure that was found to be best is outlined in Table 19. The liquor was weighed and transferred into the system that had been evacuated to about 200 mm He by suction through a hose connected to the bottom drain valve of the vessel. The actual mass of liquor charged was determined by difference in weight of the liquor container before and after loading. The pressure controller was set to the pressure desired, the cooling water to the condensers turned on, the load cell zeroed, and the stirrer motor started. The heating mantle was turned on to heat the liquor and the temperature was observed as the liquor heated. When the liquor began to boil, the heating mantle voltage was adjusted to give the desired boiling rate; this could be determined approximately by counting drops of condensate from the reflux condenser over a short period of time (after some experience with the apparatus, this rate could be preset almost exactly). If the unit were to be run as a concentrator, the cooling water to the reflux condenser was shut off and the water drained from this condenser. The vapor was then condensed by the shell and tube condenser, the condensed mass was collected in the receiver, and this mass was recorded continuously.

At the end of the run, the liquor remaining in the vessel was drained and weighed, the condensate in the receiver was weighed, the cold trap was drained and the trapped condensate weighed, and the solids content of the liquor remaining in the vessel was determined. From these data and the starting mass and concentration of liquor, the mass balance for the system provided by the continuously recorded mass of condensate in the condensate receiver could be checked. Also, any error resulting from not condensing all of the vapor could be compensated from measurement of the condensed mass in the cold trap by assuming that this mass had been collected at a constant rate during the evaporation.

If the mass balance did not check, the data was discarded. Normally, the mass balance closed very well. The evaporation rate normally remained very constant over extended concentration ranges. If the unit were run under conditions of total reflux, the reflux condenser was used, the boiling rate was set to a very low value with stirring at as high a rate as practical, and the system run at constant pressure until thermal equilibrium was established.

For pre-evaporated and skimmed liquors, the condensate contained only traces of organic carbon, at most, which indicated that there was virtually no entrainment.

6.4 Normal Mode of Operation and Typical Results. For our liquors made in our pulping experiments and for most mill liquors studied, liquors used in the vapor-liquid equilibrium and boiling point elevation studies were pre-evaporated in our pilot scale evaporator and soap skimmed. For data for liquors at concentrations below about 30 % solids, the liquors were diluted with distilled water before study. The liquor to be studied was loaded as described previously, brought to boiling, and data for vapor-liquid equilibria collected at pressures ranging from 125 to 760 mm He. The pressure cycled between two limits at about two minutes/cycle and the temperature followed this cycle with about a five second lag. The average values of pressure and temperature were used as the true data points.

These data were regressed as log pressure vs. reciprocal absolute temperature as linear and second order regression equations. The second order term was very small. Data at low pressures that deviated substantially from the regression established by data taken above 200 mm Hg was discarded. because this is evidence of error resulting from air leakage. Correlation coefficients for these data were very near to 1.0. and we found that data could be extrapolated to as high as 2300-2800 mm Hg (3.0 to 3.68 atm.) with confidence.

Normally, after completing data collection for vapor-liquid equilibria. the liquor was cooled to a temperature below the boiling point at some lower pressure. After the liquor had cooled, the reflux condenser was drained. the pressure was set at a constant value, the heater was turned on again. and concentration was begun with the evaporation rate set at a low value. Concentration was allowed to proceed at a constant evaporation rate and constant pressure while recording the temperature and the load cell voltage as a function of time.

Since the initial mass in the vessel and the solids concentration of this mass were known and since the condensate mass could be calculated at any time from the load cell voltage reading, the solids concentration of the liquor in the vessel could be determined by material balance as a function of time. Since the temperature is also recorded as a function of time. the boiling point (and hence. the boiling point elevation) of the liquor vs. concentration at that pressure could be determined. The limits for concentration were set by either the volume of the condensate receiver (about 2200 grams) or by the final volume in the vessel (about 600 ml).

At the completion of the concentration step, the liquor was again allowed to cool to a temperature below the boiling point at a low pressure, normally a pressure of 150 to 200 mm Hg. After cooling, vapor pressure equilibrium data were taken for the liquor at the

final concentration. The system pressure was then raised to atmospheric pressure, the liquor cooled to below about 100C, drained, weighed, and sampled for solids concentration determination.

The concentrated sample was packaged in high density polyethylene bottles, blanketed with nitrogen, sealed, and placed into cold storage for use in properties measurements.

A boiling point vs. concentration curve at one constant pressure from a concentration of about 10% solids to as high as 87% solids was determined for every liquor from concentration data collected from a series of concentrations made at the same pressure. Usually, a second curve was determined from concentration data collected at a second constant pressure. Vapor pressure equilibrium data were collected for each liquor at five to ten different concentrations over the concentration range studied. The quality of the data proved to be excellent. Often, inflections in the boiling point elevation curve could be observed that were related to association or to precipitation in the liquor. The vapor pressure equilibrium data were shown to be thermodynamically consistent with other thermal properties.

The vapor pressure data collected at different concentrations and the boiling point elevation curve determined at one constant pressure permitted boiling point elevation vs. concentration curve at different pressures to be estimated with confidence. This technique has been used for study of mill liquors to provide data for multiple effect evaporator design with success a number of times for pressure operation as high as 3.5 atm. The vapor pressure equilibrium data can also be used to determine the boiling point of the liquor at the furnace firing guns, an important parameter for good droplet formation.

The liquor boiling point has been correlated as a function of pressure and solids concentration for many softwood kraft black liquors derived from Slash Pine (Zaman, 1996). The correlation for the two sets of lines involves three constants that are a

function of pressure for one liquor. These constants have been related to the pulping conditions to permit one to predict the boiling point behavior of these liquors for a given set of pulping conditions.

The experimental techniques have been used successfully for kraft liquors from softwoods, hardwoods, bamboo, and agricultural wastes, and for liquors from carbonate, sulfite, semi-chemical, and TMP pulping. However, the data reduction techniques used successfully for kraft liquors were not successful for semi-chemical or TMP pulping liquors above about 30% solids, probably due to the effects of precipitation and/or association in the liquor at higher concentrations.

7.0 THERMAL PROPERTIES

Thermodynamic transition temperatures (such as freezing points and second order transitions), heat capacities. heat of mixing and/or solution. specific volume or density. thermal coefficients of expansion. heat of combustion or reaction are very important, not only for engineering design, but also for providing information useful in understanding the behavior of any material. In this study, all of these properties were determined except heats of reaction. In most cases, these properties were determined extensively for many different liquors. In many cases, these measurements were made accurately over the entire solids concentration range for the first time by methods that were developed or adapted for work on black liquors for the first time.

Not only were extensive data collected, but data reduction correlations were developed that are based upon sound theories and correlations for the data reduction correlation constants developed that related the property ultimately to the liquor solids composition or to the pulping conditions used for Slash pine. In most cases, the methods and data reduction correlations have been applied successfully to liquors from other wood species and to liquor derived from other types of chemical pulping. Therefore, the experimental methods and the data reduction correlations have been shown to have general utility.

7.1 Density and Thermal Expansion. The first of these measurements that will be described is the measurement of density and thermal expansion. While not the most important of the thermodynamic properties, these are the most easily understood, and the measurements made in this work are the first reported for liquors over the entire range of solids concentrations from 0 to 100% solids. The measurement of density as a function of concentration at constant temperature was the measurement that was most desirable from our point of view. There are two problems in making such measurements directly. The first is that liquors at high solids concentrations are very viscous at lower temperatures and cannot be loaded into pycnometers easily. The second is that it is very difficult to

control the temperature of the liquor in the pycnometer to 0.1C or better during the measurement. By using a combination of pycnometers and by using thermal expansion data, these problems could be eliminated and very accurate data for density as a function of concentration at constant temperature obtained. Therefore, these techniques will be described as a unit with a discussion of the methods used for correction.

Glass pycnometers with ground glass jointed thermometers graduated in 0.1C increments and side arms with covers were used to determine density directly for liquors that were fluid enough to be loaded into the pycnometers with no inclusion of air. The temperature limit for loading was about 36C. The pycnometers were calibrated by filling them with distilled water at the temperature of interest, determining the mass of water, and calculating the pycnometer volume using literature values for the density of water. This was done for the temperature range from about 23 to 36C. The exact procedure used for glass pycnometer measurements is described in detail in Table 20, including the equation for the density of water as a function of temperature that was used and the calculation for the volume of the pycnometer at the temperature of calibration.

One must be extremely cautious in excluding air for the calibration as described. the method described closely follows TAPPI 625 cm-85. The calibrated glass pycnometers were then used to determine the density of liquors that were fluid enough to be loaded into the pycnometers so as to completely fill the pycnometer. The pycnometer was filled with liquor, the temperature allowed to equilibrate while the pycnometer was immersed in a bath, the pycnometer removed and wiped clean and dry, and the pycnometer quickly weighed on an automatic balance with the liquor temperature recorded to the nearest 0.1C. Thermal expansion data taken later was used to correct this density to the density corresponding to a given temperature, such as 25.0C. This basic density was never corrected for a temperature change of more than about 10C.

Glass pycnometers cannot be used successfully to determine densities of liquor with high viscosity. A variety of types of pycnometers designed for absolute measurement

TABLE 20

Density by Glass Pycnometer

Densities at 50% solids or lower concentrations could normally be determined easily and accurately with glass pycnometers. The method used follows Tappi Method T 625 cm-85 closely.

Method:

1. Choose a glass pycnometer complete with the thermometer and the glass top for the side arm. Be sure they are clean and dry. Record the #'s on the pycnometer set.
2. Find the tare weight of the pycnometer and record this as X.XXXX grams.
3. Fill pycnometer with DI water. making sure there are no air bubbles in it, insert the thermometer. Set aside for a minute so the temperature can equilibrate. Do not hold it because your body temperature will cause the temperature to rise.
4. Record temperature.
5. Wipe the pycnometer dry on the outside. At side arm, skim top of arm lightly to remove excess water. Squirt outside with acetone and dry in air stream. Put top on side arm.
6. Weigh pycnometer with water in it and record this.
7. Dump the water out and dry the pycnometer using acetone and air for a final drying. Warm the pycnometer in your hands a little to return it to room temperature.
8. Mix the liquor sample thoroughly but do not shake it in order to minimize the air trapped in the sample.
9. Fill pycnometer with liquor sample. Again. be sure no air bubbles are in the sample. Tap the pycnometer gently but firmly on the counter top to help dislodge any air or use a cotton swab to remove the more stubborn ones.
10. Gently insert the thermometer. Check for air bubbles. Set aside for temperature to equilibrate. Record the temperature.
11. Rinse the outside of the pycnometer with water, then acetone and finish with air stream. Put the top on the side arm.
12. Weigh the pycnometer and liquor and record this weight.
13. Clean the pycnometer and repeat with fresh sample.
14. Do the analysis in triplicate, calculate the density and average the results.

Calculations:

Equation for Volume of Water at 1 atm (from *Handbook of Chemistry and Physics 63rd Ed*, p. F-6)

$$\rho, \text{kg m}^{-3} = (999.83952 + 16.945176t - 7.9870401*10^{-3}t^2 - 46.170461 * 10^{-6}t^3 + 105.56302 * 10^{-9}t^4 - 280.54253 * 10^{-12}t^5) / (1 + 16.879850 * 10^{-3}t)$$

$\rho, \text{g/cm}^3 = (\rho, \text{kg m}^{-3}) / 1000$ $\text{cm}^3 = \text{ml}$ $\rho = \text{g/cm3 or g/ml}$

To find volume of chosen pycnometer, calculate density of water at temperature tested.
Subtract tare weight of pycnometer from full pycnometer to get weight of the water.
Divide grams water by density of water to get volume of pycnometer.

$$\rho_{sample} = g_{sample} / ml_{pyc}$$

of density of viscous fluids were tried for liquors without success. These included TMA methods. The method that was finally found to be successful and that was adopted for this work was comparison pycnometry using permanent gas displacement. Fortunately, a new instrument, Micromeretics' Accupyc, became available, and it was adapted for our use.

The principle of comparison pycnometry is simple. Two chambers of known volume are connected by a line containing a valve. A sample of known mass of the material whose density is to be determined is placed in one of the two chambers. The chambers are flushed with a permanent gas and closed to the surroundings. The valve between the chambers is closed and additional gas is introduced into the chamber that does not contain the sample to raise the pressure in this chamber. The pressure difference between the chambers is measured as well as the absolute pressure in the chamber that does not contain the sample. The valve between chambers is opened, the pressure allowed to equilibrate, and the final absolute pressure measured. Since the initial pressures, the final pressure, and the chamber volumes are known, the volume of the mass of sample can be calculated by the simple application of the ideal gas law.

The Accupyc 1330, manufactured by Micromeretics, was found to be ideal for our work with some minor modifications. In this device, helium at elevated pressure is used as the permanent gas. Both chambers are contained in a massive aluminum block for temperature uniformity and the temperature of the block is measured by a resistance thermometer. The pressures and the pressure differences are measured by electronic pressure transducers of very high sensitivity. The instrument is supplied with aluminum sample holders that fit snugly into the chambers. These were replaced with stainless steel sample holders. Aside from this, the instrument was found to be suitable as supplied by the manufacturer.

Sample loading still required refinement. Samples in the intermediate range of solids concentration (40-60%) could be heated, poured into the sample container, cooled,

and then used for measurement. Samples in the higher solids range (60-80%) had to be formed into a "dollop" carefully, and the "dollop" loaded into the sample holder, cooled, and then used for measurement. Samples in the highest concentration range (80-100%) were cooled to low temperature, powdered, the powder loaded into the sample holder, warmed, and then used for measurement.

The Accupyc must be calibrated and sample holders must be of equal mass (equal volume) if more than one sample holder is used. Four stainless steel sample holders were used and these were matched in mass to the nearest 0.1 mg. Specially ground spherical balls made of Invar that were supplied by Micromeretics were used for calibration. The volume of these balls was known to better than 1 part per million. The balls were washed, dried, and weighed to within 0.02 mg when used to insure that the balls had not changed. The calibration procedure used is described briefly in Table 21. More complete details can be obtained from the instrument manual and were also described in one of our research publications (Zaman, 1994). The instrument includes a microcomputer for making density calculations from the measurements. A sample holder (or cup) is placed in the measuring chamber and the volume of the sample holder determined just as one would determine a sample volume. Since the initial pressure in both chambers, the high pressure in the gas chamber, and the final pressure in the chambers are known, the effective empty volumes of the gas chamber and of the sample chamber containing the sample holder can be calculated by application of the ideal gas law. These volumes are recorded in the memory of the computer. An Invar calibration ball (or balls) is then placed in the sample holder and the volume of the chamber containing the sample holder and the ball (or balls) is determined. Since the volume of the chamber and the sample holder are known, the volume of the Invar balls can be calculated by difference and compared to the known value. If values agree, the instrument is calibrated and the calibration constants for the instrument are automatically entered into the microcomputer program.

TABLE 21

Density by Micromeretics Accupyc 1330 Helium Pycnometer

Densities of liquors at solids concentrations above about 50% solids are very difficult to determine at low temperatures due to viscosity. Procedures have been developed for these measurements with an instrument based upon the principle of gas displacement pycnometry.

Start-Up and Calibration:

This must be done each time the instrument is turned on.

1. Turn Accupyc on.
2. Open valve to Helium tank (blue). Make sure the pressure regulator is set for ~20 psi.
3. Choose one of the 4 numbered sample cans to calibrate.
4. Place empty cup into chamber and press the white button, followed by "calibrate".
5. Make sure the volume of the calibration standard is correct.

   Volume for ball #1 and #2 is 2.095028 cm^3 for each one with a combined volume for both of 4.190056 cm^3
6. Make sure the can is empty, clean and dry. Press **enter** twice.
7. When the instrument beeps, place the calibration ball(s) into the sample can and follow directions.
8. Because each of the four numbered sample cans are of equal mass, they can be all be used for analysis without recalibrating the instrument. If a different can is used then calibration must be repeated using that can.

Sample Can Loading:

1. Weigh the clean, dry sample cans and record weights (see step 8 above). Make up 3 sample cans for each sample and run the analysis on each can to get an average density.
2. For Samples in the 40-60% Solids Range:
   a. Heat the sample bottle at about 80-110°C until the liquor pours easily (~ 30 min).
   b. Pour heated liquor into the tared can until 1/2 to 3/4 full.
   c. Firmly tap the can on the counter top to dislodge any air bubbles from the sample.
   d. Weigh sample in can, and subtract the can tare weight to obtain the sample weight.
   e. Cover can with Parafilm, and allow the sample to cool to room temperature.
3. For Samples in the 60-80% Solids Range:
   a. Get a small glass sample jar (the short, fat kind with a plastic lid).
   b. Fill jar with liquor sample. It is helpful to use a screwdriver or the "heavy" spatula
   c. (with the spoon on the end) to scoop out the liquor. Put lid on jar.
   d. Place glass jar in an oven at about 80-90°C for ~ 30 minutes or until sample is fluid.
   e. After the sample is fluid, scoop out the sample with a spoon shaped spatula.
   f. Try to form a "dollop" ; as the sample cools, use fingers to pull/stretch into a raindrop shape.
   g. Allow the sample to cool slightly and place in can.

   Weigh sample in can, and subtract the can tare weight to obtain the sample weight.

   Cover the can with Parafilm and allow the sample to cool to room temperature.

Analysis:

1. Remove Parafilm cover from can.
2. Place sample in Accupyc, press the white button, followed by **analyze**, then enter sample ID and sample mass, ending with the **enter** button to start the analysis.
3. When the instrument stops its automatic operation, it will beep 3 times and display a **reload** message. Press the **choice** button.
4. Record the sample density and the standard deviation.
5. Record the ambient temperature.
6. Repeat the analysis using the next two cans and record the density/deviation of each.
7. Average the 3 runs to obtain the density of the sample.

Replicate measurements were always made using identical sample holders. The samples were loaded into the sample holders as described in Table 21, cooled or heated to the measurement temperature, weighed, and the density determined. The temperature of measurement and the measured density were recorded. The entire instrument was contained within a plexiglass enclosure to minimize ambient temperature transients; normally temperature transients were not detectable and the temperature of measurement was well within 0.1C of the ambient temperature. Replicate measurements normally agreed within 0.06% or less. When one considers the problems of loading, the fact that weighings and instrument calibrations must be done, and that the measurement itself is subject to error, this is quite remarkable precision.

There was one uncertainty with respect to use of this device with black liquor- the question of volatilization. Even though vapor pressure data were available that could be extrapolated to low temperatures, the effect of volatilization on the measurement could not be estimated precisely, because the extrapolation was large and the measurement itself is of short duration. Therefore, measurements were made on liquors for which measurements could also be made by glass pycnometry; that is, in the 40-50% region of solids for some liquors. Measurements made on these liquors resulted in very close to exact agreement for density as determined by the two methods. This is evidence that the volatility of the liquors does not introduce error in the measurement by comparison pycnometry for solids concentrations greater than 40%.

One should also note that the comparison pycnometry method gives the true density of the material, regardless of the sample shape or size, as long as there is no occluded void volume within the sample. Therefore, if proper care is exercised in excluding occluded air from the sample, a true density can be obtained, even for powders. One should also note that replicate measurements were always made; therefore, occluded void volume would be noted, because this would result in large differences in the measured densities of replicate samples.

Thermal expansion was also determined for the liquors. A variety of techniques were examined. TMA analysis as it is presently used for polymers and solids was found to be unsuitable, since the liquor is too fluid and reacts with liquids normally used for sealing fluids. Therefore, absolute dilatometry was used. A variety of dilatometer designs were tested. The dilatometer adapted for our use was a dilatometer intended for fats and for plymer reacion determinations.

Numerous attempts were made to try to use the dilatometers with liquor only. For a variety of operational reasons, this could not be done, and measurements were made using mercury as a seal fluid. Multiple dilatometers were used. These were placed in a well stirred temperature control bath using silicone oil at the bath fluid. The bath temperature could be controlled to within better than 0.1C from 10 to 130C. Levels in the dilatometer capillaries were measured to within 0.01mm with a cathetometer located on a firm stand within 1 m of the cathetometers.

Each dilameter was calibrated with mercury. The procedure is given in detail in TABLE 22. The dilatometer was filled with a known mass of mercury (about 200 gms +/- 0.003 gms or about 15 parts per million). The loaded dilatometer was placed in the bath and allowed to reach temperature equilibrium with the bath. The height of the zero mark and the height of the mercury level of the capillary of the dilatometer were measured with the cathetometer to determine the height of mercury in the dilatometer capillary above the zero mark. This was repeated at intervals of about 10C for the entire temperature range from 10 to 130C.

Since the density of mercury as a function of temperature is known accurately, the volume of fluid in the dilatometer as a function of fluid height above the zero level in the dilatometer could be calculated. This begs the question of the effect of temperature on the change in volume due to the expansion of the glass. Even though the manufacturer assured us that this was negligible, this effect was checked. The change in volume of the glass apparatus was estimated by using the equation recommended for expansion of glass

TABLE 22

Procedure For Dilatometer Calibration

1. Load Dilatometer with known mass of deionized water and place in temperature bath.
2. Set temperature at lowest temperature to be used. allow temperature to equilibrate, measure reference height and water height in capillary arm with a cathetometer. record temperatures and differences in heights.
3. Repeat step 2 at 5-10°C increments to 90-95C.
4. Regress height difference vs. temperature.
5. From handbook value of density for water ar 25C. determine volume of dilatometer corresponding to height difference in capillary at 25C.
6. Using handbook values for density of water. determine volume correponding to height difference in capillary at each temperature.
7. Regress volume vs. height difference in capillary.
8. Load Dilatometer with known mass of mercury.
9. Set temperature at lowest temperature to be used. allow temperature to equilibrate, measure reference height and water height in capillary arm with a cathetometer. record temperatures and differences in heights.
10. Repeat step 2 at 5-10°C increments to 90-95C.
11. Regress height difference vs. temperature.
12. From handbook value of density for mercury ar 25C, determine volume of dilatometer corresponding to the height difference in the capillary at 25C.
13. Using handbook values for density of mercury, determine volume correponding to the height difference in the capillary at each temperature.
14. Regress volume vs. height difference in capillary.
15. If regressions do not agree, repeat procedure.

Normally, the calibration with mercury was more accurate. The calibration regression was nearly linear and precise to better than 1 part per thousand.

apparatus from the Chemistry and Physics Handbook. The calibration was done with slightly different volumes of mercury. Finally, the thermal expansion of water was measured and compared with the accepted literature values.

In all three cases, the effect of glass expansion was shown to be negligible compared to errors in measurement of fluid mass and fluid height in the capillary. The calibration with mercury was replicated and the calibration of dilatometer volume vs. capillary height used for further work. This was repeated for each dilatometer used in this work. Calibrations for each dilatometer were determined and fitted to second order polynomials relating dilatometer volume to capillary height above the zero mark.

The procedure used for thermal expansion measurements of black liquor is detailed in Table 23. The level of the cathetometer was always checked and the cathetometer leveled, if necessary. The bath temperature was set to the lowest temperature to be used, usually 20C, but sometimes 0 to 10C. The dilatometer was loaded with a known mass of mercury (determined by difference of two weighings) and the mercury was drawn up into the measuring capillary a short distance above the zero mark. Black liquor was then poured carefully into the dilatometer to fill it and the ground glass cap fitted into place and sealed so that no air was included in the dilatometer volume.

The outside of the dilatometer was carefully washed and cleaned and the loaded dilatometer placed in the temperature bath and allowed to come to thermal equilibrium with the bath. One should note that the mass of liquor loaded into the dilatometer was not determined directly by weighing. The detailed procedure given in Table 23describes the steps necessary to insure that no air is present in the dilatometer volume. The sample identification, the dilatometer number and dilatometer cap number, and the mass of mercury in the dilatometer were all recorded. At each temperature of measurement, the height of the zero mark and the height of mercury in the dilatometer capillary were measured using the cathetometer. The difference in cathetometer readings gives the

TABLE 23
Thermal Expansion of Black Liquor
Procedure:
1. Make sure cathotometer is level.
2. Turn on cooler for oil bath.
3. Turn on oil bath heater. Set temperature for ~ 20°C.
4. For samples in 60-80% solids range, heat samples so they can be well-mixed.
For samples <60% solids, mix well, but try not to incorporate air into the sample.
5. Weigh out 30-40g mercury in a tared, 11-ml vial. Record mass of mercury.
6. Carefully pour the mercury into a clean, calibrated dilatometer. Check for air bubbles trapped
in capillary tube or in the bowl of the dilatometer. Use a rubber bulb to force mercury to travel into the
column until the bubble is removed. Use a fine wire to displace air bubbles if necessary.
7. Coat the cap of the dilatometer with vacuum grease. Do not get any on the bottom part of the
cap since that will change the volume of the dilatometer. Insert cap into seat of dilatometer to
coat the ground glass wall where contact occurs. Remove cap and wipe excess from the
bottom edge where contact doesn't occur.
8. Carefully pour the liquor into the bowl of dilatometer until it is almost overflowing. Insert dilatometer
cap allowing air bubbles and excess liquor to escape over top of bowl. The mercury will be
displaced up the capillary tube. Check mercury height in the tube; it needs to be over the
0-mark and less than ~1/3 height of tube to allow for expansion. If this is not the case, either
remove cap and either add more liquor or release a little to adjust the volume. Check for air in
mercury column. If air is caught in column, release cap, add more liquor if necessary and
reseat cap.
9. Rinse liquor off the closed dilatometer and secure dilatometer cap using available springs.
10. To check for air bubbles in liquor, bounce the bowl of the dilatometer firmly in your palm. Watch
the mercury height. If it also bounces, air is present in the liquor bowl. A visual check can also
be used. Fill a 500ml graduated cylinder (~1/3 to 1/2 full) with gasoline (do this under the hood),
immerse dilatometer in the gasoline and look for any air bubbles. The gasoline has an index of
refraction close to glass and you can see easily into it.
11. After air has been removed, secure dilatometer in the oil bath by means of the clamps.
12. Record sample ID, dilatometer # and dilatometer cap # (they must either match or have been
calibrated together), mass of the mercury, height of the 0-mark, height of the mercury column
after temperature has stabilized, and the temperature of the oil bath.
13. After the 20°C reading has been made, turn off the cooling unit, raise the temperature in 5-7°
increments, record mercury height and temperature of oil bath. Continue this until 90-100°C
has been reached.
14. Turn off oil bath heater.
15. Remove dilatometers and release the liquor. Save mercury and rinse it clean. Put it in a
separatory funnel with soap, shake sep funnel and drain off mercury. Store in Nalgene bottle.
Clean the dilatometers immediately since NaOH in the liquors can pit the glass.
If the cap will not come off, soak dilatometer in gasoline to help loosen cap.

height of mercury in the capillary above the reference. This was repeated at temperature intervals of 5 to 10C from the lowest temperature to the highest.

An example of data and data treatment is given in Table 24. Note that the sample and the solids concentration are clearly identified. The dilatometer and dilatometer cap numbers are recorded to insure that the proper calibration is used. The constants for the second order calibration equation relating dilatometer total volume to capillary height above the reference mark are given (note that the second order term is extremely small). The mass of mercury loaded is given to the nearest 0.1 mg and the second order equation for the density of mercury as a function of temperature determined from literature values for mercury density is given.

For any one temperature, the volume of mercury can be calculated from the known mass and the density equation, the total volume of fluid in the dilatometer can be calculated from the height of fluid in the capillary above the zero(or reference) mark, and the volume of black liquor in the dilatometer determined by difference. The values for black liquor volume at different temperatures are fitted to a second order polynomial relating volume in the dilatometer to temperature. The density at one temperature will have been determined by one of the two pycnometer methods used at some temperature between 20 and 35C. The regression equation relating black liquor volume in the dilatometer to temperature is used to calculate the volume in the dilatometer at the temperature at which the density is known (in the example given, this is at 22.9C). From these two values, the mass of black liquor in the dilatometer can be calculated very accurately. The mass of liquor in the dilatometer is a constant for any one set of measurements. This constant can then be used to transform the relation between liquor volume and temperature to yield a second order regression equation relating black liquor density to temperature.

This is repeated for the same liquor at different solids concentrations to develop a complete mapping of liquor density vs. concentration and temperature. In most cases,

TABLE 24

Thermal Expansion of Black Liquor, Example

Dilatometer # = 254/254

Dilatometer Calibration: Vol. Dil.= 11.95724+0.002684*Ht +0.00000406*Ht^2

Mercury Volume: Vol Hg = 13.59548569-0.00247057*T+0.00000038*T^2

Mass Hg Loaded: 155.0206 gms

Dilatometer Data:

Temp	0 Mark	Hg Ht	Δ Hg Ht	Vol. Hg	Vol. Total	Vol. BL
deg C	mm	mm	mm	cm^3	cm^3	cm^3
23.6	21.77	68.42	46.65	5.054149	12.09128	7.037134
35	21.77	69.35	47.58	5.064591	12.09414	7.029544
32.15	21.77	73.59	51.82	5.06198	12.10723	7.045246
45.2	21.77	81.43	59.66	5.073939	12.13182	7.057877
59.2	21.77	89.85	68.08	5.086777	12.15878	7.072004

Regress Black Liquor Volume (Vol BL) vs. temperature

Vol BL = 9.862409+0.003731*T+0.0000248*T^2

From pycnometer data: density at 22.9°C (g/cm^3): 1.2933

Calculated Vol. BL (cm^3) at 22.9°C: 9.960845

Calculated Mass BL (g): 12.88236

Calculated Density at 25°C (g/cm^3): 1.29196

Since the mass of liquor in the dilatometer is constant (12.8824 gms) and the volume of the dilatometer is known at each temperature, the vol Bl data can easily be converted to density BL vs. temperature.

problems with exclusion of air limited measurements to concentrations below about 80% solids. One should note that a large number of direct measurements are involved. Even though care was exercised in making each of these as carefully and as precisely as possible, any one value for density at a given temperature is probably accurate to only about 0.05%.

It was of value to calculate density as a function of solids at constant temperature for the liquors. This was always done for a temperature of 25C. Virtually all liquors exhibited similar behavior. From zero to some concentration in the range of 60-70% solids, the relation between density and concentration was linear. Above this concentration, the relation could be represented by two straight lines for different solids concentration regions, and the slopes of the three straight lines needed to fit the data were not equal. This indicates that the derivative of density with respect to concentration at constant temperature and pressure has two discontinuities; that is, there are two second order thermodynamic transitions for the liquor at different concentrations. The first (the one that occurs at about 60-70% solids at 25C) is apparently related to the transition that occurs in phase transition at low temperatures from freezing to glass transition. The second (the one that occurs at 80-85% solids at 25C) is apparently a transition from fluid behavior to plasticized glass behavior.

In the lowest concentration region, the density and thermal expansion data can be reduced and treated successfully by using corresponding states principles, but these cannot be used for the data at higher concentrations. The line relating density to concentration in the highest concentration region has the lowest slope, as one would expect for the plasticized glass region for a polymer. Theoretically, it should be possible to determine the relation between temperature and concentration for each of the two second order transitions by using the thermal expansion data. This has not been done to date. It is of interest to try to do this.

Above the second transition, the liquor can be expected to exhibit very strong viscoelastic behavior that would make droplet formation virtually impossible which would define the upper limit for application of present recovery furnace operation. Between transitions, the liquor can be expected to exhibit non-Newtonian behavior that, while not making present furnace operation impossible, could limit operation to certain conditions.

7.2 Heats of Combustion. The heats of combustion of liquors were determined using a Parr 1241 automatic adiabatic bomb calorimeter by a method that is very close to TAPPI Method T 684 pm-84. Normally, freeze dried samples of black liquor at 100% solids were used, although some tests were run with liquors at 65-85% solids that had been prepared by evaporation in our small scale evaporator. The detailed procedure used in given in Table 25.

Solid samples were pelletized using the pellet press supplied with the instrument. Normally, 1-1.5 gms of sample was pelletized. The pelletized sample was placed in a vial and redried in the freeze drier to insure dryness.

The bomb was cleaned, the fuse wire put in place, the weighed sample placed in the sample holder, and the bomb closed. The bomb was then charged with oxygen automatically to 425-450 psig and then was closed. The calorimeter bucket was tared and filled with 2000 gms of water. With the thermometer in place and the stirrer on, the bucket and jacket were allowed to reach thermal equilibrium. The Parr 1710 controller was turned on and the operator was prompted step-by-step through the combustion operation that was conducted automatically. When the process was completed, the bomb was removed from the bucket, opened, the unburned fuse removed and weighed, and the bomb washed with a known volume of distilled water. The washings were tested with methyl orange or methyl red indicator. If a pink color developed, the washings were titrated with 0.070 N sodium carbonate solution to determine an acid correction term for sulfur. The sample mass and temperature rise were recorded to be used to calculate the

TABLE 25

Heat of Combustion Measurements

Parr 1241 - Adiabatic Bomb Calorimeter

This system has several parts: the pellet press, the bomb, the autocharge system, the calorimeter controller, the calorimeter and the heat/cool system associated with it.

Procedures:

The Pellet Press:

1. When measuring freeze-dried samples, use the pellet press to form the sample into an easily handled pellet.
2. Weigh out about 1.25 grams sample in a small plastic weighboat or beaker.
3. Pour the sample into the stainless steel die, beveled side up, which should be sitting on the flat side of the die holder.
4. Set this assembly on the pedestal and compress the sample. The lever should require a firm push all the through its full stroke. If it does not move a full stroke, lower the pedestal by turning the pedestal clockwise. If the lever moves through a full stroke but there is no resistance, the pedestal is too low. Raise it and try again. The sample may require several strokes to tamp it down to a firm pellet.
5. Raise the lever and slide the die and holder off the pedestal. Reverse the holder and return the die and holder to the pedestal. Raise the pedestal a few turns.
6. Lower the lever gently to eject the pellet. The pellet may need to be sliced off the end of the punch. Use a flat spatula if necessary.
7. Remove the pellet carefully with forceps and place it in a tared 30ml vial.
8. Find the mass of the pellet and record this number. The mass should be ~1 gram.
9. Clean and dry the punch, die and die holder.
10. Remember, when working with black liquor, that it is hydroscopic and will absorb water quickly. If the pellet-making process takes a while, place the finished pellet in a 30ml short, fat vial, cover top with a small piece of Kim-wipe and secure it with a tiny rubber band (found in freeze-dry appartus drawer), and return this assembly to the freeze-dryer for a final drying before measuring the mass.

Loading The Bomb:

1. Before using the bomb, ensure that it is clean, the surfaces are smooth and look polished, the seals look good, and the threads are in good shape.
2. Set the bomb head on the support stand and attach a 10cm length of nickel alloy fuse wire to the electrodes. Pinch the center of the fuse wire and bend it to a straight line with a *u* or *v* shape in the middle that will touch the sample pellet.
3. Move the sample pellet from the vial to the sample holder. Place the sample holder in the ring formed by the electrode. Push the fuse wire down until it makes good contact with the sample.
4. Lift the entire head assembly and carefully lower into the bomb body. Do not tilt.
5. Lower the screw cap over the head and onto the bomb body and tighten the cap firmly by hand as far as it will go.

Filling the Bomb Using the Parr 1841 AutoCharge System:

1. Turn on oxygen tank. The regulator should be set to ~475psig.
2. Connect the hose from the autocharger to the bomb inlet valve (the smooth, solid peg on top with the small hole in the side) by just sliding it over the peg.
3. Press **Start**. The autocharger will fill the bomb to 450psig. If the charge goes correctly, the yellow light will glow to indicate a full charge. If the charging pressure does not reach the range of 410-425psig, the low charge light will come on. Check pressure in oxygen tank and make sure valve is open. If these are not the causes of the low fill, look for gas leaks.

TABLE 25 (continued)

Heat of Combustion Measurements (continued)

Parr 1241 - Adiabatic Bomb Calorimeter (continued)

Procedures: (continued)

Setting the Calorimeter for a Bomb Run:

1. Lift the bucket thermometer by pulling the black release button and sliding it up until it clicks. The thermometer will remain in place until it is lowered again.
2. Just below the motor on the lid is another black release button. Pull it and lift the lever to allow the lid to swing open to the right. Release lever and remove the bucket.
3. Tare the calorimeter bucket and fill with 2000 g DI water.
4. Set the bucket in the calorimeter with the two dimples to the back and the one dimple to the front. Make sure the ignition wires remain free.
5. Plug the ignition wires into the two outlets on the bomb top and lower the bomb into the bucket taking care to span the circular boss on the bottom of the bucket. Shake off into the bucket any water that remains on handle or fingers.
6. Close the calorimeter cover and return thermometer to its former position.
7. Turn on the power switch to start the motor and let it run for 4 or 5 minutes until the jacket and bucket reach equilibrium.
8. Turn on the Parr 1710 calorimeter controller and press the **Start** key.
9. The EE light will flash asking for a bomb letter designation, A or B. Push the correct letter and the controller should produce the EE value stored. If the power has been disconnected, the EE values will be lost and need to be reentered by pressing **Reset** followed by A or B and the corresponding EE values.
10. The next request is for sample weight. Enter this data now.
11. The PRE light will show and this is a check for thermal equilibrium.
12. As soon as this has been met, the FIRE light comes and ignition hopefully begins. This light operates for 50 seconds and a temperature rise of 0.05 °C is required for the operation to continue.
13. If firing is confirmed, the POST light comes on and the instrument waits for a final equilibration. An end of test signal will sound and the system returns to its starting configuration and a preliminary test result will be displayed. Record this number and the total rise in temperature.
14. The calorimeter can now be opened and the bomb removed for clean-up.
15. Remove bomb to the hood and slowly open the bleed valve and let the gas release.
16. After pressure is released, untighten the cap and remove the bomb head.
17. Rinse interior parts of bomb head, fuel capsule and bomb interior itself with DI water. Retain these washings in a clean, Nalgene bottle.
18. Check washings with methyl orange or methyl red indicator. If pink color develops titrate with 0.0709 N Na_2CO_3 solution. Record this information.
19. Set fuel capsule under running hot water to dissolve any residue left from bomb.
20. Remove remaining fuse wire from the electrodes and record their length.
21. Perform all tests in triplicate.
22. Enter data in the computer as follows

Sample I	Run #	Bomb ID	Smp Mas	E	ΔTemp	fuse rem	pH	ml tit	Corr Hg
4344 -80	1	A	1.3341	4970.75	1.5326	5.4	3.3	1.3	4963
	2	B	1.3057	4993.8	1.5082	2	7	0	4980
	3	A	1.3253	4990.93	1.5287	2.4	8.16	0	4978
						Average Corr Hg			4973
						Standard Deviation			7.54

TAPPI Method T 684 pm-84.

uncorrected heat of combustion. The unburned fuse wire mass and the equivalents of sodium carbonate used to neutralize the washings were recorded and used to correct the heat of combustion measurement. Measurements were normally made in triplicate and the average value reported. The standard deviation was normally about 0.1 to 0.2%, depending upon the solids concentration. An example of data for one liquor sample is shown in Table 25.

Heats of combustion for a number of liquors were determined at different solids concentrations between 65 and 100% solids. These data were plotted vs. solids concentration to verify that heat of combustion is a linear function of solids. This proved to be correct. Thereafter, heats of combustion were determined using 100% solids samples that had been prepared by freeze drying. Heats of combustion were determined for liquors resulting from pulping Slash pine at various pulping conditions and heat of combustion was successfully correlated as a function of pulping conditions and as a function of solids composition for these liquors.

Surprisingly, heat of combustion did not correlation as a additive function of components in the liquor solids as has been assumed in the past, but correlated as a non-linear function of solids composition. Also, heat of combustion varied considerably with pulping conditions or solids composition, indicating that change in pulping conditions can result in changes in heat of combustion of the liquor solids that is considerably greater than is currently accepted by many practitioners.

7.3 Transition Temperature Measurements. A Perkin-Elmer System 7 Differential Scanning Calorimeter (DSC) was used in the Differential Thermal Analysis (DTA) mode to determine transition temperatures. The System 7 is a true differential calorimeter in that the heat flux to a standard and to an unknown sample is measured by difference at identical temperatures for the standard and unknown, rather than by measuring the temperature difference between the standard and unknown for identical heat flux to both

as is done in DTA. Using DSC in the DTA mode is preferred, since transition temperatures can be determined more accurately and precisely in this manner. The change in heat flux between the standard and the unknown as the temperature of both is increased or decreased determines the difference in enthalpy needed to keep the temperatures identical. If there is no transition in the standard, the difference will be a smooth curve if there is no transition in the unknown. If the unknown undergoes a first order thermodynamic transition (such as freezing or melting), the heat flux difference will exhibit a spike (in the ideal case, go to infinity) at the transition temperature. The spike will be exothermic for freezing and endothermic for melting, for example.

Normally, the first order transition occurs over a temperature range during this measurement. The range is defined by the smooth curves that exist on each side of the transition temperature region. The transition temperature is normally taken as the mid point of the defined region. This is a dynamic measurement used to define a thermodynamic quantity. Experimentally, the measurement should be repeated at different rates of temperature change (scanning rates), the transition temperature plotted vs. the rate of temperature change (scanning rate), and the resulting line or curve extrapolated to zero rate of temperature change (zero scanning rate).

Second order thermodynamic transitions (such as glass transitions and strong short order rearrangement transitions) can also be determined using DSC in the DTA operating mode, if the transition results in a relatively significant change in heat capacity change with temperature or density change with temperature. In DSC, this will be shown by a region of rapidly changing difference in enthalpy between standard and unknown over a small temperature interval, usually with an inflection in the difference in enthalpy in the region as the temperature is increased. Smooth curves for the enthalpy difference are drawn through the data on each side of the region and extrapolated into the region. The upper and lower temperatures where the data departs from these curves defines the temperature region for the transition. The transition temperature is taken as the mid point of this region.

Again, this is a dynamic measurement used to determine a thermodynamic quantity (the transition temperature). Therefore, the experiment should be repeated at different rates of temperature change (scan rates), the results plotted as a function of scan rate and extrapolated to zero scan rate to determine the transition temperature. This method was followed in most of our work.

Both first order and second order transition temperatures were determined in this work with important consequences. Massee (1984) showed that black liquors would undergo a first order thermodynamic transition (freezing) only at concentrations below about 42% solids and further demonstrated that this behavior was general for solutions of non-polar and polar amorphous polymers. Also, he demonstrated that freezing occurred at practical temperatures only up to about 30% solids. This research resulted in abandonment of work in freeze concentration of black liquors to high solids which saved DOE considerable research expenditure.

It has also been demonstrated that the quantitative behavior of freezing point with concentration at low solids concentration is a function of the composition of the solids. Glass transition (a second order thermodynamic transition) has been determined for black liquors as a function of solids concentration up to and including 100% solids, for purified lignins, and for solutions of purified lignins. The relations of glass transition vs. solids for black liquors have been used successfully as the reference temperature for correlating high solids rheology data in the form of master curves, as has been done for polymers and concentrated polymer solutions.

7.4 Heat Capacity Measurements. Heat capacities of black liquor and of purified lignins were determined from differential scanning calorimeter (DSC) measurements using sapphire as a standard. Measurements were made using the Perkin-Elmer System 7 DSC unit in the DSC mode of operation. Unknowns and standards were loaded into stainless steel pans with gasketed sealed covers. Quantitative determination of heat capacity requires several individual scans to calibrate the instrument and to determine the heat

capacity of the unknown by comparison to the standard. Moreover, the heat capacity can only be determined after the rate of temperature change (the scan rate) has been established at a constant value and measurements are only valid for the temperature range in which no first order thermodynamic transition occurs. In this section, the procedure used is described in detail, since the procedure required considerable development and because it is not in general use.

Sample loading is very important. Detailed instructions for sample loading are given in Table 26. An M-3 Mettler Microbalance sensitive to 0.001 mg was used for all weighings. Sample pan bottom, top, and O-ring seal supplied by Perkin-Elmer were each weighed. Since there were small variations in mass for the parts, these were carefully selected to match weights as closely as possible and the metal parts were filed to match weights exactly in many cases. The sample was loaded into the bottom of the pan with an Eppendorf micropipette if liquid or a small spatula if solid. A sample size of 8-30 mg was typically used. The pan top containing the O-ring was then placed on top of the pan bottom, the assembly placed in a press, and top and bottom pressed together to form the seal. The assembled pan and sample were weighed and then placed in a sealed glass vial until used. The standard, a sapphire disc of certified purity supplied by the National Institute of Science & Technology, was sealed in a pan in a similar manner with weights determined as described.

Quantitative determination of heat capacity by DSC requires three separate determinations: a "blank" run to set the base line, a standard run to determine the standard with the standard sapphire, and the sample run to determine the sample heat capacity. Each are run in a similar fashion by the steps described in Table 27 for "Operating Instructions for DSC 7-Perkin-Elmer 7500". In the "blank run", no pans are placed on the pan holders and the sample mass is set at 0.000 mg. A temperature scan is run with the instrument controlled by the computer to maintain the temperature difference between pan holders at zero and to maintain the rate of temperature increase constant at

TABLE 26	
Sample loading for DSC Measurements	
1	Use Mettler M3 microbalance for all weighings.
2	Use Part Numbers 319-1525 (bottom), 319-1526 (top), and 319-1535 (O-ring) for each sample.
	Do not handle these parts with bare fingers since the oil from your skin can affect the analysis.
3	Use tweezers to manipulate the parts and use a vial to transport the loaded sample pan to the DSC.
4	Weigh and record weight of empty pan (top and bottom).
5	Weigh and record weight of empty pan (top, bottom and O-ring).
6	Insert the O-ring into the top pan.
7	Place the bottom pan on circular impression milled into the surface of insert for press.
8	For liquid samples, use 100µl Eppendorf to fill bottom pan.
9	For more solid samples, use a tiny spatula to add sample to the bottom pan.
	Working quickly to minimize any evaporation, invert top pan with O-ring and place on bottom pan.
10	Place press insert into press.
11	Gently squeeze press handle so that the top and bottom are sealed. Don't squish the pan.
12	Weigh and record total mass of pan plus sample. Subtract out pan mass to get sample mass.
	Pan Correction Factor = PCF
	PCF = (sample pan - blank pan) * 0.0823

TABLE 27	
Operating Instructions for DSC 7 - Perkin-Elmer 7500	
Run Procedure:	
1	Turn on Nitrogen.
2	Open DSC purge valve.
3	In this order, turn on DSC7 (instrument), TAC7 controller (bottom shelf), plotter. then computer.
4	Type: **idris**, hit **enter** key.
5	Type: **tas7**, hit **enter** key.
6	At prompt, hit return or **enter** key.
7	After a short time, upper lefthand block should be red and read **T1 DSCA _.___mw**
8	If it does not, shutdown system, following protocol, and repeat startup.
9	Open furnace area by lifting handle and swinging gate to the right.
10	Lift covers from pan holders using the fine tip right angle tweezers to insert into cover holes.
	(Remember their orientation and replace exactly as they were. This will increase reproducibility.)
11	Remove any pans from pan holders using tweezers. Do not use your fingers to hold them.
12	Place pans into appropriate vials.
13	Replace covers.
14	Close furnace gate.
15	In running samples, you need a blank run for correction, a standard run and the sample run.
	Each of these should be done using the same setup and method.
16	Set up or recall method for blank. (No pans)
17	Check that the sample weight is 0.000mg. If not, use soft keys **Sample Info**, then **Sample**
	Weight, then **Type in Weight**. Type weight used in sample (in this case, 0.000) then hit **Enter**.
17	Check that the mw reading in red block of left-hand corner is stable. If it is not, allow it to
	equilibrate before starting run.
18	Hit the soft key labeled **Start Run.**
19	Graph can be viewed by hitting **View Parameters** key at top left-hand of keyboard. This key
	toggles back and forth between the chosen parameters of the method and the graph.
20	After run is finished, give the graph a name (5 alphanumeric lowercase letters) to save file.
21	Open gate to furnace. remove covers, and place the standard in the left-hand holder and the
	blank pan in the right-hand holder. Replace lids exactly as removed. Close gate.
22	Set up or recall standard method.
23	Check that the sample weight agrees with the weight on the vial that the standard was stored in.
	If not, change it now.
24	Let mw reading stabilize before beginning run.
25	Hit the soft key labeled **Start Run.**
26	After run is finished. save file by giving it a name.
27	Open gate to furnace. remove covers and remove standard pan from the left-hand holder to its
	appropriate vial. Place the sample to be run in the left-hand holder and replace cover and gate.
28	Set up or recall method.
29	Hit soft keys **Sample Info, Sample ID, Sample Weight** and enter appropriate data.
30	Let mw reading equilibrate before beginning run.
31	Hit the soft key labeled **Start Run.**
32	After run is finished. save file by giving it a name.
Shutdown procedure:	
1	Hit **shutdown** key at top left of keyboard.
2	Computer will ask, "Are you sure ...?". Hit **Yes** key at upper right of keyboard.
3	Computer will say, **login:** Type **shutdown**.
4	When a blue bar at the bottom of the screen shows **OK to Power Down**, turn off computer.
5	Turn off Plotter, TAC7 and DSC.
6	Turn off nitrogen.

the desired scanning rate. The difference in heat input necessary to accomplish this is recorded as a function of time (temperature) in a file in the computer. The pan containing the standard is then placed in the sample pan holder and an empty pan assembly with a mass equal to the pan assembly holding the standard is placed in the reference pan holder. The control program is called and the mass of the standard is entered into the computer. A temperature scan is run under computer control as before and the heat input necessary to maintain zero temperature difference between sample holders is recorded as a function of time (temperature) in a file in the computer as before. The pan containing the unknown sample is then placed in the sample pan holder with an empty pan assembly of equal mass to the sample pan placed in the reference pan holder. The control program is called, the sample mass entered, and the scan run as before with data recorded in a computer file as before. These data are used to calculate the heat capacity of the sample as a function of temperature.

It is very important to allow the instrument to equilibrate between runs; this can be verified by letting the mv reading of the instrument reach a steady value. After each test, the pans containing the sample and the standard should be placed in glass vials and sealed to be retained for further testing, if necessary.

A pan correction factor is calculated, based on the difference in masses of the blank and standard pans without O-rings as given in Table 26. Obviously, this correction will be zero if the pan masses are perfectly matched. In most cases, they were not. In the example data layout given, the pan correction was 0.94% of the sample mass. The correction factor was used in the computer program to eliminate the error introduced by this difference.

A scanning rate of 3-10C per minute was normally used. For the data layout given, the scanning rate was 4C per minute. The enthalpy response (delta Y) for the standard and sample are as recorded in the computer files, corrected for base line effects determined in the blank run. The enthalpy responses (delta Y) are corrected for

differences in pan masses by using the pan correction factors. The enthalpy response (delta Y) scale is calibrated in enthalpy units from the run with the standard of known mass and heat capacity. This calibrated scale is used to calculate enthalpy for the unknown sample from the corrected unknown sample scan (corrected delta Y). The description of user interaction with the computer program to perform these calculations is given in Table 28 under the heading of "Data Processing".

The data are not optimized, since there are still differences resulting from slight differences in base line, start of scan, etc. These are eliminated or corrected for by using the computer program outlined in Table 28.

The first step is to align the beginning of the scans. The second step is to align the end of the scans. The third step is to set the base line by subtracting the blank curve. The results are two scans (one for the standard and one for the unknown) with matched beginnings and endings and a common baseline.

Using the scan for the standard to calibrate the ordinate of the scans, the unknown sample scan is quantified over the temperature span for which the rate of temperature change (the scan rate) is constant. This optimizes the data for the unknown so that the heat capacity can be calculated from the known mass of the sample and the quantified scan. These values, along with the scan results, the standard and sample masses, and the pan corrections are stored in a computer file. The calculated heat capacity results are transferred to another file as the experimental data of interest.

The computer program supplied with the 7500 control unit by Perkin-Elmer was satisfactory, but not ideal. Dr. Mark Stoy, as part of his PhD research, wrote a program in BASIC that is an improvement for data calculation. This program sources the raw data from the control unit and calculates heat capacity as a function of temperature using automatic routines for setting beginning and ending points, baselines, and calibrations for the scans rather than by using visual matching of scans for these corrections.

The program listing for Stoy's program is given in Table 29, which is an improvement over the program supplied by Perkin-Elmer that is outlined in Table 28.

Normally, a steady state rate of temperature increase could be established by the time the sample reached 35C from a starting temperature of about 25C. Occasionally, steady state was not reached until a temperature of 40C had been attained. At the other end of the temperature scale, evaporation from the sample in the pan became a problem, even though the vapor formed did not escape from the pan. When evaporation occurs, the heat of vaporization as well as sensible heat must be added to raise the sample temperature; therefore, the onset of vaporization was obvious from the results, since the calculated heat capacity (assuming no vaporization) begins to increase very rapidly when vaporization begins significantly.

Scans were always run to about 125C, but heat capacity data could normally be obtained to only 100C for most samples. Since the heat capacity of nearly all liquors proved to be a linear function of temperature at constant solids concentration up to at least 85% solids, this was not a severe limitation; the relation can be extrapolated to estimate the liquor heat capacity up to as much as possibly 150C.

Of more concern was the effect of scan rate, since this is a dynamic experiment that is being used to determine a thermodynamic function. Also, this is a comparative rather than an absolute method which introduces the possibility of additional error in measurement.

Replicate measurements were made and the total probable error estimated from the results. The determination of heat capacity for a given sample is estimated to have a maximum probable error of about 2%; in most cases, the error can be expected to be slightly in excess of 1%. Replicates were made at different scan rates using the same unknown. The optimum scan rate appeared to be 4-6C per minute.

TABLE 28	
Operating Instructions for DSC 7 - Perkin-Elmer 7500	
Data Optimization:	
1	If instrument is not running, turn on DSC, TAC 7 controller, plotter and computer, in that order.
2	Type: **idris**
3	Type: **tas7**
4	Press: **enter**
5	**T1 DSCA** will come up in red in the upper lefthand corner of the screen. Soon soft keys will light.
6	Press: **Recall Data**
7	Press: **Recall 1st**
8	**DSC7 Data** will be highlighted. Press: **Get Directory**
9	The files available on the hard drive will be listed. Recall the one you want by selecting it using
	the arrow keys on the right-hand side of the keyboard, then press **Recall File**. Start with the
	current standard reference.
10	Press: **Recall 2nd**
11	**DSC7 Data** will be highlighted. Press: **Get Directory**
12	This time select the current blank, and press **Recall File**.
13	After the files are recalled and on the screen, press **Exit**.
14	Press: **Optimize Data**
15	Press: **Shift Y**. This series of steps will let you adjust the lst graph to align with the blank.
16	Press: **Align 1st-2nd**. This step aligns the beginning of the curves.
17	Press: **Exit**
18	Press: **Slope**. This step lets you align the end of the curves.
19	Press: **Change Step Size.** The screen message will read **The current value is 10.**
20	Type: **1** then **enter**. Use arrow keys to change where the end of the 1st curve will be once
	the curve is sloped. If the 1st curve end is too high, use the down arrow to allow the curve to be
	sloped that direction. If the 1st curve end is too low, use the up arrow to raise it.
21	Press: **Slope**. Check alignment of curves and repeat if necessary.
22	Press: **Exit**
23	Press: **Exit** again.
24	Press: **Change Curvetype**
25	Press: **Subtract**
26	Press: **Replace 1st Curve**. The blank will be subtracted from the standard curve.
27	Press: **Exit**
28	Press: **Recall Data**
29	Press: **Erase 2nd**. This erases blank curve and leaves only the standard curve with the blank
	subtracted from it.
30	If a plot is desired, press **Plot** (above number pad on keyboard). Screen message
	says **Calculating**.
31	When message appears, position paper and press **Enter** on plotter to begin graph.
32	Press: **Exit**
33	Press: **Select Calc**
34	Press: **Delta Y**
34	Press: **Type in Limits**
36	Screen message reads **Enter new left limit. Current value is 0.00**, type in desired start of
	calculation. Example: **8** This will be 8 minutes into the analysis.
37	Screen message reads **Enter new right limit. Current value is 29.49**, type in desired end of
	calculation. Example: **26** This will be 26 minutes into the analysis.
	Screen will add delta Y data to the graph. Record T and Y for both ends of analysis.
38	Press: **Type in Limits**, repeat new limits in increments of 1 minute up and down until curve is
	finished and you now have a record of delta Y for entire curve.
39	Press: **Exit**
40	Press: **Exit**

TABLE 28 (Continued)	
Operating Instructions for DSC 7 - Perkin-Elmer 7500 (continued)	
Data Optimization (continued):	
41	Press: **Recall Data**
42	Press: **Recall 1st.** Repeat the entire process using the sample and the blank this time.
43	After the delta Y for the sample is calculated, leave this part of the system by pressing **Exit** twice
	followed by **Shutdown** hard key located in upper left corner of the keyboard.
44	The screen message will read **Are you sure you want the TAS7 software to shut down**
	(Yes or No)? Press hard key **Yes** above the number pad on keyboard.
45	Screen message will read **login:** Type **user** if you want to process data.
46	Type: **shutdown** if you are ready to leave the system.
47	Wait until the screen message reads **OK to Power Down** before turning off computer and DSC.
Data Processing:	
1	Before processing data. you must have Standard and Sample masses, pan correction factors
	for both Standard and Sample pans. the number of data points and the Delta Y for Standard and
	Sample.
2	The pan correction factor is calculated on the mass of the empty pans (no O-ring).
	0.118cal/gK * 10K/min * 1min/60sec *4.184 J/cal * (standard pan - blank pan(mg)) = mW
3	At the **login** prompt, type **user**.
4	At **$** prompt, type **ed testcpin.dat**.
5	The screen will show 5 lines of single numbers followed by sets of 3 numbers separated
	by commas.
	The first line is the number of data points.
	The second line is the mass of reference standard in milligrams.
	The third line is the mass of the sample in milligrams.
	The fourth line is the sample pan correction factor.
	The fifth line is the reference standard pan correction factor.
	The remaining lines are Temp K, delta Y reference, delta Y sample. The number of lines here
	must total the number entered in the first line.
6	Overwrite any data in this file and delete any unused lines.
7	When data entry is finished, press **file.**
8	At **$** prompt, type **basic**.
9	At **ready**, type **load "cpcal.bas"**.
10	Press **enter.**
11	At **ready**, type **run.**
12	Screen message will read **Enter name of data input file -> ?** Type **testcpin.dat**, press **Enter.**
13	Screen message will read **Enter name of data output file -> ?** Type filename**.dat**, press **Enter.**
14	Program will calculate and print to screen the **Temp K, Y smpl, Ystd, Cp smpl** for each data
	line. Record these numbers.
15	To leave data processing, type **system** and at the **$** prompt, type **shutdown.**
16	Wait until screen message reads **OK to Power Down** before turning off computer.

TABLE 29

Data Processing Program (by M. O. Stoy) for DSC 7 - Perkin-Elmer 7500

This program is on the P-E 7500 Hard Drive under the names "cpcal.bas" and "bjs.bas".

```
10  defint j,k
20  dim temp( 20), refscan( 20), smplscan( 20), corref( 20)
30  dim corsmpl( 20), index( 50), smplcp( 20)
40  input "Enter name of data input file-> "; infile$
50  input "Enter name of data output file-> "; outfile$
60  open "i", #1, infile$
70  input #1, npts&
80  input #1, refmass
90  input #1, smplmass
91  input #1, smplcor
92  input #1, stdcor
100 open "o", #2, outfile$
110 print #2, npts&; refmass; smplmass; smplcor; stdcor
120 for j = 1 to npts&
130 input #1, temp(j), refscan(j), smplscan(j)
140 next j
150 for j = 1 to npts&
160 corref(j) = refscan(j) - stdcor
170 corsmpl(j) = smplscan(j) - smplcor
180 next j
190 for k = 1 to npts&
200 xtemp = temp(k)
210 gosub 380
220 smplcp(k) = cp*corsmpl(k)*refmass/corref(k)/smplmass
230 print#2, temp(k); smplcp(k)
240 next k
250 print " "
260 print "number of data points ="; npts&
270 print "mass of reference ="; refmass
280 print "mass of sample ="; smplmass
285 print " "
287 print tab( 10); "Temp"; tab( 24); "Ysmpl"; tab( 39); "Ystd";
288 print tab( 53); "Cpsmpl"
289 print " "
290 for k = 1 to npts&
300 print tab( 9); temp(k); tab( 22); corsmpl(k); tab( 37); corref(k);
310 print tab( 52); smplcp(k)
320 next k
330 close #1
340 close #2
350 end
360 rem subroutine for determining interpolation values
370 rem and reference sapphire heat capacity
380 test& = fix(xtemp)
390 test = fix(xtemp)
400 for i = 1 to 5
410 if i = 1 goto 440
420 test& = test& - 1
430 test = test - 1
440 if ( fix (test/5) - test/5) <> 0 then 520
```

TABLE 29 (continued)

Data Processing Program (by M. O. Stoy) for DSC 7 - Perkin-Elmer 7500 (continued)

```
450   if ( fix (test/2) - test/2) = 0 then 490
460   x1 = test& - 5
470   x2 = test& + 5
480   goto 530
490   x1 = test&
500   x2 = test& + 10
510   goto 530
520   next i
530   open "i", #3, "cpindex"
540   open "r", #4, "cpstnd"
550   field #4, 10 as cpref$
560   input #3, nrecs&
570   for j = 1 to nrecs&
580   input #3, index(j)
590   next j
600   for j = 1 to nrecs&
610   if x1 = index(j) then 630
620   next j
630   rec1& = j
640   rec2& = j + 1
650   get #4, rec1&
660   let z$ = cpref$
670   let cp2 = val(z$)
680   get = #4, rec2&
690   let z$ = cpref$
700   let cp2 = val(z$)
710   cp = (xtemp - x1)*(cp2-cp1)/(x2-x1) + cp1
720   close #3
730   close #4
740   return
```

Data were taken for a very large number of liquors and for some purified lignins. For each liquor, data were taken at concentrations ranging from about 8% solids to 100% solids with six to twelve concentrations for each liquor. The results for 100% solids and literature values for water were used to show that black liquor heat capacity is not an ideal additive function with respect to concentration, as has been assumed. The behavior is non-ideal, and the excess heat capacity exhibits a maximum in the vicinity of 80-85% solids.

One will recall that this is the concentration region for which a second order thermodynamic transition was identified from density data at 25C. Two models for the solution were proposed that led to two forms for the excess heat capacity relation. These were both successfully applied to the data for many liquors. The relations involve three constants each. These constants, together with the constants for the relation for heat capacity of 100% solids as a function of temperature, are functions of the liquor solids composition.

We have successfully correlated these constants to pulping conditions and to liquor solids composition to yield a totally generalized relation for heat capacity of Slash pine black liquors. Furthermore, the data have been shown to be thermodynamically consistent with other results. Therefore, we believe that this work establishes a frame work that can be used to develop similar quantitative relations for black liquors derived from other woods are from other types of pulping with a great deal less effort than was expended in this work.

7.5 Heats of Dilution. Black liquor is a complex solution containing many polar compounds that should exhibit non-ideal solution behavior; indeed, this has been shown to be true from measurements of heat capacity and density measurements. Therefore, there was every reason to believe that the interactions occurring during mixing or concentrating

should result in enthalpy changes for the liquor; that is, the heat of mixing (or dilution) is not zero. Only two single point measurements of the heat of mixing of black liquor solids and water had been reported prior to our work. Although the measurements were questionable with respect to the quantitative values reported, this work did show conclusively that the heat of mixing is not negligible. Still, accepted practice in design of concentration processes for recovery systems is to ignore the heat of mixing, presumably because no data for this thermodynamic quantity exists. In addition, the heat of mixing must be known for thermodynamic completeness if thermodynamic consistency for various models for properties is to be checked.

Obviously, models that can be shown to be thermodynamically consistent are likely to be more general and can usually be extrapolated with greater confidence, which is very useful for designers. Also, models that are shown to be thermodynamically consistent can usually be used by researchers to interpret solution behavior with greater certainty and generality, which is important for such a complex and variable a solution as black liquor. For these reasons, a major objective of this program was to develop a method for measurement of the heat of mixing (or dilution) of black liquor and to apply the method to measure heats of dilution for liquors with a wide range of solids compositions.

The development of the method required nearly two years (Stor, 1993). Firstly, all experimental methods that had been or possibly could be used for measurement of heats of solution were reviewed thoroughly. One should remember that heat is a flux (energy in transit) that severely complicates any absolute measurement of the heat of solution. In the end, it became clear that the only method likely to be useful for accurate measurements was the Calvet absolute microcalorimeter method. In this method, the heat evolved or absorbed by a change, such as heat evolved or absorbed in mixing, is transferred totally from the container holding the solution to a heat sink or source through thermopiles that serve as a heat flux meter. There are several manufacturers of such instruments. Samples of black liquor were submitted to each manufacturer with requests

for exploratory measurements. None of the results were really satisfactory, but the results of tests made by Setaram were most promising. Setaram is a French company whose US representative is Astra Scientific International located in Pleasanton, CA. A Setaram C-80 Calvet Calorimeter mounted on a rocking stand was selected as the best choice for our work and was purchased and installed. The cells purchased for use were model 31/1419 cells made of stainless steel and designed specifically for measurements of heats of reaction, heats of solution, and heat capacity with liquids and solids.

The thermal block of the instrument that serves as a heat source or sink and that is maintained at a constant temperature above the ambient is cylindrical and is mounted on a stand with a rocking device that can rock the instrument through 180^0 for mixing components to initiate experiments. Two cells, one for the sample for measurement and the other for a reference or blank, are mounted symmetrically in the heat source block in the heat flux measurement sections. The heat flux meters surround each cell. The outputs of the flux meters are connected in a differential manner such that the output is the difference. The cells are identical in geometry, material, and mass; therefore, the blank serves to cancel out the effect of the cell on the measurement automatically, and, since the placement of both the sample and blank cells are exactly symmetrical, other very minor differences due to very small heat losses are compensated for automatically. Finally, by filling the blank cell with material with about the same sensible heat properties as the sample, the effects of any differences in sensible heat can be minimized.

In the particular cell used, there are two chambers that are separated by a "lid". One chamber holds one of the components to be mixed and the other holds the second. The lid is normally sealed with a liquid "seal fluid" that is inert in the experiment. The lower chamber, the insert, has a usable volume of 1.35 ml. The upper chamber has a usable volume of 3 ml if the minimum volume of seal fluid is used. In our experiments, we loaded the reference cell with an equivalent volume of seal fluid and of one of the components. Two trials were made. In one case, the material used to fill the blank cell

was water. In the other case, the material used to fill the blank call was black liquor at the final concentration. There were no differences in results for the two trials. Therefore, very small differences in sensible heat are not important.

Mercury is the sealing fluid normally used, since its properties make it ideal for most studies. Its density, thermal conductivity, and surface tension are high and its viscosity is low. It seals well, transfers heat well, and does not interfere with mixing. It can also be separated easily from the final solution after the experiment is completed. Unfortunately, mercury reacts with some components of black liquor and is not suitable as a sealing fluid for work with black liquor. Another sealing fluid had to be found, and this proved to be a non-trivial problem.

After an exhaustive search involving a great deal of experimental testing, a fluorinated oil was found to be the best available material to use as a seal fluid. The oil is a perfluoralkylpolyether that is a saturated chain and that consists of only carbon, oxygen, and fluorine with a density at ambient temperatures of about 1.88 gm/ml. This meets one of the requirements that the seal fluid be denser than either component to be mixed. The oil is available in a wide range of viscosities, depending upon the degree of polymerization and has a reasonably high thermal conductivity. It is completely inert with respect to black liquor, but is does have a relatively low surface tension. On balance, a reasonably low viscosity oil was selected to prevent interference with the mixing process, but the oil dispersed in the final solution as a result and could not be separated easily. This did not interfere with the mixing experiment, but did prevent us from analyzing the final liquor for solids concentration as an experimental check.

The particular instrument and cells that we used were checked for accuracy and precision using inorganic salts and water with mercury as the seal fluid. The microcalorimeter proved to be extremely accurate. Most tests were run with potassium chloride certified by the National Institute of Science and Technology and water with mercury as the seal fluid. The certified heat of solution for a 0.111 mol/kg solution of this

material at 298.15K was 235.86+/-0.23 kJ/kg. The experimental result with our calorimeter, after an accepted temperature of mixing correction had been made, was 236.01+/-1.01kJ/kg at the 95% confidence level. This is essentially exact agreement. When we used the fluorinated oil in the same experiment, the experimental result was a value of 234.94+/-0.72kJ/kg at the 95% confidence level. This mean value is 0.39% lower than the mean value certified by NIST, and, even though the confidence intervals overlap, the difference is statistically significant. The difference was so small, however, that we considered the system to be used to be of acceptable accuracy.

Another problem was establishing the best temperature for measurement. Even though the quantity sought is a thermodynamic quantity, the measurement itself is dynamic. If dissolution is too slow, the rate of heat release or absorption will be low and the heat flux signal will be low, resulting in increased error due to integration of a low signal over a long period of time. On the other hand, it is desirable to conduct the experiment at as low a temperature as possible to prevent any pressurization in the cell and to minimize extrapolation to lower temperatures in constructing enthalpy relations. With black liquor, 80C was chosen as the best temperature for mixing experiments. Figure shows a typical power curve for mixing of black liquor. The heat of mixing is obtained by integrating the power curve.

After the cells had been prepared and loaded into the calorimeter, the system was allowed to come to complete thermal equilibrium as indicated by a stable baseline. The cell was then rocked to begin the mixing process and rocking continued for five minutes or less. The power curve was recorded until the signal returned to the base line. This usually took 40 to 60 minutes, but could require up to 400 minutes at high solids concentrations where mixing was more sluggish. At initial solids concentrations of less than 60%, the

TABLE 30
Heats of Dilution Measurements
Setaram C-80 Absolute Microcalorimeter
The Setaram measures the heat of dilution of black liquor and water. The two liquids are separated by being in different chambers and separated by a loose steel cap and Krytox oil. Upon inversion, the steel cap overturns and the two fluids mix. The heat of dilution is measured and compared to a reference chamber containing only water and Krytox.
Deatailed Procedures:
Sample Setup:
1. Weigh entire reaction vessel and record weight.
2. Carefully disassemble the reaction vessel. Do not attempt to loosen the top by twisting the long *fragile* tube on top of the vessel.
3. Weigh the lower container and record weight.
4. Nearly fill the lower container with liquor to be tested, weigh and record weight.
5. Insert lower container into main body and tighten.
6. Seat steel cap.
7. Weigh this much of the assembly and record weight.
8. Add ~1 milliliter Krytox and record new weight.
9. Add desired amount of water for mixing, weigh and record weight.
10. Finish assembly of reaction vessel. Make sure not to invert or tilt it.
11. Repeat this process using the reference vessel and leaving out the black liquor. Usually, the reference vessel can be done once and saved for later analysis.
12. Place Sample vessel in the pre-heater to bring temperature close to that of the calorimeter.
13. Install reaction vessels into the calorimeter. After the first run, the only vessel removed is the Sample vessel. The reference vessel can stay in place.
14. Let sample and reference vessels equilibrate and thermal stabilization occur.
15. Go through ASI software and set up run information, sample ID, mass and run criteria.
16. Begin run and let a stable baseline run for 3 minutes before turning on mixer to the calorimeter.
17. Allow the calorimeter to finish the analysis and stop mixer in the upright position.
18. Use the ASI software to calculate heat of dilution.
Using the ASI Software:
1. Turn on the computer.
2. At the C:> prompt, type ASI
3. Hit any key to continue to the Main Menu.
4. Using the function keys F1, F2, ect..., you select which task to perform.
5. Hit F1 to collect data.
a. Enter filename for collection (up to 8 characters + 3 for extension).
b. The sample name.
c. Sample ID.
d. Date and time collected (automatic entry from computer clock).
e. Operator.
f. Collection Interval. Enter 2 seconds.
g. Sample Mass. Enter sample mass in mg.
h. Power Amplification. Entry depends on dilution and expected needs, check similar dilutions to get range required.
i. Collection Type: Choose isothermal.
6. After entering this data, press enter to go to the time setup screen.
a. Length of Collection. Enter 90 minutes.
b. Isothermal Temperature. Enter 25 °C.

TABLE 30 (continued)
Heats of Dilution Measurements (continued)
Setaram C-80 Absolute Microcalorimeter (continued)

Using the ASI Software:

7. Press F10 to exit and return to main menu.
8. Wait for instrument to completely equilibrate before beginning collection.
9. To perform a region analysis on a sample run, press F3.
10. Press F1 Set New.
11. Enter filename desired, confirm Yes or No as indicated. Hit Enter key to go on.
12. Respond to the prompts on the next screen as desired for analysis. These two screens screens deal with x and y axis, scaling, normalizing and smoothing. When finished, press Enter and the graph will be plotted.
13. Set area of interest using these keys.

End	moves only left line
Down Arrow	moves both lines
Pg Dn	moves only right line
Left Arrow	moves current line(s) left
Right Arrow	moves current line(s) right
Pg Up	determines # of data points each line will move
Delete	prevents these functions from working. DO NOT USE.

14. Choose F1 for Enthalpy calculation. Press enter to go on.
15. If option exists for next prompts, select the number that matches the option and enter that. Otherwise, just hit Enter key to go on.
16. The final Enter key activates the regional analysis and the computer calculates the enthalpy. This is given in several units so choose the one you need and record the information.
17. A new region can now be set or hit F10 to return to menu.
18. Hit F10 to return to Main Menu and again to exit program.

black liquor was placed in the lower chamber. At higher initial solids concentrations, water was placed in the lower chamber and liquor was placed in the upper chamber. A detailed procedure is given in Table 30. Heats of solution were measured in increments of concentration; that is, a liquor at a given solids concentration was mixed with a given quantity of water and the heat of solution was measured for this process. This was repeated for a number of increments of concentration change and the increments plotted on an arbitrary scale so that the end points of each increment were connected. Dilutions were made down to concentrations as low as about 1.5% solids. Typically, there was a large release of heat during dilution from 5 to 1.5%. Below 5% solids, the pH drops rapidly from 12-12.5, and lignin association must occur.

This is not the normal state for lignin in black liquors. We had originally intended to dilute the liquor so as to extrapolate the data to zero solids to establish a reference for solids at infinite dilution at 80C. Extrapolation of the experimental data, however, would not give a reference state that is equivalent for the solids in solution at concentrations above 5%. Therefore, the data above 5% solids was extrapolated to zero solids to establish a reference state at 80C with the solids in the same form as at higher solids. This was established as the reference state and the solids assigned a value of zero enthalpy in this state. The data were then fitted with a smooth curve to yield the heat of dilution of black liquor at 80C as a function of solids concentration. A preferred reference would have been 100% solids at 80C; however, this proved to be essentially impossible to establish experimentally, since 100% solids are highly hydroscopic and dilution of 100% solids with the maximum amount of water that could be used resulted in a very viscous final solution whose heat of dilution could not be accurately measured with our present techniques.

7.6 Enthalpy-Concentration Relations. Although not an experimental procedure, calculation procedures used for enthalpy-concentration relations are important, since the

relations depend upon the reference states used. The reference state for solids, as previously described, was solids at infinite dilution in the same state as present above 5% solids and at 80C. The reference state for water was water at 0C under its own vapor pressure. Enthalpies are zero for the two components under these conditions. With respect to its reference state, the enthalpy of water at 80C is 334.5 kJ/kg (79.95 cal/gm). This is then the enthalpy at zero solids for the heat of dilution isotherm at 80C that defines the enthalpy of the solution at 80C as determined from the heat of dilution experiments. The heat capacity data are used to calculate enthalpies at other temperatures up to the boiling points, as determined for the liquor. The liquor is treated as a binary of water and solids. Heat capacity data at particular constant solids concentrations, or heat capacity correlations as previously determined, are used to calculate enthalpies at other temperatures by normal thermodynamic calculation procedures.

The validity of treating a liquor system as a pseudobinary can be tested for thermodynamic consistency. This can be done by using the enthalpy results, an equation of state for water, and a normal boiling point curve for the liquor to calculate the fugacity of the solids at a number of constant solids compositions. Vapor pressures of the liquor at other temperatures can then be calculated by using the fugacities and the equation of state for water. This was done and the calculated vapor pressures at a number of constant solids concentrations were compared with experimentally determined vapor pressures at solids concentrations ranging from 30 to above 70% solids. Experimental and calculated vapor pressure curves agreed almost exactly, which is an indication that treating kraft black liquor as a pseudobinary solution of water and non-volatile solids is thermodynamically consistent (Stoy, 1994).

8.0 RHEOLOGY

Rheology of black liquors is an extremely important property or set of properties that are very important for design and operation of recovery systems, particularly at high solids concentrations. Black liquors of interest are complex solutions of polar polymers in an ionic solution over a very wide range of concentrations of organic components and of ionic inorganic components. One should expect the rheological behavior to be complex and it is. Development and adaptation of instruments for measurements, development of experimental procedures, experimental measurements, and development of data reduction and correlation methods were an important part of our overall program. As a result, a total of eight instruments were developed or adapted for use with black liquors to permit measurement of rheological properties of liquors from 10 to more than 85% solids, temperatures from about -120C to more than 150C, pressures up to 600 psia, and shear rates from about 0.01 to as high as 6,000 sec^{-1}. Moreover, these adaptations were made with the objective of determining viscosity within about +/-5%, and this objective was met in nearly every case. Sufficient data with different instruments were taken to demonstrate that results obtained from different instruments were in agreement. Experimental data were taken for many liquors. Typically, data for a single liquor were taken from 10 to 80% solids, from 40 to up to 150C, and shear rates from 1 to 1,000 sec^{-1}.

The basic premise used to reduce and to correlate the data was to consider black liquor to be a polymer solution. This proved to be very successful, and permitted us to rationalize behavior and to develop reduction and correlation methods that are fundamentally sound and that are in agreement with theory. In the course of this work, the first measurements of black liquor viscosity at high solids concentrations were made, the first experimental evidence of the non-Newtonian behavior of black liquor was collected, the first viscoelastic measurements for black liquor were made, the first measurements of viscosity at temperatures above the normal boiling point were made, the

instability of liquors at high solids and temperatures was discovered, and the first systematic study of the effects of solids composition and lignin characteristics was made. This is a long list of firsts with many being significant contributions to the study of black liquors.

8.1 Instruments. The instruments and techniques used to measure viscosity or viscoelasticity with each instrument are important, and these are described in detail in this section. These will be taken individually; however, there are some generalities with respect to handling liquors. Liquors were normally heated in sealed containers at a temperature sufficient to make the liquor fluid or, at least, deformable. The heated liquor was loaded into metal transfer syringes or formed in molds to the shape required for the instrument to be used. The liquor was then transferred to the instrument, brought to thermal equilibrium as rapidly as possible, and the measurement made within a limited time so that measurements were made without the complication of changes in the liquor characteristics. This latter point is important. At high solids concentrations and high temperatures, measurements on a single sample had to be made within as little as 20 minutes after thermal equilibrium was established in order to make measurements at constant liquor characteristics. This, combined with the wide range of viscosities of interest required that many instruments be used.

8.1.1 Glass Capillary Viscometers. Glass capillary viscometers were used for two purposes: to check standard Newtonian fluids used to calibrate other viscometers and for measurement of viscosity of black liquors at lower solids concentrations and temperatures where the liquor was Newtonian and well below the normal boiling point of the liquor. Sets of standard Cannon-Fenske and Ubbelohde viscometers were used. The particular viscometer used for a viscosity was chosen so that the fluid acceleration effects on the measurement were negligible. The viscometers were maintained at constant temperature for measurements by placing them in a constant temperature bath filled with water or silicone oil and maintaining the bath temperature within 0.1C or less of the desired

temperature. Viscosities could normally be measured with a precision of 0.3% or better. Glass capillary measurements were used extensively to measure black liquor viscosity at solids concentrations below 50% and at temperatures up to 80-90C.

8.1.2 Open cup Haake Viscometers. A Haake RV-12 system equipped with open cup coaxial cylinder viscometers of various geometries and cone-and-plate and parallel plate geometries was used for many measurements. These were particularly useful for measurements of black liquors that were non-Newtonian, but non-elastic, at intermediate solids concentrations and at temperatures from about 30 to 90C. A variety of cups and bobs were available for use so that a wide range of shear rates could be used. Three torque measuring devices with different torque ranges were used to give a torque range of more than three orders of magnitude with very good accuracy and precision for torque measurement. The measuring system was thermostatted and silicone oil circulated from a temperature controlled bath through the thermostat around the cup to maintain a constant temperature for measurement. Temperature could be maintained at a constant value within +/- 0.1C or less.

The torque measuring devices were calibrated by Haake at the factory and the calibration checked in our laboratories by using weights and pulleys according to the manufacturer's recommended procedures. Each viscometer combination was calibrated and end effects determined for the coaxial cylinder combinations using standard fluids with viscosities certified by NIST whose calibration had been checked with glass capillary measurements as previously described. The effects of viscosity and shear rate on end effects were determined. The level of fluid in the viscometer for measurement was carefully controlled and the fluid was protected by covering the top of the viscometer with a paraffin film or covering the fluid with a thin layer of a lighter non-volatile fluid to prevent or retard evaporation when making measurements with fluids containing volatiles. Normal precision was +/-2% or better with accuracy, as determined by using standard fluids or by comparison with measurements made with other viscometers, of +/-5% as a

general rule for all checks of accuracy made. It should be emphasized that this is very good accuracy for viscosity measurements.

These systems were used extensively for determining black liquor viscosity at up to about 60% solids at lower temperatures where volatility of the liquor was not a problem. The effects of shear rate on apparent viscosity could be determined by using these viscometers. Shear rates from about 5 to up to 1000 sec^{-1} could be investigated at these liquor conditions; higher shear rates could not be used, because secondary flow effects within the viscometer interfered with the measurement. A typical example of calculated data obtained for a black liquor with an open cup coaxial cylinder viscometer is shown in Figure .

8.1.3 Pressurized Cell Haake Coaxial Viscometer. Haake supplies an enclosed coaxial cylinder viscometer for use with the RV-12 system in which the cylinder is mounted on sapphire bearings and the cylinder contains magnets that permit it to be magnetically coupled to the viscometer drive that is external to the cell. The torque range is more limited than that for the open cup coaxial cylinder, because the magnetic coupling permits the use of only two of the three drive; therefore, the torque range is limited to a little more than two orders of magnitude with precision of +/-2% or less. The pressure limit of the cell is 580 psi.

The major problem with the unit as supplied by Haake is temperature control. Haake supplies an instrument with a temperature jacket around the cylinder and recommends that oil be circulated from a temperature bath through the jacket to maintain a constant temperature in the cell. Following the recommendations from Haake, we found that there were temperature variations within the cell of up to 15C with an oil temperature of about 115C. This was totally unacceptable. We removed the jacket and immersed the cell in a large, well stirred oil bath. This arrangement proved to be satisfactory and temperature could be controlled to within +/-0.1C at up to 150C with this arrangement. It

is worth noting that data collected with the instrument thermostatted as recommended by Haake has been reported in the literature.

While our arrangement proved to be satisfactory, experimental use was awkward and time consuming because of the necessity of bringing the entire viscometer mass to thermal equilibrium before data could be collected. The time required for the entire cell mass to reach thermal equilibrium was too great to permit measurements with black liquors whose rheology changed rapidly with time at high temperatures. Therefore, we redesigned the cell and changed the thermostatting system.

The cylinder and top and bottom flanges of the cell were jacketed with spiral baffles in the jackets. Space was left unjacketed in the top and bottom flanges for connection of the cylinder drive and for connections for loading and unloading of fluids. The internal geometry of the cell was unchanged. Silicone oil from a constant temperature bath was circulated through the jacket by using a gear pump to supply oil at a flow rate sufficient to maintain turbulent or transitional flow within the cell jackets. Temperatures of the oil into and out of the jacket were measured, and the oil flow rate set to maintain a temperature drop of 0.1C or less. The temperature of the fluid in the cell was measured at the cell midpoint. This arrangement proved to be very satisfactory, and was used extensively for measurements with black liquor.

The pressurized cell requires some changes in techniques for calibration and use. The bearings introduce some frictional resistance. This is minimized by filling the bearings with a high temperature silicone grease. The torque measuring system is operated with no fluid in the cell and the torque due to friction determined as a function of cylinder rotational speed. This frictional torque is subtracted from the torque reading when making viscosity measurements. The unit is then calibrated for end effects by using Newtonian fluid standards of known viscosity. Normally, end effect corrections are +/-6% or less with an uncertainty on end effect correction of less than 5% (less than 0.3% on the viscosity reading).

The pressurized cell is brought to the measuring temperature with no fluid in the cell. The fluid to be measured is then injected into the cell and the cell closed. The fluid reaches the measuring temperature within about 3 minutes, and measurements can be made for a black liquor sample for a minimum of 30 minutes before the character of the liquor begins to change significantly. This is more than sufficient to permit as many as 15 measurements at different shear rates (different cylinder speeds). The cell is then opened, the fluid drained or displaced with hot solvent (hot water in the case of black liquor), flushed with hot solvent, and allowed to dry by leaving the cell open while the solvent evaporates. The bearing friction is then checked at one speed to insure that it has not changed. The cell is now ready for reuse. If desired, the temperature of measurement can be changed. The time required for the cell to reach a new thermal equilibrium is about 20-30 minutes. Normally, the cell can be operated in this manner for up to 10 cycles. After that, the cell must be opened, the bearings regreased, and the frictional calibration repeated.

When operated in this manner, this unit is capable of producing results with a precision of about 2% and an accuracy of about +/-5%. The unit is capable of operation at temperatures from 40 to 230C, but has been used with black liquors up to only about 150C. The shear rate range that can be used for measurement is affected by the level of the apparent viscosity, but the overall range is about 8 to 1000 sec^{-1}. The upper limit on shear rate is due to the secondary flows that develop in the fluid. It is worth noting that every Couette viscometer in which the cylinder is rotated is subject to error due to secondary flows at high shear rates and to errors due to viscous heating within the fluid due to shearing. Temperature can be controlled and maintained uniform in the fluid to within +/-0.1C. With careful attention to technique, this unit can be used to measure viscosities ranging from about 20 to over 4000 cp with accuracy of +/-5%.

While this unit was the first unit to be developed and adapted for precise measurements of fluids under pressure, other units made by Contraves, Bohlen, and Rheometrics are now available and the unit made by Contraves has been used in some studies of black liquor viscosity. However, it is not clear that any of these other units have been subjected to the close scrutiny with respect to temperature control, precision, and accuracy that the modified Haake unit in our laboratories that has been used in our work has received.

8.1.4 Brookfield Coaxial Cylinder Viscometer. Brookfield Engineering Laboratories developed a closed cell coaxial cylinder viscometer in which the cup is rotated rather than the cylinder while our work was in progress. This viscometer was obtained with funds made available by a different research project, and has been used for measurements with black liquor as well as for other measurements.

The torque developed in the viscometer due to viscosity of the fluid is measured by measuring the degree of twist of the shaft connected to the viscometer cylinder. The cup is driven by a constant speed drive. The system is sealed by a mechanical seal between the cup drive shaft and the cylinder holding the torque shaft. The system can be pressurized with a gas cap above the fluid in the fluid measuring gap of the coaxial cylinder formed by the cup and cylinder. The entire assembly is temperature controlled by immersing it in a controlled temperature bath. The rotation of the cup during operation increases heat transfer for temperature control during operation. A variety of coaxial cylinder geometries are available and the torque measuring shafts can be changed to change the range of the instrument. In our case, a Fann coaxial cylinder geometry is used with the standard torque measuring shaft normally supplied by Brookfield.

This instrument has advantages and disadvantages vis-a-vis the Haake pressurized cell unit. The torque measurement is not quite as precise (precision is about +/-1%). End effect corrections are about the same, but there are no bearing corrections to be made as had to be made for the Haake, because there are no bearings involved in the torque

measuring system. Therefore, overall, the Brookfield closed cell rotational viscometer is as precise as the Haake pressurized cell viscometer. Since the viscometer must be loaded with fluid and then immersed in the temperature bath and brought to thermal equilibrium, the time available for measurement with fluids that are temperature sensitive is less; a maximum of about 20 minutes is available for measurement with a black liquor at high solids and temperature. The present experimental set up can be operated from about 30 to 150C, which is a lower temperature than can be used in the Haake. This unit is easier to load with a sample and easier to clean after use. The pressure limit of the Brookfield is 200 psi as compared to 580 psi for the Haake. This unit has no theoretical upper limit on shear rate that can be used, because there are no secondary flows generated, since the cup rather than the cylinder rotates. The upper limit on shear rate that can be used is due to viscous heating of the sample being measured. Experimentally, we have determined that the Brookfield can be used successfully to measure apparent viscosities at up to 4000 sec^{-1} for fluids with viscosities as high as 1000 cp. This is a considerably higher shear rate limit than for the Haake system. The lower limit of viscosity that can measured with an accuracy of about +/-5% is about 25 cp with the Brookfield as compared to about 20 cp for the Haake pressurized cell, although the Brookfield can be used at viscosities as low as about 12 cp with decreased accuracy. A detailed procedure for using this instrument is given in Table .

The Brookfield has been used extensively for measurements of viscosity of polymer solutions, coatings, and suspensions with good results, as well as for black liquor, in our laboratories. It is an instrument that could have many uses for quality control in integrated mills.

8.1.5 Rheometrics RMS 800 Mechanical Spectrometer System. The Rheometrics RMS-800 system was purchased with funds made available through a separate research grant for general use for rheological measurements, but it has been used extensively for measurements with black liquor. This system is basically a speed controlled (shear rate

controlled) system with capability to measure torque response and principal normal stress response in steady state operation, but also capable of measuring oscillatory torque response when in oscillatory shear operation. The unit in our laboratories is equipped with two torque measuring transducers with different ranges; each transducer has a range of about three orders of magnitude. Tooling is available to permit measurements for cone-and-plate and parallel plate geometries. Cones with angles between 0.5 and 2.5^0 and diameters of 25 to 75 mm are available to increase the range of the instrument. Plates are available at diameters from 25 to 75 mm so that measurements can be made at different ranges using parallel plate geometry. The instrument is equipped with means to measure and set the gap between parallel plates to within 50 microns or better from zero to about 10 mm.

The instrument is equipped with computer control that permits the shear rate to be held constant or oscillated at constant frequency, that permits the temperature of the measuring portion of the system to be changed at any desired rate (for so-called temperature sweeps), or that permits the shear rate of frequency of oscillation of shear rate to be changed at any desired rate (for so-called shear rate or frequency sweeps). The maximum strain used during shear rate or frequency experiments can be set and maintained by computer control to values as low as 3% with 0.5% precision. The temperature of the measuring system is measured by means of an RTD mounted in the bottom plate. Soft ware is included, not only for control, but also for data collection of temperature, strain, torque, and normal force as a function of time. The computer software, when supplied with instrument constants, calculates shear rate, shear stress, and normal stress when in steady rotational operation mode and shear rate and torque vs. time when in oscillatory operation mode. Raw data is collected at a rate of about 2000 points per second and averaged by running average methods. The averages are retained in the computer memory for analysis.

Our system is equipped with three environmental chambers for temperature control. One chamber uses liquid nitrogen as a temperature control fluid. Liquid nitrogen is fed through an efficient heating system and then is introduced into a chamber surrounding the measuring system. With this setup, the instrument can be operated, according to the manufacturer, from -160C to 300C. We have actually operated the system from about -60 to 330C. Nitrogen consumption is extreme (about 2 liters/hour of liquid nitrogen) with this chamber. However, air can be used in place of nitrogen, but this restricts the temperature range to about 30 to 330C. The second chamber is called a sub-ambient chamber. The chamber is surrounded by a jacket through which a temperature control fluid can be circulated. The unit is equipped with a circulating bath with a temperature range of -10 to about 150C. The advantage of this system is that there is not a high gas flow around the tooling as is the case with control chamber using nitrogen. Thedisadvantage is that the temperature control is not as precise. The third chamber is the so-called solution chamber. This chamber is thermostatted in a manner similar to that used for the sub-ambient chamber, but the chamber is much more enclosed and the thermostatting is better. The useful temperature range for this chamber is about 20 to 100C.

Detailed procedures for operation are extensive. The procedures used for measurements concerned with our black liquor program follow the manufacturer's recommendations as detailed in the operations manual, and will not be repeated, but changes in the recommended procedure that were found to be necessary or useful for work with black liquor will be described as exceptions to the recommended procedures. These changes include loading, setting of operational parameters, and provisions for minimizing the effects of loss of solvent (water).

Calibration of the stress measuring devices is necessary whenever the transducers are exchanged and periodically during operation with any one transducer. Normally, the transducer calibration was checked about every four weeks. Stress measuring devices are extremely sensitive and must be handled with care to insure good operation.

When used for rheology, this device is a rotational device employing cone-and-plate or parallel geometries. A coaxial cylinder cell is available from Rheometrics for use with this device, but our unit is not equipped with a coaxial cylinder cell. Cone-and-plate and parallel plate geometries can only be operated under conditions of creeping flow, which limits the app licable shear rate range to low values. Although the unit can operate at rates as high as 100sec^{-1}, valid data cannot be taken in steady shear at these high rates. The actual limit is about 10 sec^{-1} in most cases. In the oscillatory mode, the instrument can operate at at frequencies as high as 100 Hertz, but signal to noise ratio decreases with increasing frequency; therefore, precise data can only be taken up to about 20 Herz in most cases. These observations are general for all types of fluids, not just for black liquors.

With low viscosity black liquors, the solution chamber is used with parallel plates. Plates are normally set at a spacing of 0.2 to 1.0 mm, depending upon viscosity. Measurements are made at 30 to 90C in steady shear, since the liquors are nonelastic at low solids concentrations. Shear rate is limited to less than 10 sec^{-1} to retain creeping flow. In many cases, the liquor is retained in the viscometer gap by a retaining ring placed at a considerable distance from the edge of the plates, about 1.5 cm. The shear rate in the fluid is not constant; it is a function of radius. Therefore, the shear stress and shear rate must be calculated using correction factors derived from the data that have been developed from theory for the hydrodynamics in the viscometer . These relations are well known and universally accepted.

With high viscosity black liquors, the solution chamber and the sub-ambient chamber were both used, depending upon circumstances. Data were taken in both steady shear and oscillatory shear modes. Parallel plates were always used with a gap of 0.5 to 1.5 mm and diameters of 25 or 50 mm, depending upon the solids concentration of liquor and the temperature of measurement. Measurements were made in steady shear with liqours at solids concentrations up to 85% solids to determine viscosity at low shear rates so that zero shear rate viscosity could be determined directly and to determine normal stresses.

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