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DR# 2246-2

DOE/CE/40606-T1
(DE84006996)

Energy

CONSERVATION

PHYSICAL PROPERTIES OF KRAFT BLACK LIQUOR

Final Report — Phase 1

By
Arthur L. Fricke

December 1983

Work Performed Under Contract No. AC02-82CE40606

University of Maine
Orono, Maine

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DOE/CE/40606-T1
(DE84006996)
Distribution Category UC-95f

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1.0 EXECUTIVE SUMMARY

Six Companies of the Pulp and Paper Industry and the U.S. Department of Energy joined in supporting research in the Chemical Engineering Department at the University of Maine to determine the Physical Properties of Kraft Black Liquors. The three year research program, which began on October 1, 1982 is divided into two phases. Phase I, the subject of this report, was completed on September 30, 1982. Phase II began on October 1, 1983 and will be completed on September 30, 1985.

The ultimate objective of the total program is to determine the physical properties - rheological, thermal, and surface - of kraft black liquors that must be known for engineering design of equipment for recovery operations, and to relate these properties to the chemical composition of black liquors in the simplest manner possible so that physical properties may be predicted. An intermediate objective is to relate physical properties of kraft black liquors to pulping conditions for specific wood species. Accomplishment of these objectives will permit the industry to design and operate recovery systems at higher final liquor solids contents with confidence so that efficiency of energy recovery can be improved.

The objective of Phase I was to perform work necessary for successful conduct of Phase II. We selected methods, installed equipment, and developed procedures for determining rheological properties; for determining thermal properties (stability, density, thermal expansion, and heat capacity); for purification and characterization of lignin (glass transition, stability, weight average molecular weight, and number average molecular weight); and for performing chemical analyses (negative inorganic ions, positive inorganic ions, acid organic salts, lignin, and total solids). A strategy for pulping to supply test liquors was developed, and a statistically designed pulping experiment was specified for a Southern softwood species. Arrangements were made for performing initial pulping work in an industrial pilot plant, and a preliminary set of pulping experiments were conducted. Liquors from the preliminary pulping experiments were used to test procedures and to determine reproducibility of the experiment. During Phase I, we also surveyed literature and made preliminary selection of designs for a pilot digester, and for equipment to determine surface tension. These units will be installed and used during Phase II.

The objective of Phase II is to use the equipment and methods developed in Phase I to prepare liquors and to determine their physical properties and chemical composition. A four variable, multi-level pulping experiment to prepare liquors from slash pine for testing is underway. The twenty-five liquors for this experiment, plus a few others, will be prepared in an industrial pilot plant, shipped to the University of Maine, and used for tests. Other experiments with other species will be conducted at the University of Maine to supply test liquors after a new digester is built at the University of Maine. All physical properties, except thermal conductivity and surface tension, will be determined experimentally for the liquors from the first pulping experiment as soon as the liquors are available. All necessary chemical analyses and lignin characterization analyses will be performed on the liquors from the first pulping experiment as soon as the liquors are available. A portion of the liquors will be stored and thermal conductivity and surface tension will be determined when the equipment necessary for these tests is available. These

tests will be repeated for liquors made from other pulping experiments with other species.

This project is somewhat unique in that an advisory group, composed of representatives from DOE and the supporting companies, is actively involved in directing a basic research program conducted entirely by a university. The advisory group met twice during Phase I and the results of the discussions were used to modify plans and schedules. This may well serve as a model for future research projects.

This is an extremely complex program. A significant accomplishment of Phase I was the collection and training of the necessary staff. Two faculty, one research associate, six graduate students, and several undergraduate students working part-time are currently engaged in the work. During Phase II, we will employ the same staff, except that one graduate student will be replaced by a laboratory technician. At that time, the total technical effort is estimated to be at least 5.5 man-years per year.

As directed by our advisory group, we conducted a preliminary experiment to evaluate the entire procedure of pulping, liquor handling, and experimental work. This was extremely worthwhile. The preliminary experiment indicated the reproducibility of pulping to be expected in the pilot plant. The experiment allowed us to evaluate handling procedures and to make necessary modifications before proceeding. It permitted us to perform analyses and tests with a liquor that should be mid-range for the first pulping experiment. Using these liquors, we modified analytical and test methods, and we estimated the necessity and time required for each chemical and physical test. The preliminary experiment required approximately four months of effort of the staff.

The statistically designed experiment for pulping slash pine is under way. One batch of wood is being used for the entire experiment. The experiment is being conducted in duplicate in four variables -- sulfidity, effective alkali, cooking temperature, and cooking time according to a rotatable composite design to produce liquors at 25 cooking conditions. The experiment is designed to cover the entire range of industrial cooking conditions to yield Kappa numbers ranging from about 25 to about 110. The liquors are blanketed from exposure to air to prevent oxidation, packaged, and shipped to the University of Maine.

Liquor handling is complex, but has been examined in detail. Liquors are mixed at the University, sampled for chemical analyses, concentrated in a large evaporator, skimmed to remove soap, packaged under a nitrogen blanket, and stored under refrigeration. Samples of the concentrated liquor are further concentrated in small laboratory evaporators and loaded into equipment for determination of physical properties, particularly viscosity. The full procedures have been tested and liquor stability evaluated. Work with liquors used in prior research indicates that, with respect to physical properties, liquors can be stored under refrigeration as described above for up to 2-1/2 years without change.

Rheological equipment for broad-range measurements has been installed, modified, and tested. Five separate instruments are used to permit us to determine viscosities at shear rates from 1 to 10^4 sec^{-1} for liquors with solids contents from about 15% to greater than 75% for a temperature range from 25 to

200°C. Viscoelastic properties can be determined for liquors with solids contents above 40% at temperatures from 25 to 90°C and shear rates from about 0.05 to about 20 sec⁻¹. These instruments have required major modification and one instrument has been designed and constructed specifically for this work. Our work indicates that measurements should be accurate to about ±5%.

Equipment for chemical analyses and lignin characterization has been installed, and most have been evaluated for our work. Methods have been developed for analyses of anions and organic acid salts using ion exchange chromatography. These methods are new and represent an advance in liquor analysis. Positive ions are being determined by atomic absorption. Improved procedures for lignin purification have been developed. Procedures for determining weight average molecular weight by light scattering and number average molecular weight by vapor pressure osmometry in organic solvents at elevated temperatures to prevent lignin association have been developed. A total elemental analyzer and a high performance liquid chromatograph have been installed to determine elemental content of liquors and saccharinic acid derivatives of liquors, respectively. Techniques for these analyses have been developed adequately elsewhere and will be applied.

Equipment for thermal analyses has been installed. A differential scanning calorimeter is being used to determine the glass transition temperature of purified lignin and to determine the heat capacity of black liquors from 25 to 100°C at solids contents from 15 to 75%. Density is being determined by pycnometry. Thermal expansion will be determined by dilatometry for solids contents below 50% and by thermal mechanical analysis for solids contents above 50%. These methods have been tested on standard materials and on black liquor. A cell for thermal conductivity measurements is under construction.

Lignin is being purified by a precipitation and solvent exchange procedure that yields a very pure lignin that is totally soluble in a number of organic solvents. The weight average molecular weight of lignin is being determined by light scattering. The procedure requires a total of five sets of measurements to determine a molecular weight. Vapor pressure osmometry is the method of choice to determine the number average molecular weight, and procedures have been developed for doing this in the same solvents that are used for light scattering.

As mentioned earlier, a digester is being designed. The digester, to be installed at the University of Maine and operating by September, 1984 will be capable of pulping 25-29 pounds of oven-dry wood at liquor-to-wood ratios of about 3.5/1 or more. The digester will be designed to simulate batch or continuous operation. It will be designed so that it can be blown and the pulp washed under a controlled atmosphere.

Surface tension measurements will not be attempted until the viscosity, normal stress, and stability of the liquors have been defined by the results of the first pulping experiment, since the choice of method is affected by these properties of the liquor.

The results of the preliminary experiment are very helpful, but only partially conclusive. The chemical analyses results indicate minor variations between cooks. These have been evaluated, and procedures have been modified. We expect very minor cook-to-cook variations in the first experiment. The main

effect of washing pulp, other than a more complete recovery of solids, seems to be to increase the recovery of potassium. During the first experiment, we will wash the pulp and combine wash and pulp liquors for each cook. Liquors can be handled adequately. Lignin glass transitions were essentially equal for lignins from all cooks of the preliminary experiment; however, there may be a difference in molecular weight of lignins produced by using frozen chips as compared to lignins produced by using unfrozen chips. Low solids viscosities and densities were the same for all liquors of the preliminary experiment; however, high solids (>50%) liquor viscosities show differences. This may be the result of differences in lignin molecular weights. Heat capacities of liquors were the same for liquors from the preliminary experiment. It is worth noting that only density of liquors at low solids agreed with data presently used for recovery system design.

The program appears to be running well. Many problems have been identified and solved. Pulpig experiments are beginning. Final installation of equipment and development of procedures will be completed before September, 1984. Data collection will begin in December, 1983 and continue throughout Phase II.

There is no reason at this time to modify the energy savings originally estimated for this project. Firing at 75% or higher solids would seem to be feasible, if properties can be defined with confidence. This should lead to energy savings of about 1.5×10^{11} Btu/yr (equivalent to 26,000 Bbl/yr of fuel oil) for the average 1000 ton/day mill, or a total savings of 7.2×10^{12} Btu/yr (1.24×10^6 Bbl/yr of fuel oil) for the U.S. and Canada, if the developments are utilized by 80% of the industry. Further, it is expected that implementation of higher solids firing could lead to production increases of 3-15% without major new capital investment for mills limited by recovery capacity. This increase could take place possibly with increased chemical recovery efficiency and decreased sulfur pollution.

2.0 BACKGROUND

2.1 OVERVIEW OF THE RECOVERY PROCESS IN KRAFT PULPING

Production of cellulosic pulp fibers from wood requires that the fibers be liberated from the structural matrix of the wood. In chemical pulping processes, this is done by reacting wood with inorganic chemical solutions at elevated temperatures. The active chemicals normally used are alkali and/or reduced sulfur ions. Approximately half of the wood is dissolved during the reaction. The cooking solution is drained from the undissolved fibers, the fibers are washed, and the exit reaction solution and washings are combined to produce a stream called "spent liquor" or "black liquor". The principal chemical pulping process used in the United States is the Kraft process, in which sodium and reduced sulfur ions are used at high pH as the active inorganic chemicals.

The black liquor leaving the pulping process contains 10-17% solids of which approximately one-half to two-thirds is organic. The organic components are partially degraded lignin in soluble or colloidal form, degraded products from hemicelluloses, solubilized cellulose derivatives, and extractives from the wood. [It is worth noting that per cent solids is an arbitrary definition that can be thought of best as those components that do not evaporate from black liquor when heated to 105°C for one to two days; not all components that do not evaporate need be solid at even moderately elevated temperatures].

For economic and environmental reasons, it is necessary to recover the inorganic chemicals and dispose of the organic by-products from pulping. This is done by concentrating the black liquor to 60-70% solids by evaporation and firing the concentrated black liquor into a furnace. In the furnace, the organic materials are burned to produce steam, and the sulfur ions are reduced. The inorganics are withdrawn from the furnace as a smelt, which is then dissolved, causticized (to regenerate caustic), and clarified. The clarified solution is recycled to the pulping process.

The combustion of organics in the black liquor can supply approximately 45% or more of the energy required for a modern integrated mill [Hurley (1978)]. Chemical pulping of wood would hardly be economical or even permitted if chemicals were not recovered and energy were not produced in the liquor recovery cycle.

The heart of the recovery process for Kraft pulping is the Tomlinson furnace [Tomlinson (1948)], which is almost universally used today. Over the years, the process has been improved and refined, but it is basically inefficient as an energy recovery process and it is hazardous to operate. One of the major reasons that it is energy inefficient is that rapid developments of the Tomlinson recovery system took place before 1973, and energy was not as valuable relative to pulp and chemicals as it is today. Therefore, there was much less incentive for improving the efficiency of energy recovery for the Tomlinson system before 1973; efforts were really directed toward improving safety and toward increasing inorganic chemical recovery to decrease pollution. The scale of recovery units has increased over the years [Hochmuth (1953), Westerberg (1968)], and it is present practice to operate units with capacities in excess of that necessary to operate a 400 tons/day pulp mill. Because of the high

capital cost and size per unit, a pulp mill capacity is normally limited by the capacity of the recovery system.

The increased costs and developing scarcity of fossil fuels, in addition to the basic problems of operational hazards and relatively low efficiency of the Tomlinson recovery process, have led to renewed interest in improving the Tomlinson process and in developing alternative recovery processes [Baldus and Edward (1978), Hurley (1978)]. Improvement or process substitution involves large capital risks because of the process scale. However, the potential return for improvement is very large: the total organic solids in black liquors that are burned in the United States probably exceed thirty million tons per year. The fossil fuel displacement represented by the black liquor recovery process is generally unappreciated outside of the pulp and paper industry.

2.2 NEED FOR KNOWLEDGE OF BLACK LIQUOR PHYSICAL PROPERTIES IN PROCESS IMPROVEMENT

To be practical, any black liquor recovery process must be capable of recovering the alkali and sulfur ions, and it must be capable of producing recoverable energy or products that have higher value and utility than their energy equivalent. Any recovery process will require liquor concentration and will usually involve some type of phase separation. Efficiency, safety, and abatement of pollution can best be improved for furnace operation by firing a more concentrated liquor to the furnace. Very large changes in the concentration of the liquor charged to the furnace will require changes in process equipment for concentrating and handling the liquor, changes in the pulping process, or both. In order to design new processes or to make significant changes in the existing process with confidence, knowledge of the physical properties of black liquors must be available; particularly, knowledge of rheological, thermal, and surface properties. Such knowledge, particularly for high solids content liquors, does not exist; there was not sufficient incentive to develop it in the era of cheap energy that existed before 1973.

Ideally, fundamentally based correlation methods should be available to predict these properties at process conditions from a knowledge of the black liquor composition in a manner similar to the methods that have been available for many years for predicting the properties of crude oils and other petroleum fractions [Hougen and Watson (1960)]. No such method currently exists for black liquors. In fact, even property determinations that are reported for particular black liquors are generally sparse and not very precise. The only apparently successful correlation that has been developed to date for black liquors is a method for predicting the heating value of black liquors from a knowledge of the content of grouped structures in black liquor [Gessner (1965)]. Even this correlation is based upon data from only a few liquors.

2.3 RESEARCH ON BLACK LIQUORS AT UMO PRIOR TO OCTOBER, 1982

Research on one of the properties of Kraft black liquor, viscosity, began at UMO in late 1978. Viscosities of a black liquor were measured from 54 to 69% solids over a temperature range of 30 to 90°C. These results showed clearly that black liquor is a non-Newtonian fluid exhibiting pseudo-plastic behavior under these conditions [Kim (1980)]. A typical result from this work is shown in Figure 2.3-1. Viscosities of other liquors produced by very different pulping

FIGURE 2.3-1 Dependence of Viscosity on Shear Rate at Various Temperatures for a Kraft Black Liquor at 66.8% Solids.

processes can exhibit very large differences in viscosity and non-Newtonian behavior, as shown in Figure 2.3-2, which is also work from the same study [Kim (1980)].

We were able, by using values of zero-shear-rate viscosity determined by extrapolation, to obtain a master curve for one black liquor based on a shift factor that includes the effect of temperature. This is shown in Figure 2.3-3. This method of generalized data treatment has been applied to different liquors at different solids contents successfully.

Wight et al (1981) determined black liquor viscosity using cone-and-plate and parallel plate viscometry. The experimental results from the cone-and-plate geometry indicated the possible presence of particles approximately 50 μ or larger at solids concentrations greater than about 55%. The parallel plate geometry was chosen to minimize the effect of particles on the determination of viscosity. These data are in agreement with results from capillary viscometry, as shown in Figure 2.3-4, and provide a means for directly determining the zero-shear-rate viscosity that is needed for data correlation.

Black liquor viscosity at temperatures up to 120°C and at solids contents up to 77% using a pressurized coaxial cylinder viscometer have been determined. These results were reported by Co et al (1982). An example of results from this study is shown in Figure 2.3-5.

Finally, the complex viscosity and steady shear viscosity and normal stress of a black liquor were determined by oscillatory and steady rotation experiments, respectively, using the parallel plate geometry [Wight (1982)]. These results demonstrate that black liquor is a viscoelastic fluid as well as pseudoplastic under some conditions. Example results are presented later in this report.

The zero-shear-rate viscosity, as determined from the capillary viscometer data, obeys an Arrhenius relation as shown in Figure 2.3-6. However, the fluid behavior is quite complicated, and an Arrhenius relation is not followed over a wider temperature range, as shown in Figure 2.3-7.

In summary, the rheological exploratory work demonstrated that:

1. Black liquor is a complex, viscoelastic, pseudoplastic fluid.
2. Black liquor can be treated as a polymer solution.
3. Black liquor rheology is affected by species and pulping conditions, as well as temperature, shear rate, and solids composition.
4. Changes in black liquor rheology with species, pulping, solids content, and temperature are very large so that rheology may be useful as the primary response for correlating properties with composition.

Since the rheology of black liquors behaves as one would expect for a polymer solution, the lignin and hemi-cellulosic polymers present in black liquor probably dominate the rheological behavior, particularly at high solids. However, the solution behavior is very complex. Solution behavior of these polar polymers must be modified by the salts present. At some concentration, solution behavior should undergo severe changes. At low solids concentration,

FIGURE 2.3-2 Dependence of Viscosity on Shear Rate at 50°C for four different Black Liquors.

FIGURE 2.3-3 Reduced Viscosity as a Function of Reduced Viscosity for a Kraft Black Liquor at 66.8% Solids. Reference Temperature = 40°C.

FIGURE 2.3-4. Dependence of Viscosity on Shear Rate for a Kraft Black Liquor at 35°C with Data Taken with Two Instruments.

FIGURE 2.3-5 Dependence of Viscosity on Shear Rate for a Kraft Black Liquor at 77% Solids with Data Taken with Three Instruments.

FIGURE 2.3-6 Dependence of Zero Shear Rate Viscosity on Temperature for a Black Liquor at 66.8% Solids.

FIGURE 2.3-7 Dependence of Zero Shear Rate Viscosity on Temperature of a Southern Softwood Kraft Black Liquor.

black liquor is a solution of organic acid salts, inorganic salts, and ion-modified lignin in water; therefore, it behaves as a more normal liquid solution. At very high solids concentration, black liquor is probably a mixture. The mixture probably contains ion-modified lignin swollen or dissolved in water or organic salts, inorganic salts in solution or suspension, organic salts, and water. Behavior under these conditions would be very complex and very sensitive to the composition of what are normally called solids. It is exactly this composition range that is of prime interest for design of equipment for high solids firing in recovery systems.

Stability of the black liquor and of the lignin in black liquor is very important to know if correlations are to be developed. Therefore, another research study on black liquors conducted at UMO prior to October, 1982 concerned the thermal stability of lignin and black liquor. Thermal gravimetric analysis (TGA) methods were used to study black liquor and lignin. Figure 2.3-8 shows the TGA curve and DA (derivative analysis of weight loss) curve for a 65% solids black liquor heated in nitrogen from room temperature to 900°C. As can be seen, there are a number of temperature regions for major weight losses. This liquor was heated to 140°C at 10°C per minute and held at 140°C for one hour, the weight approached a constant value of 65% of the initial weight after 40 minutes, as can be seen from Figure 2.3-9. When cooled and reheated, the black liquor exhibited no further weight loss until the sample temperature exceeded 140°C. Work with lignin was similar.

While TGA studies indicate stability with respect to degradation by loss of small molecules (chain unzipping) if there is no weight loss, TGA studies cannot reflect changes in molecular structure, such as chain scission, in which there is no weight loss. However, rheology of the liquor at high solids should reflect changes due to chain scission. Black liquors stored for more than two years at 40°F under nitrogen in glass and high density polyethylene (HDPE) containers have been tested periodically. These tests show no changes in the rheology. Tests run at 60°C for up to 100 hours show no major changes for the first 40-60 hours. Further high temperature stability tests have to be run.

The results of the thermal stability tests indicate that liquors can be stored for at least two years at 40°C under nitrogen without change that affects rheology. Tests also indicate that changes at higher temperatures are very likely slow enough to permit rheological data to be collected without the complications of chemical changes in the liquor.

Research on black liquors prior to October, 1982 has been summarized and presented in theses [Kim (1980), Snow (1982), Wight (1982)], papers [Kim (1980), Wight (1980), Co (1981), Fricke (1981), Snow (1981), Fricke (1983)] and publications [Kim (1981), Beckwith, et. al., (1981), Wight (1981), Co (1982)].

2.4 OBJECTIVE

The overall objective of this work is to determine the physical properties--rheological, thermal, and surface--of black liquors over a wide range of conditions and relate them to the composition of the liquors so that correlations for predicting properties with sufficient accuracy for engineering design purposes from the liquor composition can be developed. In the course of the work, liquors are to be made by pulping a known wood under known pulping conditions so

FIGURE 2.3-8 Thermal Gravimetric Analysis (TGA) and Derivative Analysis (DA) Results for a Kraft Black Liquor. Analysis Made at 10°C/Minute in a Nitrogen Atmosphere.

FIGURE 2.3-9 Thermal Gravimetric Analysis (TGA) and Derivative Analysis (DA) Results for a Kraft Black Liquor at 65% Solids When Heated at 10°C Per Minute to 140°C in Nitrogen and Held at 140°C.

that liquor physical properties can be related to pulping conditions, which serves as a secondary objective.

When correlations have been successfully developed, black liquor recovery systems can be designed and/or modified for firing higher solids (>70%) liquors with confidence. This will lead to increased energy recovery and should lead to increased capacity and decreased pollution for black liquor recovery systems.

The objectives for the first phase of this work, which is covered in this report (October, 1982 to October, 1983), were to:

1. Design, purchase, install, calibrate, and test all rheological equipment necessary to permit viscosity to be determined from room temperature to 200°C, from 1 sec⁻¹ to 10⁴ sec⁻¹, and from 15% solids to at least 80% solids; and to permit complex viscosity to be determined from room temperature to 90°C, from 50% to at least 80% solids, and over as wide a frequency range as possible with both types of determinations to be made at accuracies of ± 5% or better, if possible.
2. Design, purchase, install, calibrate, and test equipment necessary to characterize the polymer properties of lignin, particularly molecular weight and glass transition.
3. Design, purchase, install, calibrate and test equipment necessary to analyze liquor composition, which is to include analyses for lignin, negative inorganic ions, positive inorganic ions, low molecular weight organic salts, higher molecular weight organic salts, and total elemental analyses.
4. Design, purchase, install, calibrate, and test equipment necessary for TGA studies of black liquor and lignin, for determination of heat capacity of black liquors, and for determination of densities of black liquors.
5. Design equipment necessary to determine the thermal conductivity of black liquors.
6. Design equipment necessary to determine the surface tension of black liquors.
7. Design and install equipment necessary for handling and storing black liquors to prevent changes in the liquor from occurring.
8. Design a digester for producing the liquors to be studied.

Most of these objectives have been accomplished completely during Phase I (October, 1982 to October, 1983) of this work. However, due to the fact that access to very good pilot plant facilities became available to us during Phase I (October, 1982 to October, 1983) of this work, efforts with respect to designing a digester, surface tension equipment, and thermal conductivity equipment were delayed in order to accelerate work on several objectives for Phase II (October, 1983 to October, 1985) of this work.

The objectives originally scheduled for Phase II that were accomplished in Phase I were:

1. Preliminary design of correlation schemes for relating black liquor properties to composition and to pulping conditions.
2. Selection of a single species for the first pulping study and design of a multi-level, four variable, statistically orthogonal pulping experiment to produce test liquors.

The progress and accomplishments with respect to each of the goals of our work during the period of Phase I (October, 1982 to October, 1983) are described in this report.

2.5 PROJECT TEAM AND INDUSTRIAL PARTICIPATION

This work is conducted at UMO with financial and technical participation from the Department of Energy and a number of industrial sponsors. The program is complex and multi-faceted; therefore, it is not surprising that staffing and co-ordination are complex and have been subject to evolutionary change.

The program organization chart as it presently stands is as shown in Figure 2.5-1. As shown, financial support flows from DOE and the participating companies to the University of Maine at Orono (UMO) office of the Vice-President of Research and Public Service. This office is responsible for financial administration of the program and for transmission of reports to the financial sponsors. The overall technical management of the program is the responsibility of the Program Manager, Dr. A. L. Fricke, Gottesman Research Professor of ChE at UMO. The technical management is conducted by Dr. Fricke with the active participation of the DOE program manager and a program officer from each of the industrial financial participants. Mr. T. E. Farrington, Research Associate in ChE at UMO is serving as a part-time Assistant Program Manager. Actual work is managed along functional lines of research as shown in Fig. 2.5-1. Staffing of each area of specific research will change as need arises.

Industrial companies participate in sharing costs at a rate of \$62,500 per company in the form of grants, and participate by actively assisting in planning the research program and evaluating results in group meetings that are held annually or more frequently, if there is need. Two review and planning meetings were held at UMO during Phase I.

The area of rheological research is directed by Dr. Fricke. Work is presently being conducted by Mr. Wight (Ph.D. student), Mr. Small (M.S. student), Mr. Farrington (Research Associate) at quarter-time, and an undergraduate student at part-time.

The area of chemical analyses of liquors is directed by Dr. M. K. Hill, Research Associate Professor of ChE, with the assistance of Dr. Fricke. Work is presently being conducted by Mrs. Krishnagopalan (Ph.D. student) and by UMO Soil Sciences. Mr. Farrington will be conducting work in this area at quarter-time.

The area of thermal properties is directed by Dr. Fricke with consulting assistance from Dr. E. Kiran, Associate Professor of ChE at UMO. Mr. M. Masse

Fig. 2.5-1 PROJECT ORGANIZATION CHART

(M.S. student) is working in this area. An undergraduate student is also working in this area part-time.

Dr. Fricke is directing work on preparations of lignin from black liquor and lignin molecular weight analyses with the assistance of Dr. Hill. Mr. Kim (Ph.D. student) is conducting work in this area with the periodic assistance of a part-time undergraduate student.

Dr. Fricke is presently responsible for research on surface tension; however, this area is not yet active.

The UMO staff has overall responsibility for pulping. Mr. Farrington will have principal responsibilities for co-ordination as part of his role as Assistant Program Manager. Since pulping experiments performed during the early part of Phase I will be conducted by the Pensacola laboratory of St. Regis, Dr. J. Wood of St. Regis will be actively involved in work in this area.

Correlation of results is principally the responsibility of Dr. Fricke as Program Manager at UMO; however, the entire UMO staff is involved.

2.6 REPORTING

Research performed in this program is to be reported in the following forms:

1. Periodic Progress Summaries that are issued at a rate of nearly one a month (nine were issued during Phase I).
2. Periodic Review Meetings with the UMO staff, DOE Program Manager, and Program Officers of Industrial Participants that are held at least annually (two were held during Phase I).
3. Annual Reports to DOE
4. Final Report to DOE after program is completed in October, 1985.
5. Presentations at Technical Meetings and Technical Publications after work has been reported to DOE and the Industrial Participants.

There is agreement that any results reported to the public domain are to have been reported first to DOE and the Industrial Participants. However, all results are to become public knowledge; the method of presentation and publication of results is to be the responsibility of the UMO Program Manager.

2.7 REPORT ORGANIZATION

Following this OVERVIEW Section, this report is organized as follows:
SELECTION OF EXPERIMENTAL RESEARCH METHODS (Section 3)
PULPING EXPERIMENTAL DESIGN (Section 4)
LIQUOR HANDLING (Section 5)
EXPERIMENTAL METHODS AND PROCEDURES (Section 6)
UNSOLVED PROBLEMS (Section 7)
TIME SCHEDULE AND STAFFING (Section 8)
TECHNOLOGY TRANSFER (Section 9)
TOTAL ENERGY SAVINGS POTENTIAL (Section 10)
APPENDICES

3.0 SELECTION OF EXPERIMENTAL RESEARCH METHODS

The first and principal activity for Phase I of this program was the selection and development (if needed) of the experimental methods to be used in research on black liquor properties. This included pulping and liquor handling; however, pulping and liquor handling are so key to the overall program that they will be discussed later. Pulping is to be conducted on known woods under known conditions and liquor is to be handled to minimize uncontrolled oxidation and changes in liquor composition.

3.1 CHEMICAL ANALYSES RESEARCH METHODS

The principal components in black liquor solids can be identified by groupings as shown in Figure 3.1-1 [Sjostrom (1982)]. It is evident that the major classes of black liquor solids components are:

1. Inorganic ions
2. Lignin
3. C₁ to C₅ organic acid salts
4. Saccharinic organic acid salts

It is necessary then to select methods for analyzing these classes of components. The degree of completeness for analysis of each class is still under review; however, it is apparent from Figure 3.1-1 that the classes formed by C₁ to C₅ organic acids and by saccharinic acids are each dominated by a few compounds. Also, we should like to analyze the black liquor with as little chemical change as possible. Methods chosen for these analyses are detailed below. In addition, some additional analyses will be performed in the early stages. A summary is presented as part of Section 4, PULPING EXPERIMENTAL DESIGN.

3.1.1 Inorganic Positive Ions

Atomic absorption and atomic emission have been chosen as the method for analyzing for elements that could form positive inorganic ions. These methods are used to analyze for sodium, potassium, calcium, magnesium, and iron. TAPPI Method T-625 will be used to analyze liquors for active alkali, sulfated ash, and organic matter.

3.1.2 Inorganic Negative Ions

Analyzing for inorganic components that could form negative inorganic ions is complicated by the possible oxidation states of sulfur and inorganic carbon ions. This area has been the subject for intensive work at UMO in Phase I.

Ion exchange chromatography has been chosen as the prime method for analysis for chloride, carbonate, and most sulfur ions. Ion selective electrode methods may also be used for certain of the sulfur ions. TAPPI Method T-625 will be used to determine sulfidity and total sulfur.

3.1.3 C₁ to C₅ Organic Acid Salts

A chromatographic method has been chosen. The method of choice is ion exchange chromatography. This method appears to be quite adequate for analyses

RELATIVE COMPOSITION OF THE ACID FRACTION, %

ACID	PINE	BIRCH
FORMIC	16	11
ACETIC	11	27
GLYCOLIC	3	4
LACTIC	11	10
2-OH-BUTANOIC	4	15
2,5-diOH-PENTANOIC	3	2
XYLOISOSACCHARINIC	4	11
GLUCOISOSACCHARINIC	39	8
MISCELLANEOUS	9	12

TYPICAL COMPOSITION OF KRAFT BLACK LIQUOR SOLIDS

FIGURE 3.1-1 Principal Components of Solids for Typical Kraft Black Liquors.
Representation Taken from Sjostrom (1982).

of these components, although complete separation of each component in this class is not accomplished by chromatography. Fortunately, it is very likely not necessary to have such a component separation.

3.1.4 Saccharinic Acid Salts

A chromatographic method has been chosen. HPLC will be used to analyze for these components. As in the case of chromatography for the C₁ to C₅ organic acid salts, separation by components will not be complete; however, complete component separation is very likely not necessary for our purposes.

3.1.5 Lignin

Lignin is a severe problem; there are no good absolute methods for determining lignin content with certainty. Relative methods have been chosen. UV-visible extinction at 280 and 205 nm is being used to determine relative concentration of lignins in black liquor. Gravimetric methods, such as ultra-filtration and acid precipitation are also under study. While relative concentration measurements of lignin in black liquor may be adequate for our purposes, the lignin is so key to rheological behavior that a more reliable method is highly desirable.

3.1.6 Total Elemental Analysis

Total elemental analysis by pyrolysis and controlled oxidation will be used to determine the elements carbon, hydrogen, nitrogen, oxygen, and possibly sulfur in black liquor solids. The CDS TEA unit installed can also be used to determine formula weights of separated components from chromatographic analyses of organic acid salts for approximate peak identification purposes.

TAPPI Method T-624 will be used to determine inorganic carbon and, as mentioned earlier, TAPPI Method T-625 will be used to determine total sulfur.

3.1.7 Per Cent Solids

Per cent solids in black liquors will be determined by TAPPI Method T-625 or by modified methods that are shown to give equivalent results.

3.2 RHEOLOGICAL RESEARCH METHODS

Determination of rheological properties over the extreme ranges of temperature, shear rate, and solids content desired requires a variety of instruments and methods. Five basic instruments have been selected as the minimum necessary. In some cases, instruments were modified or designed completely. In all cases, procedures have been developed and the instruments tested. The ranges of usefulness are outlined below; in every case, overlap of results from instrument to instrument has been provided for so that the final results can be combined.

3.2.1 Glass Capillary Viscometers

Glass capillary viscometers have been installed for determining viscosity of black liquors at 50% solids or less over a temperature range from 30 to 100°C. These will be used for determinations only in the Newtonian behavior region.

3.2.2 Instron Rheometer

The Instron Capillary Rheometer will be used to determine viscosity of black liquors at solids contents above 50%. The instrument is limited to those conditions for which flow through the capillary requires a force in excess of approximately 25 psi. This instrument will be used to determine viscosity at 30 to 100°C of liquors containing more than 50% solids when undergoing shear at rates from 100 to 10^4 sec^{-1} .

3.2.3 Haake Viscometer

The Haake Viscometer will be used primarily to determine the viscosity of black liquors at solids contents above 50%. The instrument is limited to those conditions for which the torque produced by shearing lies between about 30 gm-cm and 500 gm-cm. It will be used basically to determine viscosities of liquors containing more than 50% solids at 30 to 150°C when undergoing shear at rates from about 20 to 300 sec^{-1} .

3.2.4 Rheometrics Spectrometer

The parallel plate geometry of the spectrometer will be used to determine zero-shear rate viscosity and normal stresses of black liquors at solids contents above 50% and at temperatures from 30 to 90°C. The instrument is limited by secondary flow phenomena to shear rates of less than about 20 sec^{-1} .

3.2.5 Dual Chamber Capillary Viscometer

This unique instrument will be used to determine viscosities of black liquors at shear rates from 100 to $5 \times 10^3 \text{ sec}^{-1}$ at temperatures up to 204°C. The instrument is limited to measurements that produce about a 100 psi pressure drop across the capillary.

3.3 LIGNIN MOLECULAR WEIGHT RESEARCH METHODS

3.3.1 Number Average Molecular Weight (M_n)

The method selected to determine the number average molecular weight of lignin separated from black liquor is vapor pressure osmometry. A Wescan model 232 VPO has been installed and tested.

3.3.2 Weight Average Molecular Weight (M_w)

The method selected to determine the weight average molecular weight of lignin separated from black liquor is light scattering. A Chromatrix KM-6 low angle laser light scattering spectrophotometer (LALLS) has been installed, calibrated, and tested for this determination. A Chromatrix KMX-16 laser differential refractometer has been installed, calibrated, and tested for determining the effect of lignin concentration on refractive index of the solution.

3.3.3 Glass Transition

The method selected to determine glass transition temperature is differential scanning calorimetry. A Perkin-Elmer DSC-2 has been used to determine the

glass transition temperatures of separated lignins.. Results of this method will be compared with results to be obtained from dilatometry.

3.4 THERMAL ANALYSES RESEARCH METHODS

3.4.1 Heat Capacity

In addition to its use in determining glass transition, the DSC can be used to determine heat capacities. The DSC has been calibrated, tested, and used to determine heat capacity of black liquor.

3.4.2 Density

Densities of black liquors at solids contents below 60% will be determined by pycnometry at temperatures from 30 to 100°C. Procedures for this have been tested. Densities of black liquors at solids contents above 60% will be determined by precision molding and volume displacement of the molding at 25°C. Densities of liquors with 60% or more solids for temperatures above 25°C will be determined by measurement of volumetric thermal expansion using mercury displacement dilatometers and a Perkin-Elmer TMS-2 thermal mechanical analyzer with a special dilatometry attachment.

3.4.3 Thermal Conductivity

Thermal conductivities of black liquors will be determined using a custom designed co-axial cylinder cell.

3.4.4 Thermal Stability

Thermal Stability will be determined in several ways. Thermal gravimetric analysis (TGA) will be used to determine stability of black liquors and lignin with respect to release of volatiles. A DuPont Model 951 TGA has been installed, programmed for real-time closed loop control and data analysis on a DEC 11/60, tested, and used to determine stability of black liquors and lignins. The tests can be run under a variety of atmospheres or under vacuum at temperatures from 30 to 900°C. Viscosity analysis will be used to determine liquor stability. Liquors can be held for long periods (100 hours or more) in the Haake viscometer at temperatures up to 250°C and the viscosity determined periodically during the holding period. Any changes in liquor that affects liquor physical properties should be indicated by a change in viscosity.

3.5 SURFACE TENSION

Selection of a research method for determining surface tension of black liquors has been postponed. The method to be used is very dependent upon the rheology of the liquor, and the techniques to be used are affected by the thermal stability of the liquor. Results are also expected to be affected by changes in some component concentration. Selection of a method will be postponed until more information on rheology, thermal stability, and composition is available.

4. PULPING EXPERIMENTAL DESIGN

It is important that the history of the black liquors to be used in this study be well documented. The wood species and chip condition must be known and the pulping conditions must be closely controlled if our work is to be most useful. Our work has shown that black liquor viscosity is affected by:

1. Wood species
2. Positive ion level
3. Sulfidity
4. Oxidation state

We also strongly suspect that viscosity is affected by cooking time and temperature. It probably is affected by liquor-to-wood ratio and chip condition. This study should be done on liquors for which these factors are definitely known. Since we believe our work will be limited to a study of 50 liquors, statistically designed experiments are essential.

Wood species definitely has an effect, since the lignin, holocellulose, and hemicellulose compositions vary with species, and we know that the rheology of black liquors follows behavior characteristic of a polymer solution. There are at least five forest belts in North America--Northeastern (U.S. and Canada from Maritimes/New England to Northern Minnesota), Mid-Atlantic/Mid western (middle U.S. from Connecticut/New Jersey to Western Illinois/Kentucky), Southeastern (Virginia to Texas), Western (West of Rockies), and Mountains/Plains (East of Rockies and North of Colorado). Even if only the dominant species are used, this still requires possible consideration of more than fifteen species.

Cooking conditions must be varied to include the effects of sodium level, sulfidity, cooking time, and cooking temperature as a minimum, and we should make every attempt to obtain the liquors in an unoxidized state so that the effect of oxidation can be determined. Cooking conditions should be set to yield pulps with a wide range of Kappa numbers.

For our first experiment, we were advised by our Industrial Participants Program Officers to choose slash pine as the species. Pulping will be done in the pilot plant of St. Regis in Pensacola, Florida under the supervision of St. Regis' Pensacola Laboratory personnel.

Since the cooking is expensive and time consuming and since the quality of the results of the studies of physical properties are very dependent on the precision of the cooking used to prepare the test liquors, we have spent a great deal of time and effort designing the experiment for slash pine so that the experiment is under as good a control as possible.

Points of concern for control of the experiment are:

1. Wood source, uniformity, and storage.
2. Digester white liquor composition.
3. Black liquor transfer.
4. Black liquor concentration, storage, and handling.

4.1 WOOD PREPARATION

The wood to be used will be mature slash pine supplied by St. Regis from a test stand. The pulpwood will be harvested, debarked, chipped, and screened under supervision of St. Regis' Pensacola Laboratory personnel. Clean chips of uniform thickness will be used. The chips will be screened (classified) by using Williams thickness screens. A typical chip size classification from this chipping system is given in Table 4.1-1. The accepted chips would fall within $+ 3/16$ -inch and $- 1 1/8$ inch. All the chips will be mixed (quartering and requartering carefully) and sampled. Each sample, one for each cook, will be packed in air-tight plastic bags and stored. To preserve chips during the course of the experiment, it is best to freeze the chips, store the chips in a frozen state, and thaw them just prior to pulping. An alternative is to store the chips at approximately 40°C so that possible changes due to freezing are avoided; however, chip deterioration would occur at a reduced rate. Since we are uncertain as to the length of the first experiment, frozen chips will be used. The effect of freezing will be checked later.

4.2 DIGESTER AND BLACK LIQUOR TRANSFER

The pilot scale digester to be used in the first experiment is St. Regis' experimental digester in their Pensacola Laboratory. The digester is a rotary (tumbling) digester that is temperature controlled by steam. The digester is loaded through a small opening at one end and closed during cooking. When cooking is completed, the digested chips are normally removed by blowing through the loading port.

In our case, since we wish to eliminate or minimize oxidation of black liquor, the digested chips will not be blown from the digester. Instead, liquor will be removed by draining and washing in the digester. The digester will be inverted, a filter fixed to the outlet of the digester to separate fibers, and the liquor drained from the digester through the filter, hose, and a heat exchanger directly into heavy-duty (heavy-wall), 5-gal. HDPE carboys, which have been purged with nitrogen. After draining, the digester will be filled with warm, degassed water, tumbled to wash the chips, and the washings drained into carboys in a manner identical to that used for the liquor. Our material balances show that the black liquor solids recovery in the drained liquor, first wash, and second wash are approximately 60%, 27%, and 8%, respectively, for a total recovery of 95%. The effects on liquor due to this procedure are considered separately. The carboys will be packaged in cardboard containers and shipped to UMO.

It appears that the wood charge will be about 25 lbs (11.34 kg) oven dry wood. At 50% yield and 4/1 liquor-to-wood ratio, total black liquor produced will be approximately 22.2 gal. (84.0 liters) at 8% solids.

4.3 WHITE LIQUOR

Synthetic white liquor of known composition will be used. The liquor will be adjusted with calcium, potassium, and carbonates.

Table 4.1-1

CHIP SIZE DISTRIBUTION AND DIMENSIONS

Ro-Tap Classification		Williams Classification		Dimensions - Inches (By Williams size classes)			Remarks
<u>Tyler Mesh</u>	<u>%</u>	<u>Class</u>	<u>%</u>	<u>Length</u>	<u>Width</u>	<u>Thickness</u>	
Normal Chips - Pilot Plant - Screened							
+2 1/2"	79.77	+1 1/8"	2.61	1.07	1.53	0.27	Test wood after screening. 1 1/2" mesh oversize, 6 mesh sawdust. Used for test cooks.
-2 1/2" +3	8.29	-1 1/8" + 7/8"	7.39	0.77	1.18	0.25	
-3 +4 mesh	7.65	-7/8" + 5/8"	27.70	0.59	0.90	0.14	
-4 +8	3.88	-5/8" + 3/8"	41.49	0.54	0.57	0.14	
-8 +9	0.21	-3/8" + 3/16"	19.13	0.47	0.28	0.08	
-9 +14	0.14	-3/16"	1.68	0.43	0.09	--	
-14 mesh	0.07						

-29-

4.4 BLACK LIQUOR CONCENTRATION, STORAGE, AND HANDLING

The liquor will be shipped to UMO by fast freight. The liquor draining and washings will be loaded into a pilot evaporator under nitrogen, mixed, and the mixed liquor sampled to provide 2 to 3 liters of an 8% solids sample for analyses. This will be stored at about 40°F (+4.4°C) for use for chemical analyses. The mixed liquor will then be concentrated by evaporation at 0 to 3 inches Hg (0 to 76 mm Hg) vacuum to 25-28% solids. The concentrated hot liquor will be transferred under nitrogen to a glass vessel where it will be allowed to cool for soap separation. The cooled liquor will be drained from the bottom of the glass vessel directly into clean, purged HDPE 5-gal. carboys. The carboys will be sealed and stored at about 40°F (+4.4°C) for use in physical properties studies.

4.5 DESIGN FOR SLASH PINE EXPERIMENT

The experiment is to be run in such a way that it is manageable, can be revised if necessary, is statistically valid, and accounts for the important variables while keeping other variables under control. The total list of variables that were considered is:

1. Wood
 - a. Species
 - b. Growth conditions
 - c. Age
2. Chips
 - a. Bark percentage
 - b. Dimensions (3 variables)
 - c. Age
3. White liquor
 - a. Active alkali
 - b. Sulfidity
 - c. Causticizing efficiency (carbonates)
 - d. Presence of other ions (chloride, other alkalis, alkaline earths)
 - e. Additives, such as anthroquinone
4. Cooking
 - a. Time
 - b. Temperature
 - c. Time to temperature
 - d. Liquor to wood ratio
 - e. Agitation or circulation and rate
5. Liquor handling
 - a. Drain vs. blow
 - b. Exposure to air
 - c. Evaporation and skimming

Most of these have been set and will be held constant. The method of handling wood and chips sets all variables with respect to wood and chips constant. Levels of carbonate (for causticizing efficiency) and ions other than

those represented by active alkali and sulfidity will be set and held constant. Synthetic white liquor will be used to insure this. The cooking will be done in a tumbling digester (speed constant), the liquor will be drained rather than blown, exposure to air will be minimized, and evaporation and skimming will be done in a uniform manner. The liquor-to-wood ratio will be held constant at 4-to-1 and the time to temperature will be held constant at some value between 40 and 60 minutes. Therefore, our experiment is one for four variables--cooking time, cooking temperature, effective alkali, and sulfidity.

4.5.1 Specific Design

The specific design chosen is an orthogonal rotatable composite design in four variables. The conditions were set to give pulps with Kappa numbers ranging from about 25 to 90 or above without exhaustion of chemicals so that conditions for producing bleachable and liner board pulps would be included. The actual variable values, statistical cooking for each variable value, and expected Kappa number for each cook in the design are given in Table 4.5.1-1.

The first 16 cooks represent a 2^4 factorial experiment. The first 8 cooks represent a half factorial experiment in these four variables that compares:

1. All variables low to all variables high.
2. High time and temperature with low chemicals (effective alkali and sulfidity) to low time and temperature with high chemicals.
3. Interaction of time and temperature with effective alkali and sulfidity.

The first eight cooks (half factorial) will be run. If time and temperature can be combined as an H-factor in their effect on liquor properties as they are in their effect on Kappa number of pulp, it will be obvious by comparing results from runs 3 and 5 with results from runs 4 and 6, respectively, and the experiment can be redesigned with time and temperature as a combined variable. At least four, if not all eight, of these runs will be duplicated to permit us to estimate the variance to be expected in our results due to cook-to-cook variations.

Assuming that cooking time and cooking temperature cannot be combined into one variable, we will perform runs 9 through 16 to complete the 2^4 factorial. Cooks for each run will be duplicated if our first half factorial results demonstrate a high variance for duplicate cook results or if our physical properties tests require more liquor than can be provided by one cook (about 22-gal. at 8% solids).

The 2^4 factorial represented by the first sixteen runs should give cooks that produce pulps with Kappa numbers ranging from about 25 to 90+, with five cooks at Kappa numbers at 40 or below and six cooks at Kappa numbers at 70 or above. There should be no exhaustion of chemicals and there is no reason to expect discontinuities in any response.

Run 17 is the center point of the design. It very likely will be run at the same time as runs 9 through 16. Results from run 17 will be used to estimate interior curvature. This should assist us in evaluating the worth of proceeding with the complete rotatable composite design, and estimates of variance from duplicates in the factorial design will permit us to assess the value of retaining design orthogonality.

Table 4.5.1-1

PULPING EXPERIMENTAL DESIGN

Run	Variable Coding				Variable Values				K no. est
	<u>t</u>	<u>T</u>	<u>EA</u>	<u>S</u>	<u>t,min</u>	<u>T,°F</u>	<u>EA,%</u>	<u>S,%</u>	
1	-1	-1	-1	-1	40	330	13	20	90
2	1	1	-1	-1	80	350	13	20	40
3	1	-1	1	-1	80	330	16	20	60
4	-1	1	1	-1	40	350	16	20	40
5	1	-1	-1	1	80	330	13	35	80
6	-1	1	-1	1	40	350	13	35	50
7	-1	-1	1	1	40	330	16	35	70
8	1	1	1	1	80	350	16	35	25
9	1	-1	-1	-1	80	330	13	20	70
10	-1	1	-1	-1	40	350	13	20	50
11	-1	-1	1	-1	40	330	16	20	70
12	1	1	1	-1	80	350	16	20	25
13	-1	-1	-1	1	40	330	13	35	90
14	1	1	-1	1	80	350	13	35	40
15	1	-1	1	1	80	330	16	35	60
16	-1	1	1	1	40	350	16	35	40
17	0	0	0	0	60	340	14.5	27.5	50
18	-2	0	0	0	20	340	14.5	27.5	100+
19	2	0	0	0	100	340	14.5	27.5	30
20	0	-2	0	0	60	320	14.5	27.5	90
21	0	2	0	0	60	360	14.5	27.5	25-
22	0	0	-2	0	60	340	11.5	27.5	90+
23	0	0	2	0	60	340	17.5	27.5	25-
24	0	0	0	-2	60	340	14.5	12.5	30
25	0	0	0	2	60	340	14.5	42.5	30

Runs 18 through 25 are the star (extreme axis) points of the composite design. These run conditions will be reevaluated after the 2⁴ factorial experiment is done. Run 18 requires a short cooking time vs. time to temperature; therefore, its validity may be questionable. Run 21 will very likely yield a very poor pulp, but it can be run. Run 22 is the one run most likely to lead to exhaustion of chemicals. Run 25 requires a very high level of chemicals. If conditions for runs 18 through 25 are changed, orthogonality for the design will be lost, unless all values for the star points are reduced proportionally; however, orthogonality will not be important if variance is estimated from replicates taken at runs for the 2⁴ factorial design. Final decision on runs 18 through 25 will be made after the 2⁴ factorial is completed.

4.5.2 Preliminary Pulping Experiment

It was considered prudent to conduct a preliminary pulping experiment to try to answer certain questions and to provide for a trial run through all procedures before starting the designed experiment.

St. Regis was to use chips of slash pine from the Pensacola mill and cook the chips according to conditions for run 17 (the design center point). Synthetic white liquor containing 14.5% effective alkali and 27.5% sulfidity was to be used. Four cooks at the conditions of run 17 were to be made. Two cooks were to be made using refrigerated chips and two cooks were to be made using frozen chips. Liquors from each cook were to be obtained by draining the digester as described earlier and shipped to UMO. Chips from each cook were to be washed once as described above and the wash liquor shipped to UMO. Because of the concern for extracting lignin from pulp by contacting with hot water for long periods, the wash conditions varied. Wash for one cook with frozen chips and for one cook with unfrozen chips were made with 150°F water for 8 minutes (short time/low temperature). Wash for one cook with frozen chips and for one cook with unfrozen chips were made with 175°F water for 180 minutes (long time/high temperature). Wash for each cook was packaged and shipped to UMO.

The objectives for the preliminary pulping experiment were to:

1. Determine the cook-to-cook variations.
2. Determine any differences in yield, Kappa number, and/or black liquor due to freezing chips.
3. Determine differences in solids contained in the black liquor and the wash, and the effects of wash time and temperature, if any, on the solids.
4. Provide a trial run for all procedures to be used.

The liquors and washes were to be analyzed at the St. Regis laboratory and at UMO by the methods summarized in Table 4.5.2-1. Evaporation, rheological, thermal, and molecular weight characterization studies were to be conducted at UMO.

This experiment, for various reasons, was only partially successful. It could not be used to conclusively determine cook-to-cook variations, the effects of freezing chips, or the differences in solids in liquor vs. wash. However, it could be used to partially evaluate the questions. It also provided invaluable experience in evaluating methods, in providing a good basis for time management planning, and for determining liquor solids yield.

Table 4.5.2-1
CHEMICAL ANALYSES OF BLACK LIQUOR, PULP, AND WOOD
PRELIMINARY PULPING EXPERIMENT

Analysis	Done at UMO	Done at St. Regis [†]
	How	How
1. Solids	Convection oven	Vacuum oven
2. Density	Pycnometer	Pycnometer
3. pH	Orion 611	Orion 611
4. Heat of combustion		Parr Adiabatic Calorimeter
5. Sulfated ash		TAPPI T625
6. Elemental analysis		
a. S	Nephthelometry & Tappi T625	Fisher combustion analyzer
b. C, H		Perkin-Elmer 240B analyzer
c. C, organic		Beckman 915B analyzer
d. Na, K, Ca, Mg	Atomic absorption & emission	Atomic Absorption
7. Alkali and Sulfidity		
a. Na ₂ S	TAPPI T625	Similar to TAPPI T625
b. free NaOH		
c. active alkali		
d. effective alkali		
e. total alkali		
8. Ions		
a. S ⁼ , (HS ⁻)	IC & sulfide electrode	HgCl ₂ titration
b. SO ₃ ⁼	IC	Differential pulse polarography
c. S ₂ O ₃		
d. SO ₄ ⁼	IC	TAPPI T623
e. CO ₃ ⁼	ICE	Beckman 915B (see 6c)
f. Cl ⁻	IC	---
g. organic acids	ICE ¹	GC of methyl esters ²
9. Volatiles		
a. Neutrals ³		Direct GC
b. Sulfur Compounds ⁴		
c. Terpenes ⁵		

Table 4.5.2-1 (cont'd.)

<u>Analysis</u>	<u>Done at UMO</u> <u>How</u>	<u>Done at St. Regis[†]</u> <u>How</u>
10. Methoxyl and Ethoxyl		
11. Lignin		
a. concentration	Ultraviolet absorption	
b. molecular weight	VPO & LALLS	
c. Methoxyl and Ethoxyl		GC of iodide derivatives
12. Tall oil		
a. dilute BL		Extraction & GC of methyl esters
b. For 25-30% BL	Extraction	
c. Tall oil skim- ming	Volume, density, others as possible	
13. Pulp		
a. Kappa number		TAPPI method
b. Yield		TAPPI method
c. Inorganic cations	Atomic absorption	
13. Wood		
a. Summative	TAPPI Methods	
b. Inorganic cations	Atomic absorption	
1. acetate, formate, lactate, oxalate 2. acetic, formic, lactic, glycolic, oxalic 3. methanol, ethanol, acetone 4. methyl mercaptan, dimethyl sulfide, dimethyl disulfide 5. Terpene compounds are expected to be lost during draining of the cooks at St. Regis. However, α - and β -pinene analysis will be done on at least one dilute black liquor.		

[†] As noted, certain analyses are being done both at St. Regis and at UMO. The purpose of the duplication is to (1) compare the state of the liquor before and after shipment from St. Regis (2) compare different methods of analyzing for the same component. In certain cases St. Regis will only do the first set of 8 samples and unless variability is seen they will not continue.

Abbreviations Used: IC and ICE refer to analyses to be done on the Dionex Ion Chromatograph; GC - gas chromatography; MW = molecular weight; LALLS = low angle laser light scattering; VPO = vapor pressure osmometry.

The description for the preliminary pulping experiment with some of the results, as reported by St. Regis, are given in Table 4.5.2-2. Results reported elsewhere are keyed to the cook number as T-2760, T-2761, etc. Washes are keyed to the cook number as T-2760W, T-2761W, etc.

Table 4.5.2-2
PRELIMINARY PULPING EXPERIMENT
COOKING CONDITIONS

<u>Cook #</u>	<u>Chips</u>	<u>Time at Temp.</u>	<u>Wash Conditions</u>		<u>Kappa #</u>	<u>Total Yield</u>
			<u>Time</u>	<u>Temp.</u>		
T-2760	Frozen	70 min.	180 min.	175°F	52.2	51.21%
T-2761	Frozen	73 min.	8 min.	150°F	50.9	52.19%
T-2762	Unfrozen	70 min.	180 min.	175°F	52.6	50.76%
T-2763	Unfrozen	73 min.	6 min.	150°F	51.8	50.86%

14.5% Effective Alkali

27.7% Sulfidity (based on AA)

117.61 g/l Effective Alkali (as Na₂O)

Liquor:Wood - 4:1

Cooking Temp. - 340°F

Time to Temp. - 60 min.

Chip dryness - 50.6%

Wood Charge - 20 kg (22 lbs) oven dry basis

Notes: (1) White liquor made from "mill stock" NaOH and Na₂S. Concentration of Na₂S reported as 60-62%. Purity of NaOH unreported as of 10/4/83. Deaerated water was used.

(2) Kappa numbers run after at least 2 days to permit pulps to stabilize.

5. EXPERIMENTAL METHODS AND PROCEDURES

5.1 OVERALL SAMPLE HANDLING PROCEDURE

Proper handling of liquor samples at UMO is extremely important and considerable effort has been devoted to planning, testing, and reviewing a scheme for sample handling. The sample procedure that has evolved is outlined in Figure 5.1-1.

When the sample arrives from St. Regis in 5-gal. HDPE carboys, it will either be placed in cold storage at 40°F (+4.4°C) or processed immediately. The first step in processing is mixing. The entire sample (liquor plus two washes) will be loaded into the large evaporator under a nitrogen blanket to give approximately 22-gal. of liquor at 8% solids. The liquor will be thoroughly mixed in the evaporator. After mixing, samples for analyses and as permanent retains will be withdrawn in containers under nitrogen and the containers will be sealed and stored at 40°F (+4.4°C) until needed. The liquor remaining in the large evaporator will be concentrated to 24-28% solids, the soap separated, and the concentrated liquor packaged and stored at 40°F (+4.4°C) until needed for rheological, density, or thermal studies.

Aliquots of the 8% solids sample to be used for analysis will be removed from the stored liquor by transferring the aliquot to the proper container in a glove box so that exposure to oxygen is minimized or eliminated.

Aliquots of the 24-28% solids sample will be removed from the 5-gal. carboy under nitrogen, but only after the sample has been thoroughly agitated. The aliquot will be transferred to the small evaporator, concentrated to the proper solids content, loaded into the proper loading device for the test to be run, and either used immediately or refrigerated and stored until needed.

These methods have been tested during the preliminary pulping experiment. Modifications have been made on the basis of our experience and the necessary equipment for conducting these sample handling procedures have been designed and installed; however, further refinements may be necessary.

5.2 LIQUOR STABILITY

Liquor stability under storage and test conditions is a very important consideration, and considerable attention has been given to this matter.

5.2.1 STABILITY OF HIGH SOLIDS SAMPLES

A number of tests for stability have been run, primarily by determining rheological behavior periodically for the same sample. The results of these tests are reported here.

An unoxidized Kraft black liquor produced from a cook of 80/20 Western softwood and hardwood was concentrated to 63+% solids, transferred to a plastic bottle and refrigerated. The cold sample bottle was removed from the refrigerator and heated in boiling water. The hot liquor was mixed with a spatula, a portion loaded into the Instron viscometer and viscosity determined at 30°C. The unused sample was returned to the refrigerator. This procedure was repeated

Figure 5.1-1
SAMPLE PROCEDURE FOR BLACK LIQUORS

twice. The total elapsed time was 17 days from the first measurement through the third measurement. Results are summarized in Figure 5.2.1-1.

An unoxidized Kraft black liquor sample produced from a cook of Southern softwood was tested at 66.6% solids. The sample was placed in loading device and held at about 60°C in the device. Periodically, viscosities were determined by transferring a portion of the sample to the Instron viscometer and running the viscometer at 50°C. The remainder of the sample was retained in the loading device at about 60°C. Test results for a holding time of 100 hours are shown in Figure 5.2.1-2. These results show a slow change occurring after about 48 hours at 60°C.

Stability of samples stored for long periods under refrigeration has also been evaluated. An unoxidized Kraft black liquor sample produced from a cook of Southern softwood and delivered to UMO at 50% solids was used. Six one-quart aliquots were taken from the liquor as received and the one-quart aliquots stored under refrigeration. This was done in April, 1981. Within 24 hours, four quarts were evaporated to given solids contents, loaded hot in the Rheometrics, or loaded into grease guns and stored hot until it could be run in the Rheometrics. The zero shear-rate viscosity was determined at 40, 60, and 80°C for solids contents of 58.3, 63.6, 69.3, and 77% solids. These data are shown in Figure 5.2.1-3.

During August, 1981 (four months later), a fifth quart was concentrated and samples taken at 58, 68, and 78% solids. The samples were bottled and refrigerated. Zero shear-rate viscosities were determined for these materials in April, 1982 (twelve months later). The zero shear-rate viscosity for 78% solids at 80°C was 13.5 Pa-Sec., as compared to 13.0 Pa-Sec for 77% solids at 80°C determined in April, 1981. Zero shear-rate viscosity determined at 68% solids and 40°C agreed exactly with the curve of zero-shear viscosity vs. solids at 40°C derived from data taken in April, 1981. Zero shear-rate viscosity was determined in April, 1982 at 50°C for 78% solids and 68% solids samples.

The samples used in April, 1982 were stored under refrigeration. In August, 1983 (thirty months after first data), the zero shear-rate viscosities for the 68% solids and 78% solids samples were determined at 50°C. The comparison was excellent. For example, the values determined for the 78% solids sample in April, 1982 and August, 1983 were 1220 Pa-Sec. and 1300 Pa-Sec., respectively. Moreover, these data for 50°C lie approximately between curves for 40°C and 60°C for data determined in April, 1981, as shown in Figure 5.2.1-3.

Stability of liquors at temperatures above 60°C is yet to be tested. These tests will be run very early during Phase II of this work. The Haake Viscometer appears to be ideal for this work and will be the preferred experimental instrument for high temperature stability studies of black liquor.

5.2.2 STABILITY OF LOW SOLIDS SAMPLES

It is startling to find that no really valid data exists for determining stability of liquors on storage at low solids. All liquors used in the early phases of this work were delivered in high solids (50% or greater) form. However, we do not expect any problems with stability of low solids samples, because the high solids samples of unoxidized liquors that have been used for

FIGURE 5.2.1-1 Reproducibility of Dependence of Viscosity on Shear Rate for an Unoxidized Southern Softwood Kraft Black Liquor at 30°C and $63.4 \pm 0.4\%$ Solids.

FIGURE 5.2.1-2 Variation of Viscosity of an Unoxidized Kraft Black Liquor at 60°C. Viscosities Determined at 30°C.

FIGURE 5.2.1-3 Stability of Black Liquor When Stored at 40°F. Zero Shear Rate Viscosities Determined Periodically by Parallel Plate Viscometry.

which stability can be determined from our records indicate no deterioration, even though fewer precautions in handling were taken in the early phases than we are taking now.

Review of our recent work indicates that samples having 24-28% solids and stored at room temperature remain homogeneous, while samples having 24-28% solids and stored at 40°F (4.4°C) exhibit solids precipitation. The amount of solids precipitated is noticeable and the density of the precipitated solids is greater than 1.12 gm/cm³, because the solids sink to the bottom of the container. Upon warming to room temperature, the solids appear to redissolve. Attempts will be made to isolate and identify these solids. Liquors will be packaged for storage and sampled for further work in a way to ensure that liquor used for any test is representative.

5.2.3 SAMPLES FOR CHEMICAL ANALYSIS

Samples used for chemical analysis are stored at 40°F (4.4°C) and 14-16% solids in sealed bottles under a nitrogen blanket. There are no indications of solids separation on storage at 40°F.

To transfer, the sample is warmed to room temperature, the bottle agitated by hand, and transferred to a glove box which has a nitrogen atmosphere. The sample bottle is opened, an aliquot taken, and the bottle is resealed and returned to refrigeration. All aliquots intended for chromatographic analysis are diluted with the proper solutions in the glove box. The solutions are made by using deionized, degassed water. Aliquots taken for lignin precipitation are placed in sealed containers and the containers removed from the glove box.

5.2.4 LIGNIN STORAGE

Lignin separation is discussed elsewhere. Separated lignin samples are stored as solids in sealed vials placed in a dessicator. Portions for analysis are transferred from the vial in a glove box.

Lignin solutions for molecular weight analysis are prepared at the proper concentrations and placed in sealed vials with septum caps. The vials are stored so as to avoid undue exposure to light. Final transfer to the analytical instruments is made by using syringes.

5.3 LIQUOR CONCENTRATION AND SOAP SEPARATION

Methods and equipment for liquor concentration are still evolving; however, we believe that methods are reasonably well developed at the time.

5.3.1 LARGE-SCALE EVAPORATOR

A schematic of the large-scale evaporator is shown in Figure 5.3.1-1. The evaporator vessel is a 316 stainless steel vessel 18-inches in diameter with a 24-inch straight side and a 6-inch deep shallow conical volume. A steam coil is mounted internally in the bottom conical section. The vessel has a 3/4-hp, 1150 rpm agitator with shaft mounted eccentrically so that a 3-inch diameter propeller is positioned within the coil at the bottom of the vessel. The overhead

FIGURE 5.3.1-1 Schematic of Large Scale Evaporator and Soap Separator.

system is constructed of 6-inch Corning glass pipe. The vapor line extends vertically approximately 3 feet, horizontally approximately 6 feet, and downward approximately 2 feet into a Corning chemplant glass condenser with about 6 ft² of heat transfer area. Condensed vapor flows by gravity into a 6-inch diameter glass receiver that is approximately 4-feet long.

Steam to the coil is pressure-regulated and flow-controlled. The evaporator is basically controlled by controlling the steam flow so as to control the evaporation rate. Water to the condenser flows through a pressure regulator and is manually controlled so as to produce sub-cooled condensate. Vacuum is supplied by a Nash Hytor pump and vacuum is controlled by bleeding air into the system at a point between the receiver and vacuum pump.

Originally, the system was built with two receivers so that condensate fractions could be collected, and the evaporator vessel was equipped with a glass pipe section in the bottom drain. We intended to separate soap by cooling the concentrated liquid in the evaporator vessel followed by draining from the bottom until the soap interface appeared. This did not work. We have revised the system. In future, only one condensate receiver will be used as a receiver. The other has been repiped so that concentrated liquor can be transferred to it from the evaporator vessel after evaporation is complete. The concentrated liquor will be cooled in the glass vessel until soap separates and then concentrated liquor transferred from the bottom of this vessel to packages appropriate for storage.

The total concentration operation requires 6 hours or less, including loading, heat-up, evaporation, and transfer. We have found that we can evaporate at a rate of about 13 lbs water/hour at 0 to 3-inches Hg vacuum and obtain a water white condensate. (The maximum evaporation rate possible without foaming and entrainment problems is about 25 lbs water/hour.) The maximum steam temperature during any of our runs is estimated to be 234°F (112°C). The evaporator vessel volume is approximately 28.5 gal. The evaporator can be operated with a starting liquid volume of as much as 22 gal. and a final volume of as little as approximately 2.5 gal. To concentrate 22 gal. of 15% solids liquor to 25% solids would require removal of about 79 lb of water, or about 6 hours of evaporation time. The total concentration operation would require a maximum of about 8 hours.

Before loading, the evaporation system is flushed with nitrogen and evacuated twice to 27-inches Hg vacuum. This leaves an atmosphere in the vessel of less than 100 ppm oxygen. The liquor is forced into the evaporator by nitrogen, mixed, heated up, and evaporated. After evaporation, the system is flooded with nitrogen, the liquor is cooled, and the liquor is drained into containers that have been flushed with nitrogen. The containers are then sealed and stored.

5.3.2 SMALL SCALE EVAPORATOR

A small laboratory evaporator has been used for vacuum evaporation of small quantities of black liquor to concentrations as high as 75% solids quite successfully, although there are problems in handling liquors easily if concentrated above 75% solids. The small scale evaporator is shown in Figure 5.3.2-1.

FIGURE 5.3.2-1 Schematic of Small Scale Evaporator.

The evaporator is essentially a 2000-ml stirred glass resin kettle that is electrically heated with a heating mantle. The kettle has a bottom drain. Vapor is condensed in a water-cooled Friedrich's type laboratory condenser with a 400-mm jacket length and the condensed vapor is collected in a graduated receiver. An aspirator or vacuum pump is used to draw vacuum through the receiver. The stirrer is driven by a variable speed motor. The temperature of the liquid is monitored.

As one would expect, foaming is a problem. Normally, a maximum of a one-liter charge of liquor can be used. The evaporation rate to prevent entrainment of liquor solids is approximately 150 ml/hour. At these conditions, liquid temperature remains in the range of 93-100°C while concentrating from about 25 to 75% solids without entrainment, and about 5-6 hours is required for heat-up and evaporation. The concentrate is then transferred to loading devices for the viscometers or to containers for storage. The useful yield from one liter of 25% solids charge is about 250 ml of 75% solids liquor.

This evaporator is being modified to provide more liquor capacity (substitute a 4-liter kettle), better agitation, better foam separation (add a clear 400-mm column), better condensation and condensate cooling (add a 400-mm Graham condenser), and better transfer (modify bottom drain). With these modifications, we hope to increase evaporation rate at higher vacuum, estimate final solids more accurately by measuring condensate, and improve liquor transfer at high solids (>70%). Evaporation and liquor handling at high solids needs further improvement.

6. EXPERIMENTAL METHODS AND PROCEDURES

The experimental methods selected, equipment used, procedures developed, and preliminary results obtained are described in this section. The emphasis has been on installation and application to black liquor studies. To this time, little actual data on black liquors has been taken. After an experimental method has been chosen and the equipment installed, our procedure has been to evaluate precision and accuracy for the method by analyzing standard or known materials before proceeding to apply the method to black liquor research.

6.1 CHEMICAL RESEARCH METHODS

There are several good general discussions of black liquor composition (Rydholm, 1965; Annergren, 1968; Wenzl, 1970; Sjoström, 1981 and 1982). Although there are many hundreds of chemicals in black liquor, these fortunately fall into only a few major categories (See Figure 3.1-1)--organic acid salts, lignin degradation products, "extractives", and inorganic components.

At the high pH's of Kraft black liquor almost all organic compounds with ionizable groups are present as sodium salts. The shaded areas in Fig. 3.1-1 represent the sodium associated with lignin and organic acids. Thus the components actually present are the sodium salts of organic acids (e.g., sodium glucoisoscaccharinate or sodium acetate), the sodium salts of lignins and the sodium salts of many "extractives" (e.g., sodium oleate or sodium abietate). Among the inorganic compounds in black liquor are Na_2CO_3 , Na_2SO_4 , Na_2S , $\text{Na}_2\text{S}_2\text{O}_3$, NaOH and NaCl . The salts of potassium, calcium and other cations are present in small amounts relative to sodium.

6.1.1 Detailed Description of Methods

Alkali and Sulfidity

At the beginning of the Kraft cook the primary inorganic constituents are NaOH and Na_2S . The Na_2S is almost totally hydrolyzed to SH^- and OH^- (Teder, 1981). The pH is near 14 whereas by the end of the cook the pH may be around 12 or lower. Thus most of the OH^- has reacted during the cook (Rydholm, 1965; Sjoström, 1981). However, although some of the SH^- is lost, 68-85% survives in the fresh dilute black liquor (Fleming et. al., 1980).

To measure surviving free NaOH , active alkali, effective alkali and total alkali in the black liquor variations on TAPPI standard T625 are typically used. (For a discussion of the terms active and effective alkali, etc., see Sjoström, 1981 or Casey, 1980). The TAPPI method involves primarily an HCl titration of the liquor. The sulfide is determined separately by TAPPI T694 PM 82 using a mercuric chloride titration.

Ion Analysis

In addition to the Na_2S and NaOH mentioned under alkali and sulfidity, black liquor contains Na_2SO_3 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ and NaCl . The Dionex Ion Chromatograph was chosen to analyze for the anions associated with Na, i.e., for CO_3^- , SO_3^- , S_2O_3^- , SO_4^- and Cl^- . In these cases, as discussed in a separate section on ion

analyses, an anion exchange column is used with, typically, a carbonate-bicarbonate eluent. The S^- (SH^-) ion is also determined on the column using a separate eluent and detector.

In addition to the ion chromatographic method the trial liquors and the first experimental liquors will be analyzed for these ions by differential pulse polarography for SO_3^- and $S_2O_3^-$; TAPPI T623 for SO_4^- ; and Beckman 915B analyzer for carbonate.

As mentioned, much sulfide survives the Kraft cook and is found in the fresh liquor. However, as the liquor stands or is handled to, e.g., effect concentration the sulfide disappears. It is converted through polysulfide and polythionate intermediates to thiosulfate. In turn thiosulfate can be oxidized to sulfite and sulfate. To obtain a better grasp of the sulfur oxidation state in the liquors it is desirable to track the level of polysulfide. The assay for polysulfide anions will be an $HgCl_2$ titration, TAPPI T694.

Elemental Analysis

The above methods are used to determine inorganic anions. However, although Na^+ is by far the predominant cation in black liquor a variety of other cations exist, e.g., K^+ , Ca^{++} , Mg^{++} , and Fe^{++} (Fe^{+++}) (Grace et. al., 1977). The elements represented by these cations come from the wood substance itself, from contaminants in the chemicals used to prepare the initial white liquor and as a consequence of recovering inorganics in the recovery cycle. Typically, and in the present study also, these elements are determined by atomic absorption or emission spectroscopy. Total sodium is also determined by atomic absorption.

In addition to the above elements which form inorganic cations, black liquor of course also contains a great deal of carbon, mostly organic but also inorganic. For the time being organic carbon will be analyzed by a Beckman 915B analyzer and total carbon and hydrogen by a Perkin-Elmer 240B analyzer at St. Regis. As the UMO lab continues to develop its analytical capacity, these analyses will be done on a Chemical Data System 1200 elemental analyzer at UMO.

Finally, total sulfur is being analyzed by the Fisher Combustion Analyser at St. Regis and--for the time being--by both Tappi T625 and by a $BaSO_4$ precipitation method at UMO. We also have the capability to analyze sulfur on our CDS 1200 system. Later, after comparisons, only one of these three methods will be used at UMO.

About 30% of wood polysaccharides are lost during kraft pulping primarily by the mechanism of "peeling" (e.g., see Sjostrom, 1981, pp 134-138). The degraded carbohydrates are found as hydroxy acid salts, formate and acetate in the approximate proportions shown in Figure 3.1-1. Details on the formation of these acids can be found in Alen and Sjostrom, 1980; Sjostrom, 1977; Friberg, 1977; or Lowendahl et. al., 1976.

As seen in Figure 3.1-1 the major acids formed in pine black liquor are glucoisosaccharinic, formic, acetic and lactic. Ideally, we would choose to measure the levels of all these acids and some of the several dozen others present in smaller quantities as well. As a practical matter for the time being, only formate, acetate, lactate-glycolate and oxalate are being measured. The

reason relates both to limited time and to the selection of an ion chromatograph as the means to scan for a variety of ions in black liquor, inorganic as well as organic. Although the ion chromatographic column used for the separation may well be capable of separating a greater number of the organic acid salts, this will take further development work.

In addition to ion chromatographic separation of liquor acid salts, the trial liquors and the first experimental liquors will be analyzed at St. Regis for acetic, formic, lactic, glycolic and oxalic acids. The St. Regis group is using gas chromatography of organic acid methyl esters for this purpose.

Lignin Analysis

The concentration of lignin in Kraft black liquor is typically measured by light absorption at 280 nm or 205 nm (Goldschmid, 1970). There is a wide variety of lignin degradation products in black liquor and other substances in the liquor also absorb in the ultraviolet. Thus it is not surprising that lignin concentration determined by ultraviolet absorption is a relative method.

A standard to which to refer ultraviolet absorbance of Kraft Liquors is prepared by precipitating lignin from liquor at low pH, purifying and drying it. Subsequently, a sample of known concentration is made up by dissolving a known weight of this lignin. The absorbancy of dilutions of this solution is measured and an extinction coefficient calculated. Literature extinction coefficients for such preparations vary.

Lignin isolated at pH 8 and at pH 2 had extinction coefficients of 24.3 and 22.6 l/g-cm, respectively (Alen et. al., 1979). By making corrections for the carbohydrate content of their fractions, McNaughton, et. al (1967) found absorptivity decreased as percentage delignification (and molecular weight) increased; they noted that the lower molecular weight material had the highest absorption. Simonson (1971), again using somewhat different means of lignin preparation, found extinction coefficients between 16.2 and 20.9. Lin and Detroit (1981) noted that lignin dissolved in methylcellulose water had absorptivities between 18.3 and 23.5. All the above authors measured absorption at 280 nm. More recently, Bobler et. al. (1981) concluded that 205 nm might be more characteristic of the "resonating system of the aromatic lignin building units".

Although it is clear from such reports that ultraviolet absorption is indeed an uncertain method, there is no method available to determine concentration on an absolute basis. For the experimental liquors to be prepared for this study we will use ultraviolet absorption measurement to estimate lignin concentration. At least for the first experimental samples we will also use a gravimetric method--precipitation of lignin at pH 2 with subsequent drying and weighing. We are planning also to take these precipitates through the next step, i.e., do Klason lignin to determine carbohydrate content. The pH 2 precipitation gravimetric methods suffers from the fact that only about 85-90% of the ultraviolet absorbing material is acid precipitable. At least part, if not most of the nonprecipitated material represents lignin degradation products.

To glean further information on the lignin in black liquor, methoxyl content will be measured on at least the first experimental samples. This will be done at St. Regis by gas chromatographic analysis of iodide derivatives.

Lignin molecular weight studies are dealt with in a separate part of this report.

Tall Oil

There are two reasons for an interest in tall oil in this project. One is related to variation in tall oil content as a function of pulping conditions. The other relates to black liquor surface properties. Some tall oil components remain soluble during the conditions used for skimming (Wenzl, 1970). That oil left behind can affect the liquor's surface properties.

The quantity of tall oil in dilute black liquor or remaining in concentrated liquor after skimming will be determined by Pulp Chemicals Association Method 25, which involves extracting the oil from an aqueous-alcohol-acetone solution in which the acidified liquor residues are soluble. This is based on a similar method (Saltsman and Kuiken, 1959). Composition of the tall oil is determined by a gas chromatographic method (Rockwell, 1981). Finally, as time permits, analyses will be run on tall oil skimmings according to TAPPI T635.

The first two procedures for dilute lignin will be done on only the first experimental liquors, unless variations as a function of pulping conditions are found. Extraction of tall oil from the concentrated skimmed black liquors will be continued in order to assess effects on surface properties.

Volatiles

The analysis of the volatile neutrals (methanol, ethanol and acetone) and volatile sulfur compounds (methyl mercaptan, dimethylsulfide, and dimethyl-disulfide) will be carried out on the first experimental liquors by gas chromatography at St. Regis. Only if variation is seen as a result of pulping conditions will these assays be continued on later samples. Terpene compounds are expected to be largely lost. However, to check out this presumption an analysis for α - and β -pinene will be done by gas chromatography on at least one liquor.

Percentage Solids

The standard TAPPI method to measure percentage solids in black liquor, T650 pm-79, is done by drying liquor on diatomaceous earth at 105°C for 5 hours or more. A number of methods have been devised to shorten the time involved. These procedures make use of drying a smaller sample on glass filter paper at 105°C (McDonald) or microwave drying (Eggers and Viljoen, 1979).

The method we used at UMO on the trial liquors is that of McDonald. For the experimental liquors TAPPI T650 will also be used. St. Regis uses a modification of the TAPPI method in which liquor is dried in weighed sand at 80°C in a vacuum oven.

Wood and Pulp Analysis

In order to have values to which to compare, e.g., black liquor concentration of K or Ca, the inorganic cation forming elements of the sample wood to be pulped will be examined. We will also measure ash, lignin, cellulose and extractives by TAPPI methods.

To determine extent of delignification, pulps will also be analyzed for kappa number and percentage yield will be determined. In both these cases TAPPI methods are used.

Other Black Liquor Components

Although all the major components of black liquor are considered in the above discussion there are other chemicals present in varying smaller quantities. For example, Simonson, 1971, reports that free (not lignin bound) hemicellulose survives kraft cooking in concentrations up to about 2.5 g/L for pine and about 5 g/L for birch liquor. If about one-third by weight of black liquor solids is organic acid salts, then a 15% liquor would have about 50 g/L of organic acid salts. Thus for a softwood liquor the maximum amount of hemicellulose would be about 5% of the organic acid content.

Nonetheless it is intriguing to wonder to what extent this percentage would vary as a function of pulping conditions. In addition, since the viscosity of polymeric carbohydrates is so much greater than that of lignin (Sjostrom, 1981), even small quantities could have a disproportionate effect on black liquor viscosity. If time permits, hemicellulose concentration (free and lignin bound) will be checked by Simonson's methods. The suggestion has also been made that some furfural polymers would be formed during cooking. At the present time we have to plan to investigate this.

Other compounds occurring in the Kraft liquor are phenolic in nature. When Lundquist, 1973, carried out Kraft cooks on spruce milled wood lignin a number of phenolic monomers, dimers and higher oligomers were found. The monomers included vanillin, acetovanillone, and homovanillic acid.

Lowendahl et. al., 1978, did Kraft cooks on spruce meal and found up to 0.6% by weight of phenolic compounds were produced. Several hundred of these compounds are produced as determined by liquid and gas chromatography, and mass spectroscopy. Amounts produced increased as cooking conditions were increased from mild to conventional to severe. As for hemicellulose, it would be intriguing to further examine these phenolic components in our experimental liquors. However, the constraints of an already very large project precludes our immediately considering this investigation.

6.1.2 Chemical Analyses of Liquors from Preliminary Pulping Experiments

Alkali and Sulfidity

Table 6.1.2-1 gives values obtained (St. Regis) for trial liquor alkali and sulfidity levels. These are expressed both as grams per liter of Na_2O and equivalents per liter. Table 6.1.2-2 gives these values for those alkali and sulfidity components that were determined for wash liquors.

No differences were noted between liquors prepared from frozen chips (T2760 and T2761) as compared to those from unfrozen chips (T2762 and T2763). Since wash liquors were prepared with water it is expected that alkali and sulfidity levels would be considerably lower than those seen in the cooking liquors.

Table 6.1.2-1
PRELIMINARY PULPING EXPERIMENT
ALKALI AND SULFIDITY FOR BLACK LIQUORS

<u>Component</u>	<u>T2760</u>	<u>T2761</u>	<u>T2762</u>	<u>T2763</u>	<u>Average with 95%¹ Confidence Intervals</u>
grams/liter as Na ₂ O					
NaOH	2.89	2.39	2.75	2.38	2.60±.41
Na ₂ S	8.05	7.46	7.70	7.66	7.72±.40
Na ₂ CO ₃	1.11	0.90	1.33	0.91	1.06±.32
Titratable ² alkali	12.05	10.76	11.78	10.96	11.39±.99
Active alkali ³	10.94	9.06	10.45	10.04	10.32±.76
Total titratable alkali (to pH 2.7) ⁴	33.63	33.29	34.21	34.08	33.80±.67
equivalents/liter					
NaOH	.093	.077	.089	.077	.084±.02
Na ₂ S	.26	.24	.25	.25	.24±.02
Na ₂ CO ₃	.036	.029	.043	.029	.034±.02
Titratable alkali	.389	.346	.38	.354	.368±.03
Active alkali	.353	.318	.337	.324	.333±.03
Total titratable alkali	1.085	1.074	1.104	1.099	1.091±.02 ⁵
% sulfidity					
(Na ₂ S)/(Na ₂ S)+(NaOH)	73.6%	75.5	73.7	76.3	74.8±2.2 ⁶

¹ The 95% confidence intervals represent the range of values in which, statistically, 95% of all values fall. For example, for 2.60±.41, 95% of the values would be found between 2.19 and 3.01.

² (Na₂S) + (NaOH) + (Na₂CO₃)

³ (Na₂S) + (NaOH)

⁴ All Na salts (inorganic + organic)

⁵ The initial white liquor charge to the chips contained 1.17 equivalents/liter. The 1.091 value equals 93% of 1.17.

⁶ The % sulfidity of the white liquor was 27.7%.

Table 6.1.2-2
PRELIMINARY PULPING EXPERIMENT
ALKALI AND SULFIDITY¹
FOR WASH LIQUORS

<u>Component</u>	<u>grams per liter</u>				<u>Average With 95% Confidence Intervals</u>
	<u>T2760W</u>	<u>T2761W</u>	<u>T2762W</u>	<u>T2763W</u>	
NaOH	1.66	1.9	1.94	1.61	1.78±
Na ₂ S	3.2	3.12	2.93	3.05	3.08±
Total titratable alkali	12.88	13.95	12.82	13.51	13.29±
	<u>equivalents per liter</u>				
NaOH	.053	.061	.063	.052	.057±
Na ₂ S	.103	.101	.094	.098	.099±
Total titratable alkali	.42	.45	.41	.44	.43±
% sulfidity (on active alkali)	66.0%	62.3%	59.8%	65.3%	63.4±

¹ Since washing was done with water, not white liquor, all of these values are considerable lower than those seen in Table 6.1.1-1.

In Table 6.1.2-3 can be seen literature values for Na_2CO_3 , Na_2SO_4 and active alkali as compared to values observed here. As would be expected, since we used synthetic white liquor composed of Na_2S and NaOH , the concentrations of Na_2CO_3 and Na_2SO_4 which we obtained are very low compared to the mill liquors studied by Grace et. al., 1977. Conversely the observed active alkali value is about the same as obtained by Grace.

Ion Analyses

The Ion Chromatograph. Ion analyses were performed by two means on the trial liquors. One of these means was the Dionex Ion Chromatograph. The Dionex Model 10101 Ion Chromatograph, purchased December, 1982, was used to prepare standard curves for carbonate, chloride, sulfite, thiosulfite, sulfate and the organic acid salts oxalate, lactate, formate and acetate. Particular columns and eluents used to separate and elute the ions of interest as well as the detectors used are shown in Table 6.1.2-5. Standard curves for the above-mentioned ions are given in the appendix.

A standard curve for sulfide ion is now being prepared as well as a restandardization for sulfite. Sulfide and sulfite ions are both easily oxidized and thus present special analysis problems. Because of the ever-present oxidation problem, black liquors that are being analyzed on the Ion Chromatograph are handled in a glove box under nitrogen. Dilutions are made using deoxygenated water.

Examples of recordings obtained on the ion chromatograph with diluted black liquor are shown in Figures 6.1.2-1 and 6.1.2-2. Data from these analyses are collected in real time by interfacing the Dionex with a PDP 1160 computer. The integration program used does not yet resolve all multiple peaks. Thus the results shown here give relative concentrations of each ion calculated from peak height. The integration program will be finished in the very near future to allow the concentration of each ion to be expressed directly as parts per million.

Figures 6.1.2-3, 4 and 5 show the relative concentrations in the trial liquors and their washes for organic acid salts, sulfur ions, carbonate and chloride. All values have been expressed on a dry liquor solids basis.

Although the differences are small, cooking liquor lactate, formate and acetate concentrations were consistently higher when frozen chips had been used. Such a difference using frozen chips did not show up when wash liquors from frozen and unfrozen chips were compared.

The difference between frozen and unfrozen chips was large for oxalate -- the liquor from frozen chips had almost twice the oxalate concentration as the unfrozen comparison. Oxalate, unlike the other organic acids found in black liquor, is present in wood. Conversely, lactate, acetate and formate are degradation products of carbohydrates formed during pulping. Thus it is possible that chip freezing may result in oxalate being more easily leached from the wood chips than is the case for unfrozen chips.

Such differences as a result of freezing do not show up for sulfur ions or for carbonate or chloride. Overall, it appears that chip freezing may slightly accentuate carbohydrate breakdown during a subsequent Kraft cook.

FIGURE 6.1.2-1 Ion Chromatogram For Negative Ions in a Kraft Black Liquor.

FIGURE 6.1.2-2 Ion Chromatogram For C₁ to C₅ Acid Salts in a Kraft Black Liquor.

FIGURE 6.1.2-3 Relative Organic Acid Salt Concentrations in Trial Liquors and Washes. Determined by Ion Exchange Chromatography.

FIGURE 6.1.2-4 Relative Sulfur Ion Concentrations in Trial Liquors and Washes. Determined by Ion Exchange Chromatography.

FIGURE 6.1.2-5 Relative Concentrations of Carbonate, Chloride, and Oxalate Ions in Trial Liquors and Washes. Determined by Ion Exchange Chromatography.

FIGURE 6.1.2-6 Lignin Concentration in Trial Liquors and Washes. Lignin Determined by UV-Visible Analysis.

Table 6.1.2-3

PRELIMINARY PULPING EXPERIMENT
OBSERVED COMPARED TO PUBLISHED VALUES
Average wt% Based on Dry Solids

<u>Component</u>	<u>Observed Value (s)</u>	<u>Literature Value¹</u>
Na ₂ CO ₃	1.2	8.7
Na ₂ SO ₄	0.45	3.2
Active alkali (as Na ₂ O)	6.8	5.95

¹ Literature values are the averages of 28 mill liquors examined by Grace et. al. (1977).

Table 6.1.2-4
CONVERSION FACTORS FOR
LIQUOR COMPONENT CONCENTRATIONS

<u>Component</u>	<u>To Convert g/l of the Compound to g/l of Na₂O Divide by:</u>
NaOH	1.291
Na ₂ S	1.258
Na ₂ CO ₃	1.712

To convert g/l expressed as Na₂O to equivalents/l divide by 31 for any of the three components. The 31 value is the weight of one equivalent of sodium oxide (Na₁O_{1/2}).

Table 6.1.2-5

COLUMNS AND DETECTORS FOR ION ANALYSIS
WITH DIONEX 10101 CHROMATOGRAPH

Ions Separated	Separator Column	Suppressor Column	Eluent	Detector
Cl^- , SO_3^- , SO_4^- , C_2O_4^- , S_2O_3^-	HPIC Anion AS3	Fiber	0.0025 M Na_2CO_3 & 0.0028 M NaHCO_3	Conductivity & Electrochemical
S_2O_3^- *	HPIC Anion AS3	None	0.008 M Na_2CO_3	Electrochemical
Lactate (glycolate), formate, acetate	HPICE ICE AS1	ICE	0.001 M HCl	Conductivity
CO_3 †	HPICE	None	Deionized water	Conductivity

* S_2O_3^- yielded an earlier and sharper peak when eluted separately under the conditions specified.

† CO_3^- is also eluted by the organic acid column but yielded an earlier sharper peak under the conditions noted.

Consistent differences do not appear when comparing cooking to washing liquor for sulfur ions, carbonate and chloride. However, organic acid salts concentrations typically are somewhat lower in the wash than in the cooking liquors. No indications of any concentration difference for any ion was seen when the 3-hour wash was compared to the 6-8 minute wash.

St. Regis Ion Analyses. Like UMO St. Regis also performed analyses on most of the above-mentioned ions but using other methods as indicated in Table 4.5.2-1. Results for inorganic anions expressed as weight % based on dry solids are shown in Table 6.1.2-6. Results for the gas chromatographic analysis of the methyl esters prepared from the acid salts are given in Table 6.1.2-7.

As noted above, under the ion chromatographic ion analyses a number of ions seemed to be present at higher levels for liquors prepared from frozen as compared to unfrozen chips. None of these differences appeared in the St. Regis results. It is too early to attach any significance to this finding as calculations for absolute concentrations of ions have not yet been made for the ion chromatograph results.

Elemental Analysis

Results of elemental analyses are shown in Table 6.1.2-8. Values for Na and S as determined by St. Regis (atomic absorption and Fisher combustion analysis of SO_2 , respectively) were within the range reported by Grace et. al., 1977, who examined the inorganic composition of 28 mill black liquor samples (Table 6.1.2-9). The UMO (Plant & Soil Science Lab) value for Na was likewise within the range given by Grace. However, the UMO sulfur value was somewhat low relative to both the St. Regis and Grace values; the procedure used was oxidation to sulfate followed by barium precipitation which could be more subject to error than the St. Regis Fisher Combustion analysis for sulfur.

Since a fresh synthetic white liquor was used for the trial cooks it is expected that the K level would be low as the only K present would be leached from the chips. However, observed Ca values which might also be expected to be low were in the range reported by Grace. However, $\text{Ca}(\text{OH})_2$ could be a contaminant of the NaOH used to prepare the white liquor. This possibility will be examined further.

To check whether total elements present added up to 100% the individual elements were summed as noted in Table 6.1.2-10. Results were compared to those reported by Annergren et. al., 1968. Results were in reasonably close approximation both to 100% and to the Annergren results.

Lignin Concentration

Lignin Concentration in black liquor is measured by ultraviolet absorption at 280 nm. The measured absorbancy is related to concentration as follows:

$$A = E c l$$

A	=	measured absorption
E	=	extinction coefficient
C	=	concentration (g/L)
l	=	path length of light (constant at 1 cm)

Table 6.1.2-6
PRELIMINARY PULPING EXPERIMENT
ION CONCENTRATIONS IN LIQUORS AS DETERMINED BY ST. REGIS¹
Wt% Based on Dry Solids

Component	T2760	T2761	T2762	T2763	Average with 95% confidence Intervals
Na ₂ S	7.04%	6.03	6.38	6.24	6.42±.70
x.4108=S ⁼ alone	2.89%	2.48	2.62	2.56	2.64±.29
Na ₂ CO ₃	1.32	.99	1.50	1.01	1.21±.40
x.556=CO ₃ ⁼ alone	.75	.56	.85	.57	0.68±.22
NaOH	2.59	1.99	2.3	1.99	2.22±.46
x.4243=OH ⁻ alone	1.10	.85	.98	0.84	0.94±.19
Na ₂ S ₂ O ₃	1.56	1.41	1.19	1.16	1.33±.30
x.7091=S ₂ O ₃ ⁼ alone	1.10	1.00	0.84	0.83	0.94±.21
Na ₂ SO ₄	0.52	.46	.41	.42	0.45±.08
x.6763=SO ₄ ⁼ alone	.39	.31	.28	.28	0.32±.08
NaCl	.28	.26	.26	.26	0.27±.02
x.6066=Cl ⁻ alone	.17	.16.	.16	.16	0.16±.01

¹ St. Regis figures were expressed as g/l. To convert to the percentages shown the following was done:

$$\text{g/l} \div 10(\text{density}) \div \% \text{ solids} \times 100 = \text{wt\% based on dry solids}$$

The percentage solids used in all cases were figures obtained by H.K. Kim.
See Table 6.1.5-1.

Table 6.1.2-7

PRELIMINARY PULPING EXPERIMENT
ORGANIC ACIDS IN LIQUORS AS DETERMINED BY ST. REGIS
Wt% of Dry Solids

<u>Component</u>	<u>T2760</u>	<u>T2761</u>	<u>T2762</u>	<u>T2763</u>	<u>Average with 95% Confidence Levels</u>
Formic	3.78%	3.46	3.63	4.22	3.77±.53
Acetic	3.01	3.46	3.34	3.26	3.27±.30
Lactic	2.10	2.22	2.3	2.17	2.2±.13
Glycolic	1.97	2.21	4.20	2.96	2.84±1.59
Oxalic	1.4	.69	1.13	1.02	1.06±.46

Table 6.1.2-8
PRELIMINARY PULPING EXPERIMENT
ELEMENTAL ANALYSES OF BLACK LIQUORS

Component	T2760	T2761	T2762	T2763	Average with 95% Confidence Intervals
wt% based on dry solids					
SODIUM					
St. Regis	18.8%	17.5%	17.7%	17.6%	17.9 ± 1.0
UMO	18.4	19.1	18.7	20.2	19.1 ± 1.25
SULFUR					
St. Regis	3.79	3.96	4.03	3.82	$3.90 \pm .18$
(UMO-P&S)	3.36	3.4	3.35	3.41	$3.38 \pm .05^1$
CARBON (St. Regis)					
Total	42.1	37.9	40.3	40.0	40.0 ± 2.74
Orgainic	45.8	43.0	44.2	43.9	44.2 ± 1.86
HYDROGEN					
(St. Regis)	4.68	4.61	4.92	5.22	$4.86 \pm .45$
NITROGEN					
(St. Regis)	0.16	0.09	0.11	0.12	$0.12 \pm .05$
POTASSIUM					
(UMO-P&S)	.104	.101	.086	.108	$0.1 \pm .02$
$\mu\text{g/g}$ based on dry solids					
CALCIUM					
(UMO-P&S)	373	446	378	357	389 ± 63
MAGNESIUM					
(UMO-P&S)	62	69	52	63	61 ± 13
IRON					
(UMO-P&S)	43	(813) ²	114	61	73 ± 59

¹ The value 3.38 is significantly lower than 3.90 at the 95% confidence level.

² This value was omitted from the average.

Table 6.1.2-9
ELEMENTAL ANALYSES:
OBSERVED VALUES FOR LIQUORS FROM
PRELIMINARY PULPING EXPERIMENT
AND LITERATURE VALUES

=====		
Component	Observed Value(s)	Literature Value ¹

average wt% based on solids		

Na		
St. Regis	17.9	18.7
UMO	19.1	
S		
St. Regis	3.90	3.83 (Range 0.35 - 6.24
UMO	3.38	
K		
UMO	0.1	1.36 (Range 0.44 - 2.7)

average ppm based on solids		

Ca - UMO	389	450 (Range 40 - 1300)
Mg - UMO	61	184 (Range 140 - 240)
Fe - UMO	73	91 (Range 56 - 120)

¹ Literature values are the results of 28 mill liquors
studied by Grace et al., 1977.

Table 6.1.2-10
ELEMENTAL ANALYSIS
TOTAL PERCENTAGES: OBSERVED VALUES FOR LIQUORS
FROM PRELIMINARY PULPING EXPERIMENT
and LITERATURE VALUES

(Each element expressed as a percentage of the total)

	Observed	Literature Value ¹
Na	18.7 - 20.4%	18.8 - 20.0%
S	3.8 - 4.0 ²	4.4 - 4.8 ²
C (total)	37.9 - 42.0	35.8 - 39
H	4.6 - 5.2	3.8 - 4.3
O	(32.3) ³	32.3 - 36.0
N	0.1	-
Others	(4.5) ⁴	-
	101.9 - 108.5%	95.1 - 104.1%

¹ Literature values taken from Annergren et al., 1968.

² The trial liquor charge used in this study was 27.9% sulfidity. Annergren's results are based on 30% sulfidity.

³ Since oxygen was not determined here, the lower Annergren value was used for illustrative purposes.

⁴ Other elements include K, Si, Ca, Mg, Al, Fe, Mn and B. The above figure of 4.5% was based on data in the Grace et al. (1977) study.

⁵ Since Annergren et al. (1965) did not report other elements, the 95.1 - 104.1% values were based only on the five elements shown.

The extinction coefficient for lignin was obtained as follows. Lignin was precipitated from black liquor at pH 2, purified and dried. A sample of the dried lignin (about 100 mg) was weighed, dissolved in dilute alkali and dilutions prepared with water. A standard curve was then prepared, absorbancy versus concentration of lignin in grams per liter. Using this procedure on three separate lignin samples prepared by H. K. Kim gave the extinction coefficient values seen in Table 6.1.2-11. Typical literature values hover around 20 liters/g-cm. The average value obtained here was 19.3.

For a chemical whose nature and molecular weight are known exactly the extinction coefficient is given as the molar extinction coefficient. However, black liquor lignin is not one chemical entity but many with a very wide range of molecular weights. Thus, results for lignin concentration are valid on a relative basis only.

The average extinction value of 19.3 was used to calculate relative lignin concentrations in the four trial and four wash liquors. Results are shown in Table 6.1.2-12. Some clear differences can be seen in this Table. The short, 6-8 minute, wash resulted in a significantly lower lignin concentration in the wash liquor than was found either for the long, 3-hour, wash or the initial cooking liquors. The 180 min. higher temperature wash, however, gave values indistinguishable from the initial cooking liquors. These results tend to indicate that more lignin was washed into the wash liquor during the long high temperature wash than that amount initially present.

There were no indications that using frozen versus unfrozen chips had any effect on lignin concentration.

Percentage Solids

Since most values are calculated as weight per gram dry liquor solids, the percentage solids is an important assay. Table 6.1.2-13 shows percentage solids in the trial black liquors. The St. Regis value was determined within hours of the liquor preparation. The other solids analyses were determinations done at UMO. One case (unfiltered liquor) percentage solids was determined on the black liquor as received from St. Regis both in our Chemical Engineering laboratory and separately by UMO's Plant & Soil Science laboratory. In addition, as some fibers were observed in the liquor a filtration was carried out through a glass filter in a Buchner funnel and percentage solids determined on the filtrates.

All three UMO assays gave closely reproducible results which were about 93% of the St. Regis values for the cook liquors and about 98% for the wash liquors. Why the UMO values for the cook liquors are 7% lower than those of St. Regis is not clear at this point. In the future we will follow the TAPPI T650 pm-79 procedure to determine black liquor percentage solids.

pH, Tall Oil and Other Black Liquor Analyses

In Table 6.1.2-14 are seen the pH measurements taken on the trial liquors. Although an Orion 611 pH meter with a Ross electrode was used at both St. Regis and UMO, pH was from 0.4 - 0.6 units higher at UMO. Calculated pH values are also shown in this table. As noted it took some time for pH values to stabilize. Considering that pH meters in general operate poorly in this highly alkaline region it is probably not surprising that these variations were seen.

Table 6.1.3-1

Extinction Coefficients of Three
Lignin Preparations*

		E
Lig 2760W		18.9
Lig 2760W-H [†]		19.1
Lig 2760-H		<u>19.9</u>
Average		19.3

* Lignin solutions on which absorbancy was measured at 280 nm varied in concentration from 0.005 -0.02 g/L.

[†] H represents the fact that a given lignin preparation was hexane extracted after the initial purification and drying.

Table 6.1.2-12
PRELIMINARY PULPING EXPERIMENT
LIGNIN CONCENTRATION IN
BLACK LIQUORS AND WASH LIQUORS

	<u>T2760</u> 180 min wash	<u>T2762</u> 180 min wash	Mean	<u>T2761</u> 8 min wash	<u>T2763</u> 6 min wash	Mean
	grams lignin/liter ⁴					
Cook Liquor	52.3	54.9	(53.6)	57.0	58.3	(57.7) ¹
Wash Liquor	22.4	23.4	(22.9)	18.7	18.5	(18.6) ²
	as wt% of dry solids					
Cook Liquor	36.3%	35.6%	(36.)	36.7%	37.7%	(37.2)
Wash Liquor	35.7	36.	(35.9)	31.5	32.6	(32.6) ³

¹ 57.7 is not significantly greater than 53.6.

² 22.9 is significantly greater than 18.5 at the 95% confidence level.

³ 35.9% is significantly greater than 32.6% at the 95% confidence level.

⁴ Values expressed as g/L varies if the determination is done on separate days. Relative differences (e.g., as shown in Fig. 6.1.4-1) are much more constant.

Table 6.1.2-13
PRELIMINARY PULPING EXPERIMENT
SOLIDS CONTENTS OF BLACK LIQUORS AND WASH LIQUORS

	T2760	T2761	T2762	T2763	Average with 95% confidence intervals
St. Regis ¹	15.11	14.85	15.39	15.64	15.25 $\pm$.54
UMO					
Unfiltered ²	13.45	14.52	14.17	14.41	14.14 $\pm$.77
Filtered ²	13.66	14.50	14.10	14.33	14.15 $\pm$.58
P&S Science lab ³					
Unfiltered	13.5	14.6	14.2	14.6	14.2 $\pm$.83
	T2760-W	T2761-W	T2762-W	T2763-W	
St. Regis	6.06	5.41	6.24	5.60	5.83 $\pm$.62
UMO					
Unfiltered	6.13	5.30	6.13	5.37	5.73 $\pm$.73
Filtered	6.15	5.24	6.00	5.33	5.68 $\pm$.73

¹ Samples run in duplicate and dried in vacuum oven for 2 hrs. at 80°C in weighed sand.

² Samples run in triplicate and dried in convection oven on weighed filter paper for 30 min (as by McDonald, 1979).

³ Samples dried overnight at 105°C (similar to TAPPI T625 ts-64).

Table 6.1.2-14
PRELIMINARY PULPING EXPERIMENT
pH VALUES OF BLACK LIQUORS

	T2760	T2761	T2762	T2763	Average with 95% Confidence Intervals
Measured					
St. Regis	12.6	12.8	12.8	12.8	12.8 $\pm$.16
UMO - Aug 4	13.15	13.22	13.22	13.19	13.2 $\pm$.05
UMO - Aug 19 ¹	13.32	13.37	13.37	13.35	13.4 $\pm$.03
Calculated					
Equivalents/ liter effective alkali ²	0.223	0.197	0.214	0.202	
Corresponding to pH	13.35	13.29	13.33	13.31	13.3 $\pm$.04

¹ Electrode standardized at pH 11. Approximately one minute was necessary for black liquor pH to stabilize.

² Equivalents/liter effective alkali was calculated from Table 6.1.1-1.

Table 6.1.2-15 shows results of other analyses performed on the trial liquors. These included density, heat of combustion, sulfated ash and methanol.

Tables 6.1.2-16 and 6.1.2-17 contain information on the tall oil level and composition of the trial liquors. Although the acid/resin ratio is somewhat higher for liquors from the frozen chips (T2760 and T2761) than from unfrozen, this difference is not statistically significant.

Wash Liquor Analyses

Fewer analyses were run on the wash than on the cook liquor analyses. Of these, the only assay showing a difference between the short lower temperature wash and the longer high temperature wash was lignin concentration (Figure 6.1.2-6). Some of the other analyses performed on the wash liquors were pH, density, Na_2S , NaOH , total titratable alkali and $\text{Na}_2\text{S}_2\text{O}_3$. None of these tests revealed any unusual information.

6.2 RHEOLOGICAL RESEARCH METHODS

Rheological equipment has been designed and installed to permit us to determine viscosity at all solids contents from 15% up to at least 75%, at temperatures from room temperature to above the normal boiling point of the fluid, and at all necessary shear rates from 1 to $5 \times 10^3 \text{ sec}^{-1}$. The equipment installed also is capable of determining normal stresses (elastic forces) in black liquors with solids contents greater than 50% at temperatures from 40 to 90°C . Finally, the equipment can possibly be used to determine changes in black liquor due to ageing at different temperatures by following changes in rheology.

6.2.1 Glass Capillary Viscometers

Means for using glass capillary viscometers have been installed to permit us to determine the viscosity of Newtonian fluids that can be used to calibrate other viscometers and to permit us to determine the viscosity of black liquors in the regions of interest where the liquors behave as Newtonian fluids.

Cannon-Fenske viscometers have been obtained. The viscometers used and the viscosity ranges in which they can be applied are:

Viscometer No.	Viscosity Range, Centi-Stokes
50	0.8-4
100	3-15
150	7-35
200	20-100
300	50-250
400	240-1200
500	1600-8000
600	4000-20,000

Table 6.1.2-15
PRELIMINARY PULPING EXPERIMENT
OTHER ANALYSES OF BLACK LIQUORS

	T2760	T2761	T2762	T2763	Average with 95% Confidence Intervals
Density (25°C)	1.0699 g/ml	1.0708	1.0716	1.0728	1.0713 $\pm$.0016
Heat of combustion	6,454 Btu/lb	6,530	6,563	6,519	6,517 $\pm$ 73
Sulfated ash (% of liquor solids)	59.2%	54.8	54.7	55.4	56.0 $\pm$ 3.4
Methanol (% of dry liquor solids)	0.70%	0.69	0.71	0.72	0.71 $\pm$.02

Table 6.1.2-16
PRELIMINARY PULPING EXPERIMENT
TALL OIL ANALYSIS OF BLACK LIQUORS BY ST. REGIS

	T2760	T2761	T2762	T2763	Average with 95% Confidence Intervals
Tall Oil					
By weight	1.77%	1.72%	1.19%	2.11%	
By titration	1.65	1.89	1.19	2.17	
Average of the two methods	1.71	1.81	1.19	2.14	1.71 $\pm$.63
Fatty Acid/Resin Acid	1.33	1.33 ¹	1.04	1.08 ¹	1.2 $\pm$.25

¹ 1.33 (the average of T2760 and T2761) is not significantly higher than 1.06 (the average of T2762 and T2763).

Table 6.1.2-17
PRELIMINARY PULPING EXPERIMENT
RESIN ACID AND FATTY ACID COMPOSITION
OF TALL OILS FROM BLACK LIQUOR BY ST. REGIS

Compound	T2760	T2761	T2762	T2763
C-12 to C-14 Fatty Acids	1.06%	0.29%	0.42%	0.37%
Palmitic	3.95	3.77	3.52	3.81
Stearic	1.07	1.15	1.16	1.02
Oleic	26.07	25.30	23.57	24.91
Linoleic	14.86	16.06	14.90	14.65
Linoleic Isomer	3.94	4.35	1.80	1.13
Linoleic C,T-Conj.	2.35	2.63	1.73	2.40
Linoleic T,T-Conj.	1.00	0.95	1.60	1.17
Behenic	<u>2.60</u>	<u>2.64</u>	<u>2.22</u>	<u>2.00</u>
Total Fatty Acids	56.90%	57.14%	50.92%	51.46%
Dextropimaric	3.91	3.46	3.68	3.88
Dihydroabietic	1.28	1.50	1.82	0.36
Levopimaric & Paulstric	6.95	6.57	6.51	5.84
Isopimaric	8.24	7.27	8.76	8.73
Dihydroabietic Isomer	0.59	0.26	0.35	0.92
Abietic	11.90	13.34	14.70	17.14
Dehydroabietic	6.53	6.32	8.30	7.69
Neoabietic	<u>3.70</u>	<u>4.14</u>	<u>4.96</u>	<u>3.98</u>
Total Resin Acids	43.10%	42.86%	49.08%	48.54%

The calibration constants of the viscometers have been determined as a function of temperature. A glass manifold system has been designed so that the viscometers can be operated under a slight positive atmosphere of nitrogen. The viscometers are thermostatted during use in a Haake Model E52 temperature bath which provides temperature control within $\pm 0.1^\circ\text{C}$.

These viscometers have been used to determine the viscosities of two trial black liquors from St. Regis at solids contents from 15 to 49% and at temperatures from 30 to 80°C . Results of these measurements are shown in Figure 6.2.1-1. These results are reproducible and precise to $\pm 3\%$ or better.

6.2.2 Instron Viscometer

An Instron Model 3211 Capillary Viscometer with change gears and three sets of capillaries has been installed. The change gears permit piston speeds from 0.0075 to 20-inches/minute to be used. Capillary sets with diameters of 0.060-inches, 0.050-inches, and 0.030-inches are available. A capillary set with diameters of 0.010-inches or 0.020-inches will soon be obtained to extend the range to lower viscosities. The viscometer is shown in Figure 6.2.2-1.

The Instron Rheometer has two design limitations for our work. Firstly, the capillary discharge is open to the atmosphere so that measurements at or above the normal boiling point of the fluid cannot be made. Secondly, the measureable pressure drop across the capillary must be greater than about 500 psi to assure accuracies better than 5% for viscosity determinations. At low pressure drops (< 3000 psi), the pressure drop must be corrected for friction between piston and barrel and for laminar flow effects in the barrel as a function of piston speed. The proper corrections can be determined and have been determined for black liquors [Kim (1980)].

A schematic diagram for a capillary viscometer is shown in Figure 6.2.2-2. A true viscosity measurement requires that we determine the pressure drop across the length in which the flow is fully developed, $(L - L_{en} - L_{ex})$, at a known flow rate. To do this, we determine the force required at the same flow rate for flow through tubes of the same diameter, but different lengths.

The total pressure drop, ΔP_T , required for steady flow in a given capillary at a given flow rate is calculated as:

$$\Delta P_T = \frac{4F_c}{\pi D_b^2} \quad (6.2.2-1)$$

where:

ΔP_T = total pressure drop

F_c = force corrected for piston friction and flow in the barrel

D_b = barrel diameter

FIGURE 6.2.1-1 Viscosity at Low Solids of Trial Kraft Black Liquors.

FIGURE 6.2.2-1 Instron Viscometer.

FIGURE 6.2.2-2 Schematic of a Capillary Viscometer.

The volumetric flow rate for steady flow, Q , is calculated as:

$$Q = \frac{\pi D_b^2}{4} X \quad (6.2.2-2)$$

where:

Q = volumetric flow rate
 D_b = barrel diameter
 X = piston speed

The data at constant flow rate for pressure drops through capillaries of the same diameter and different lengths can then be used to determine the true shear stress for fully developed flow through use of the equation [Bird, 1977]:

$$\Delta P_T = 4 \tau_R \left(\frac{L}{D} \right) + C \quad (6.2.2-3)$$

where:

τ_R = true shear stress at the capillary wall
 L = capillary length
 D = capillary diameter
 C = constant

When equation 6.2.2-3 is plotted as ΔP_T vs. L/D for constant flow rate and capillary diameter, the slope of the line is $4\tau_R$. A plot of this type for a black liquor is shown in Figure 6.2.2-3.

Several steps are necessary to determine the shear rate for each line for a plot such as Figure 6.2.2-3. We first calculate an apparent shear rate for each line as [Bird, 1977]:

$$\dot{\gamma}_A = \frac{4Q}{\pi R^3} \quad (6.2.2-4)$$

where:

$\dot{\gamma}_A$ = apparent shear rate
 R = capillary radius

We then plot τ_R vs. $\dot{\gamma}_A$ for the conditions of each line in Figure 6.2.2-3 to obtain a plot such as Figure 6.2.2-4. We then take the slope, n , of this smooth curve at values of Q corresponding to flow rates for the lines in Figure 6.2.2-3. [Bird, 1977]. n is the "flow index" of the fluid. The true shear rate at the capillary wall is then [Bird, 1977]:

FIGURE 6.2.2-3 Example Plot of Experimental Capillary Viscometer Data to Determine Shear Stress.

FIGURE 6.2.2-4 Typical Shear Stress vs. Shear Rate Curve for Viscosity of a Kraft Black Liquor by Capillary Viscometry.

$$\dot{\gamma}_R = \dot{\gamma}_A \left[\frac{3n + 1}{4n} \right] \quad (6.2.2-5)$$

where:

$\dot{\gamma}_R$ = shear rate at the capillary wall.

Viscosity, η , can then be calculated as:

$$\eta = \tau / \dot{\gamma} \quad (6.2.2-6)$$

A plot of the viscosity vs. shear rate for the data of Figure 6.2.2-3 is shown in Figure 6.2.2-5. Each point in Figure 6.2.2-5 represents data from a line on a plot such as Figure 6.2.2-3. Figure 6.2.2-5 shows data for three separate determinations of viscosity for a black liquor. This is representative of the reproducibility of the results.

A semi-empirical method can be applied to these data to combine the effects of shear rate and temperature on viscosity, if the liquors behave as polymer solutions or suspensions [Bischoff, Catsiff, and Tobolsky (1955), Ferry (1961), and Bird, Armstrong, and Hassager (1977)]. Application of the method requires that the zero shear-rate viscosity, η_0 , be determined. These values can be estimated from capillary viscometry data by plotting $\log \eta$ vs. τ_R and extrapolating to zero, as shown in the example represented by Figure 6.2.2-6, which are data taken at different temperatures for a black liquor. The experimental viscosity data are then normalized by preparing a plot of $\log \eta(T) / \eta_0(T)$ vs. $\dot{\gamma}$, where η is the viscosity at T for a given $\dot{\gamma}$ and $\eta_0(T)$ is the zero shear-rate viscosity at T . An arbitrary reference temperature, T° , is then chosen as some temperature within the range of the experiment and all curves for data at temperatures other than T° are shifted horizontally to superimpose on the normalized viscosity curve at T° . The distance each curve is shifted represents a multiplying factor, a_T , which is called the shift factor and is a function of temperature.

Molecular theory [Ferry (1961)] predicts that the shift factor should be given by:

$$a_T = \frac{\eta_0 T^\circ \rho^\circ}{\eta_0 T \rho} \quad (6.2.2-7)$$

where:

- T° = reference temperature
- η_0° = zero shear-rate viscosity at the reference temperature, T°
- T = temperature
- η_0 = zero shear-rate viscosity at temperature, T
- ρ° = fluid density at the reference temperature, T°
- ρ = fluid density at temperature, T

FIGURE 6.2.2-5 Typical Reproducibility of Dependence of Viscosity on Shear Rate for a Kraft Black Liquor by Capillary Viscometry.

FIGURE 6.2.2-6 Example of Extrapolation of Capillary Viscometer Data to Determine Zero Shear Rate Viscosities of a Kraft Black Liquor.

This method of data treatment, which is a reduced variables method, has been applied successfully to black liquors. An example of the treatment for a black liquor is shown in Figures 6.2.2-7, 6.2.2-8, and 6.2.2-9, which are plots of the zero shear-rate viscosity (η_0) vs. $1/T$, the shift factor (a_T) vs. $1/T$, and the master curve of reduced or normalized viscosity (η/η_0) vs. the shifted shear rate ($a_T\dot{\gamma}$), respectively.

The significance of this result is that methods used successfully for polymers and polymer solutions are shown to be applicable to black liquors, at least over the restricted temperature range that can be studied. The practical advantage is that the complete dependence of viscosity with respect to temperature and shear rate can be described by three pieces of information:

1. A master curve of η/η_0 vs. $a_T\dot{\gamma}$.
2. A plot of η_0 vs. T .
3. A plot of a_T vs. T .

This is beneficial in that it reduces the amount of data necessary to determine the viscosity and in that it can be used to extrapolate to conditions of shear rate and temperature for which measurements of viscosity cannot conveniently be made. However, extrapolation should be made with caution; theory requires that there be no change in phase or composition of the fluid.

The Instron viscometer will be used to determine viscosities of black liquors at concentrations above 55% solids for temperatures from 30 to 90°C. At these conditions, measurements will be made at shear rates from about 50 to 10^4 sec^{-1} .

6.2.3 Rheometrics Spectrometer

A Rheometrics Mechanical Spectrometer RMS-7200 system has been installed, which has capability for steady shear and oscillatory shear measurements of viscosity and normal stress for fluids. A special environmental system has been designed and installed to control temperature and humidity of the surroundings of the sample during measurement. The Rheometrics and the environmental system are shown in Figures 6.2.3-1 and 6.2.3-2.

The purpose of using the Rheometrics is to determine the zero shear-rate viscosity of liquors directly and to test liquors for elastic behavior. The Rheometrics affords the only experimental instrument adaptable by us that can be used to quantitatively observe elastic behavior of liquors. A schematic of the Rheometrics is shown in Figure 6.2.3-3. A function generator and electronics drive unit is used to control speed or oscillation frequency and to condition output signals from the instrument. Output signals are fed to a DEC-11/03 computer and results calculated. A schematic of the environmental control system is shown in Figure 6.2.3-4. The actual test sample is contained in the tooling placed within the environmental chamber. For most of the work with black liquors, the parallel plate geometry (shown in Figure 6.2.3-5) will be used. The actual sample is represented by the cross-hatched area.

The precision and accuracy of the instrument was tested by determining the viscosities of standard Newtonian fluids. Using silicone oils, our first tests showed an accuracy of ± 1 to $\pm 5\%$ with silicone oils having viscosities ranging

FIGURE 6.2.2-7 Dependence of Zero Shear Rate Viscosity of a Kraft Black Liquor on Temperature at 66.8% Solids.

FIGURE 6.2.2-8 Dependence of the Shear Rate Shift Factor of a Kraft Black Liquor on Temperature at 66.8% Solids.

FIGURE 6.2.2-9 Dependence of the Reduced Viscosity of a Kraft Black Liquor on Shear Rate at 66.8% Solids.

FIGURE 6.2.3-1 Rheometrics 1200 Mechanical Spectrometer.

FIGURE 6.2.3-2 Environmental Control System for the Rheometrics Spectrometer.

SCHEMATIC OF MECHANICAL SPECTROMETER

FIGURE 6.2.3-3 Schematic Diagram of Rheometrics 1200 Mechanical Spectrometer. Reproduced from Rheometrics Manual.

FIGURE 6.2.3-4 Schematic of Environmental Control System for the Rheometrics Spectrometer.

FIGURE 6.2.3-5 Parallel Plate Geometry Used on Rheometrics Spectrometer.

from 0.3 to 22.0 Pa-sec (300 to 22,000 cp). Later work with black liquor demonstrated that this was not sufficient, because black liquor viscosity is much more sensitive to temperature changes. The temperature control system was revised and new tests for precision and accuracy made using mineral oils, which have nearly the same temperature sensitivity as black liquors. Tests with mineral oils now yield viscosity measurements with an accuracy of 0.5 to 5% for mineral oils with viscosities from 0.4 to 5.0 Pa-sec (400 to 500 cp), which is the precision we now expect for black liquors.

Using the parallel-plate geometry, we have determined the viscosity of black liquors at different temperatures and solids contents. Methods for calculation of the viscosity and normal stress from the experimental measurements of angular velocity, torque, and total normal force are given in many standard sources [cf. Bird (1977)]. The final equations to be used for measurements with the parallel plate geometry are:

$$\eta_R = (T H/2\pi R^4 W) \{3 + d[\ln T/2\pi R^3]/d[\ln RW/H]\} \quad (6.2.3-1)$$

where:

T = torque

W = angular velocity

H = gap height (plate separation)

R = plate radius

η_R = viscosity at the shear rate at the plate rim,

$\gamma_R = RW/H$

(6.2.3-2)

where: γ_R = shear rate at the plate rim

and

$$\Psi_1 - \Psi_2 = (FH/\pi R^4 W^2) \{2 + d[\ln(F/\pi R^2)]/d[\ln(RW/H)]\} \quad (6.2.3-3)$$

where:

F = total normal force required to maintain constant gap height

$\Psi_1 - \Psi_2$ = difference in primary and secondary normal stress coefficients
(normal stress)

The results for measurement of viscosity of a Softwood black liquor using the cone-and-plate and parallel-plate geometries are shown in Figures 6.2.3-6 and 6.2.3-7. The results for cone-and-plate and parallel-plate geometries are in good agreement; however, the parallel-plate geometry will be used for nearly all of our work to prevent any anomalies due to possible solids precipitation.

These results show that zero-shear rate viscosity can be determined for liquors at solids contents from about 55 to 75% solids quite precisely at temperatures up to 70°C. Work is now proceeding at temperatures as high as 90°C. The range of the instrument can also be extended by the use of a transducer capable of measuring higher torques. The torque limit for any one transducer is two decades of stress or less.

FIGURE 6.2.3-6 Zero Shear Rate Viscosities of a Kraft Black Liquor at 68% Solids as Determined Directly Using the Rheometrics Spectrometer.

FIGURE 6.2.3-7 Zero Shear Rate Viscosities of a Kraft Black Liquor at 50°C as Determined Directly Using the Rheometrics Spectrometer.

Oscillatory shear experiments are very useful in defining the nature of fluids. In this type of experiment, one plate is displaced sinusoidally about the rest position such that:

$$\theta = \theta^{\circ} \sin wt \quad (6.2.3-4)$$

where:

θ = angular displacement at t
 θ° = maximum angular displacement
 w = frequency
 t = time

We define a function, called the complex viscosity, η^* , such that [Bird (1977)]:

$$\tau^{\circ} = \eta^* \dot{\gamma}^{\circ} \quad (6.2.3-5)$$

where:

τ° = amplitude of stress
 $\dot{\gamma}^{\circ}$ = amplitude of strain rate
 η^* = complex viscosity

The complex viscosity has real and imaginary parts:

$$\eta^* = \eta' - i\eta'' \quad (6.2.3-6)$$

where:

η' = real part; associated with energy dissipation
 η'' = imaginary part; associated with energy storage

For a Newtonian fluid, there is no energy storage; therefore $\eta' = \text{viscosity}$ and $\eta'' = \text{zero}$.

For the parallel-plate geometry, the torque varies sinusoidally as:

$$T = T^{\circ} \sin (wt + \psi) \quad (6.2.3-7)$$

where:

T = torque
 T° = maximum amplitude of torque
 ψ = phase shift angle

The real and imaginary parts of the complex viscosity are calculated as follows:

$$\eta' = (T^{\circ} H \sin \psi / 2 \pi R^4 \theta^{\circ} w) \{ 3 + \{ d[\ln(T^{\circ} \sin \psi / 2 \pi R^3)] / d[\ln(R \theta^{\circ} w / H)] \} \} \quad (6.2.3-8)$$

$$\eta'' = (T^{\circ} H \cos \psi / 2 \pi R^4 \theta^{\circ} w) \{ 3 + \{ d[\ln(T^{\circ} \sin \psi / 2 \pi R^3)] / d[\ln(R \theta^{\circ} w / H)] \} \} \quad (6.2.3-9)$$

The imaginary component of the complex viscosity is often represented in another form as the storage modulus, G' . G' is calculated as:

$$G' = w \eta'' \quad (6.2.3-10)$$

Measurements of the complex viscosity for a Softwood black liquor containing 68% solids are shown as η' vs. w and G' vs. w in Figures 6.2.3-8 and 6.2.3-9, respectively.

Data for η' and G' can be superimposed by a temperature shift to give single curves for each percent solids, as shown in Figures 6.2.3-10 and 6.2.3-11, in a manner that has been used successfully for low molecular weight, uncross-linked polymer solutions.

6.2.4 Haake Viscometer

A Haake RV-12 rotational viscometer system with a pressurized cell has been installed, which has the capability for steady shear viscosity measurement at temperatures up to 300°C and pressures up to 40 atmospheres. The Haake viscometer and partially disassembled pressure cell are shown in Figure 6.2.4-1.

The pressurized cell is a coaxial cylinder viscometer that is supplied with two cylinders. One cylinder is 48 mm in diameter by 155 mm high. The other cylinder is split; only the bottom section is used for measurements. The bottom section is 48 mm in diameter by 60 mm high. The cylinders are interchangeable in the cell. The cylinders form a 1.0 mm gap with the chamber wall, which is the main area for shearing the fluid.

The speed of the cylinder is electronically controlled. The cylinder is driven from an external drive through a close-coupled magnetic clutch. The resultant torque is measured directly by torsion bars. A 150 gm-cm drive head and a 500 gm-cm drive head are available for use. Special loading cylinders have been devised for black liquor for transfer of material into the pressurized cell.

This device is not a primary instrument and measurements must be corrected for end effects. This is done by using Newtonian fluids of known viscosity to determine the torque experimentally at different speeds. The lengths equivalent to those needed to produce the measured torques at various speeds are calculated and are used as the lengths for calculations of viscosities of unknown fluids. The equivalent length vs. speed for the 155 mm bob are given in Figure 6.2.4-2. This relation has been checked extensively and is precise within $\pm 2.2\%$.

Once the equivalent length is known, viscosities of unknown fluids can be determined. The basic procedure is to measure the torque produced by shearing the fluid at constant speed. After the fluid is loaded and brought to a uniform temperature, measurements over the entire speed range, including measurements to eliminate the very small hysteresis effects that exist in the measuring head, require 15 to 20 minutes.

The shear stress at a given speed is calculated as:

$$\tau_1 = T/2\pi R_1 l_e \quad (6.2.4-1)$$

where:

τ_1 = shear stress at wall of inner cylinder

T = measured torque

R_1 = radius of inner cylinder

l_e = equivalent length of inner cylinder at speed, Ω

FIGURE 6.2.3-8 Dependence of the Real Part of the Complex Viscosity of a Kraft Black Liquor on Frequency at 68% Solids.

FIGURE 6.2.3-9 Dependence of the Storage Modulus of a Kraft Black Liquor on Frequency at 68% Solids.

FIGURE 6.2.3-10 Dependence of the Reduced Real Part of the Complex Viscosity of a Kraft Black Liquor on Shifted Frequency. Reference Temperature = 50°C.

FIGURE 6.2.3-11 Dependence of the Storage Modulus of a Kraft Black Liquor on Shifted Frequency. Reference Temperature = 50°C.

FIGURE 6.2.4-1 Haake RV-12 Viscometer with Pressure Cell.

FIGURE 6.2.4-2 Example of Determination of Equivalent Length for Coaxial Cylinder for Haake Viscometer.

The shear rate must be calculated with corrections for non-Newtonian effects and for curvature of the shear rate gradient in the gap between the cylinders. This can be done by using one of several correction methods that have been developed. One method that has been used in this work to calculate the shear rate at the wall of the inner cylinder is [Bird, 1977]:

$$\dot{\gamma}_1 = (\Omega / \ln \epsilon) \left\{ 1 + \ln \epsilon \left(\frac{d \ln \Omega}{d \ln \tau} \right) + \left[\frac{(\ln \epsilon)^2}{3} \frac{\Omega}{d \ln \tau} \right] - \left[\frac{(\ln \epsilon)^4}{45} \Omega \right] \left[\frac{d^4 \Omega}{d (\ln \tau)^4} \right] + \dots \right\} \quad (6.2.4-2)$$

where:

- $\epsilon = R_1 / R_0$
- R_1 = inner cylinder radius
- R_0 = outer cylinder radius
- Ω = angular velocity
- $\dot{\gamma}_1$ = shear rate at wall of inner cylinder

The viscosity can now be calculated as:

$$\eta = \tau_1 / \dot{\gamma}_1 \quad (6.2.4-3)$$

Considerable work has been done with black liquors using the Haake system to define the practical limits of the device. Typical results for black liquors are presented in Figures 6.2.4-3 and 6.2.4-4. Figure 6.2.4-3 illustrates the magnitude of the mechanical hysteresis of the system. Values are obtained by approaching the given speed in different directions, the high and low values at each speed are averaged to remove the hysteresis effect. Figure 6.2.4-4 presents results for three softwood liquors at 120°C.

A very detailed analysis of the Haake pressurized cell indicates a temperature variation within the cell of as much as 13°C at 100°C. We have demonstrated that results are inconsistent, even though reproducible to high precision. The cell has been redesigned to eliminate temperature variations and a new cell is being built. The new cell will be thermostatted to $\pm 0.5^\circ\text{C}$ and is expected to yield precision of $\pm 5\%$ or better.

It appears that data can be taken for black liquors at shear rates from about 20 to about 300 sec^{-1} . Fluids with viscosities ranging from about 0.1 to about 30 Pa-sec. (100 to 30,000 cp) can be tested. There has been no evidence of change in liquor viscosity with time within the time required for loading, equilibrating, and measuring a liquor at temperatures up to 120°C. Further temperature stability work must be done. There has been no problem in preparing or handling Softwood liquor samples up to about 72% solids and Hardwood/Western Softwood liquor samples up to about 80% solids. Techniques for preparation and transfer of samples at solids levels above these limits need further refinement.

6.2.5 Dual Chamber Capillary Viscometer

A special viscometer has been designed, built, and tested with standard fluids. The viscometer is designed to permit us to determine the viscosity of fluids as a function of shear rate at conditions at or above the boiling point of the fluid. The viscometer is shown in Figures 6.2.5-1 and 6.2.5-2.

FIGURE 6.2.4-3 Dependence of Viscosity of a Trial Draft Black Liquor at 120°C and About 76% Solids. Hysteresis in Measurement is Illustrated.

FIGURE 6.2.4-4 Dependence of Viscosity on Shear Rate for Trial Kraft Black Liquors at 120°C and about 76% Solids.

FIGURE 6.2.5-1 Dual Chamber Capillary Viscometer.

FIGURE 6.2.5-2 Dual Chamber Capillary Viscometer.

The basic design of the viscometer is shown in Figure 6.2.5-3. The sample of fluid to be tested is confined in two sample cylinders (the sample barrels) that are connected by the capillary. The piston in the sample cylinder on each side of the capillary is rigidly connected to a piston in a hydraulic cylinder. In normal operation, hydraulic fluid is metered into the hydraulic cylinder on the right hand side, which drives the test fluid from the sample cylinder on the right hand side through the capillary into the sample cylinder on the left hand side. The hydraulic fluid pressure in the hydraulic cylinder on the left hand side is held under constant pressure by the pressure controller. The linear motion of the sample cylinder piston is measured directly by means of a linear potentiometer. The pressure in each sample chamber is measured during flow to measure the pressure drop across the capillary. The pressure on the hydraulic fluid in the cylinder on the left hand side is set to give a pressure in the left hand sample cylinder (the cylinder on the downstream side of the capillary during measurement) that is higher than the boiling vapor pressure of the fluid. When the sample has been transferred totally from the right hand side to the left hand side, hydraulic valving is reversed, and the sample is transferred from left to right so that new measurements can be made with the same fluid.

The basic design premises used were:

1. Sample size = 0.56 liters maximum
2. Capillary diameter = 0.031 to 0.125 inches
3. Capillary length = 6 to 72 inches
4. System static pressure = 350 to 1750 psig
5. System pressure, maximum = 15000 psig
6. System temperature = 25 to 204°C
7. System flow rate = 0.004 to 0.24 liters/min

The limits of temperature, pressure, and flow rate can be increased with modifications of the instrument as constructed using proven, standard components to make the necessary modifications.

Each design premise was analyzed and control systems devised to provide the ranges needed with precision. This required that:

1. Hydraulic fluid not be exposed to high temperature
2. Hydraulic fluid be metered at a constant rate ($\pm 0.2\%$ or better) over a range of flow rates equivalent to a sample flow rate range of 0.0041 liters/minute to 0.236 liters/min
3. Temperature of the sample barrels and capillary be controlled $\pm 1^\circ\text{F}$ or better
4. Hydraulic back pressure (fluid static pressure) controlled to within ± 2 psi from 350 to 1750 psig
5. System pressure drop to be measured to $\pm 2\%$ or less.

The requirement that hydraulic fluid not be heated and that flow rate be controlled very closely over nearly a range of 60X led us to choosing Zenith gear pumps driven by an SCR regulated speed drive as the prime mover. In normal operation, the hydraulic fluid is pumped into the hydraulic cylinder on the right hand side so as to drive the sample fluid through the capillary, as shown in Figure 6.2.5-3. The hydraulic system is protected by a pressure relief valve set at 3000 psig. While the metering pumps provide flow at $\pm 0.1\%$, the actual

FIGURE 6.2.5-3 Schematic of Hydraulic Drive and Metering System for Dual Chamber Capillary Viscometer.

flow rate is affected by the static pressure in the sample cylinder. Therefore, movement of the piston is measured by a linear potentiometer. The metering pump and potentiometer provide a constant flow rate that is measured to $\pm 0.1\%$ over the flow rate range of 0.0041 to 0.236 liters/minute. The hydraulic cylinders and sample cylinders are different diameters. The sample cylinder pressure is 7.11X the hydraulic pressure; therefore, a hydraulic pressure of 3000 psig produces a system pressure on the upstream side of 21,300 psig. The system is now set for a maximum hydraulic pressure of 2100 psig (14,900 psig system pressure). To conserve sample, the system is reversible (as shown in Figure 6.2.5-3) so that the test fluid can be driven from the left hand sample cylinder to the right hand sample cylinder for further measurements.

The static pressure in the downstream (left hand normally) sample system must be maintained at a constant value that is above the boiling vapor pressure for the fluid. This is accomplished by using the "back pressure control" system shown in Figure 6.2.5-3 and shown in more detail in Figure 6.2.5-4. A PDI controller is used with two control valves for different ranges of oil flow. Pressure in the cylinder is controlled at 45 to 350 psig. The static pressure in the downstream static cylinder is controlled to ± 1 psig under these conditions.

Temperature on each of the sample cylinders and on the capillary are controlled separately. These control systems are shown in Figures 6.2.5-5 and 6.2.5-6. Temperatures in the sample systems are controlled by electric heating, as shown in Figure 6.2.5-5. Each sample barrel has four heating zones with current supplied through variacs to balance the heating. Current for all four zones on a cylinder is controlled by a PDI controller that controls on the metal temperature in the middle zone of the barrel. Temperature can be controlled to within a range of 1°F with this system at temperatures up to 204°C . The temperature of the capillary is controlled by circulating hot oil through the capillary jacket. Oil is in turbulent flow in the jacket. The hot oil control system shown in Figure 5.2.5-6 provides temperature control of better than 1°F up to 204°C .

This system is now operational. Calibration has been attempted with 0.0625 inch diameter capillaries at 2 foot and 4 foot lengths using mineral oils of known viscosity. Calibration of the 2 foot was not successful with the fluid used, because the pressure drop was too low (< 50 psi in most cases). Calibration with the 4 foot length using a higher viscosity mineral oil yields calculated viscosities that are accurate to $\pm 5\%$. Further calibration work is proceeding.

With this system, it is estimated that viscosities can be measured from 30°C to 204°C for shear rates from 10^2 to 10^4 sec^{-1} . Within these limits, we should be able to obtain measurements for fluids exhibiting viscosities from 0.1 to 100 Pa-sec (100 to 100,000 cp) by using different combinations of capillaries.

Data is treated in a manner similar to that used for the Instron capillary viscometer data, except that end effect corrections are not needed for most of the data. Most experiments will be run with capillaries having L/D values from 380 to 2300; therefore, end effects are negligible.

Final calibration and trials with this instrument should be completed by December, 1983 or before.

FIGURE 6.2.5-4 Schematic of Back Pressure Control System for Dual Chamber Capillary Viscometer.

FIGURE 6.2.5-5 Sample Barrel Heating and Temperature Control Systems for Dual Chamber Capillary Viscometer.

FIGURE 6.2.5-6 Hot Oil Circulation for Capillary Temperature Control for Dual Chamber Capillary Viscometer.

6.3 LIGNIN MOLECULAR WEIGHT RESEARCH METHODS

Lignin content of black liquors and the molecular characteristics of the lignin have a very important influence on the properties of black liquor, particularly the rheological properties. Analysis for lignin content is discussed elsewhere. This section is concerned with purification and molecular weight analysis of lignin. We have spent considerable effort in refining techniques for lignin purification and in developing methods to determine lignin molecular weight.

6.3.1 Lignin Purification

Lignin must be separated from black liquor as completely as possible and purified in such a manner as to render it completely soluble in some solvent if molecular weight is to be determined successfully.

We are presently separating lignin by precipitating it from black liquor with H_2SO_4 to a pH of 2. The precipitated lignin is washed with H_2SO_4 at a pH of 2 and then freeze-dried. The freeze-dried lignin is extracted with hexane in a Soxhlet extraction apparatus and redried under vacuum at about $0^\circ F$ ($-17.8^\circ C$). It is then placed in a sealed container and stored in a dessicator. The apparatus for lignin purification is shown in Figure 6.3.1-1.

Lignin separated and purified in this manner is completely soluble in DMF, DMSO, THF, and pyridine. Presently, we are using solutions of lignin in DMF for molecular weight determinations, since DMF is more suitable than THF or DMSO for both M_n and M_w determinations and is less hazardous than pyridine.

To reduce inorganic contamination to the lowest possible level, we plan to precipitate lignin with HCl at a pH of 2 and wash lignin with HCl at a pH of 4 in the future.

6.3.2 Number Average Molecular Weight (M_n)

Our approach has been to attempt to determine the number average (M_n) and weight average (M_w) molecular weights. The number average molecular weight (M_n) is defined as:

$$M_n = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} \quad (6.3.2-1)$$

where: N_i = number of molecules with molecular weight, M_i

It can be determined by measurement of a colligative property of the polymer solution.

The Wescan Model 232 Vapor Pressure Osmometer (VPO) has been installed and prepared for use with lignin solutions. This is shown in Figure 6.3.2-1. In this instrument, pure solvent and the solution are fed to wicks surrounding

FIGURE 6.3.1-1 Lignin and Solvent Purification Units.

FIGURE 6.3.2-1 Wescan 232 Vapor Pressure Osmometer.

separate resistance thermometers in a thermostatted chamber that contains both liquid and vapor phases of the solvent. The solution has a lower evaporation rate than the pure solvent; therefore, a temperature difference between the two thermometers is established. This temperature difference is a function of the type and quantity of solute present. The equation that can be used to determine molecular weight is:

$$\frac{\Delta v}{c} = \frac{K}{M_n} + ac + bc^2 + \dots \quad (6.3.2-2)$$

where: Δv = voltage difference between thermistors
 c = solution concentration
 K = instrument constant for the solvent used at the temperature of measurement
 a, b = constants specific to the solvent - solute pair at the temperature of measurement

As can be seen, if K is known, the value of M_n can be determined by measuring Δv for several concentrations and determining the intercept of the curve of $\Delta v/c$ vs. c .

The instrument was first tested for accuracy and precision by measuring the M_n of several polystyrene samples obtained from Pressure Chemicals Company. The values of M_n of these samples were known to $\pm 5\%$. The instrument constant for toluene at 50°C was determined using sucrose octaacetate as the solute. The molecular weight of sucrose octaacetate is known and is equal to 678.6. The plot for $\Delta v/c$ vs. c for sucrose octaacetate in toluene at 50°C is shown in Figure 6.3.2-2. The intercept of the curve is $K/678.6$, which serves to determine K as 38436. Figure 6.3.2-3 is a representative curve of results for determination of M_n of polystyrene. The measured M_n value of 2121 is within 4.5% of the value reported by Pressure Chemical. The measured value of 2121 is reproducible to within 3%. Measurements have been made successfully for polystyrene with M_n values from 2220 to 10,000. At this point, we accept our instrument as accurate.

Measurements of K for sucrose octaacetate in DMF at 70 and 80°C have been made. The instrument has been shown to reach steady state for a single measurement for DMF within 20 minutes if very dry DMF is used. M_n for lignins have not been measured yet due to work on determining M_w .

FIGURE 6.3.2-2 Example of Calibration of the Vapor Pressure Osmometer. Instrument Constant Determined for Toluene at 50°C Using Sucrose Octaacetate.

FIGURE 6.3.2-3 Experimental Determination of Number Average Molecular Weight of Polystyrene by Vapor Pressure Osmometry with Toluene at 50°C.

6.3.3 Weight Average Molecular Weight (M_w)

The weight average molecular weight (M_w) is defined as:

$$M_w = \frac{\sum_{i=1} M_i w_i}{\sum_{i=1} w_i} = \frac{\sum_{i=1} M_i^2 N_i}{\sum_{i=1} M_i N_i} \quad (6.3.3-1)$$

where: w_i = mass of molecules of molecular weight M_i
 N_i = number of molecules of molecular weight M_i

and is determined by light scattering. We chose the Chromatrix Low Angle Laser Light Scattering (LALLS) Spectrophotometer Model KMX-6 for this measurement because:

1. Sample requirements are small
2. Measurement is absolute
3. There is little or no effect of molecule shape on the result
4. Measurements can be made at elevated temperature.

Use of this instrument requires that the effect of solute concentration on refractive index be determined at the same wave length and temperature as is used for the light scattering measurement; therefore, a Chromatrix KMX-16 Differential Refractometer has also been installed. These instruments are shown in Figures 6.3.3-1 and 6.3.3-2.

The basic relationship for M_w for light scattering is:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} (1 + ac + \dots) \quad (6.3.3-1)$$

where: $K = \frac{2\pi^2 n^2 (\partial n / \partial c)^2}{N_A \lambda^4}$

$$R_\theta = \text{excess Rayleigh Ratio} = R_{OSn} - R_{OSv}$$

$$R_{OSn} = \text{Rayleigh Ratio of solution}$$

$$R_{OSv} = \text{Rayleigh Ratio of solvent}$$

$$R_o = r^2 I_o / V I_i$$

C = concentration of solution

λ = wave length of incident light

N_A = Avogadro's number

I_o = intensity of scattered beam

I_i = intensity of incident beam

FIGURE 6.3.3-1 KMX-6 Low Angle Laser Light Scattering Photometer.

FIGURE 6.3.3-2 KMX-16 Chromatrix Differential Refractometer.

- V = solution scattering volume
- r = scattering distance
- n = refractive index of solvent at λ and T
- $\partial n / \partial c$ = change of refractive index of solution with respect to concentration at λ and T
- a = constant dependent upon solvent-solute pair, T, and λ .

Light scattering is a very difficult measurement if precise and accurate results are to be obtained. We worked with the polystyrene-toluene system first to determine the accuracy to be expected from our instruments. At least three different measurements must be made:

1. Determination of the Rayleigh Ratio for the solvent, R_{0Sv} .
2. Determination of the change of refractive index for the solution, dn/dc .
3. Determination of the Rayleigh Ratio of the solution, R_{0Sn} , as a function of concentration.

The Rayleigh Ratio for toluene was determined with the KMX-6 a number of times. The values determined all lay within $\pm 3\%$ of the accepted value. The value of dn/dc for polystyrene-toluene was determined at 24°C as 0.105 ml/gm , as shown in Figure 6.3.3-3. Measurements of excess Rayleigh Ratio for the solution, R_{0Sn} , were made at various concentrations of polystyrene in toluene at 24°C . The results were plotted according to Equation 6.3.3-1, as shown in Figure 6.3.3-4, and used to determine the M_w for the polystyrene. A value of $M_w = 97,640$ was obtained, which is within 4.9% of the value reported by Pressure Chemicals for this sample. Our reproducibility is within $\pm 3\%$. Therefore, we have accepted our system as capable of precise and accurate measurement.

We then began work with the lignin-DMF system. dn/dc for lignin in DMF was determined at various temperatures. A typical plot of Δn vs. c is shown in Figure 6.3.3-5, which is for one lignin sample at 70°C . As expected, dn/dc is not sensitive to lignin molecular weight and has only a very slight dependence on temperature.

Measurements of excess scattering for lignin-DMF were attempted at 60 to 90°C . There are problems. Lignin apparently associates in DMF at lower temperatures and the solution must be filtered to remove salt particles. Figure 6.3.3-6 demonstrates this effect. We were most successful in using a teflon filter reinforced by high density polyethylene; however, this filter deteriorates badly at temperatures above 70°C . The lignin does not associate in DMF at 70°C , as shown by the positive slopes of the lines in Figure 6.3.3-6. If we filter at 24°C and then heat the filtered solution to 70°C before measurement, rather than heating the solution to 70°C and then filtering before measurement, the molecular weight determined is lower. That is, filtration at 24°C removes some of the lignin that is associated. Therefore, the solution must be heated before filtration.

The molecular weight determined for the lignin used was $M_w = 84,050$. However, there can be other complicating factors. These are:

1. absorbency of the solution
2. fluorescence
3. polarization.

FIGURE 6.3.3-3 Refractive Index Increment for Polystyrene in Toluene at 24°C and 6328 Å.

FIGURE 6.3.3-4 Determination of Weight Average Molecular Weight of Polystyrene by Light Scattering in Toluene at 24°C and 6328Å.

FIGURE 6.3.3-5 Changes in Refractive Index of Dimethyl Formamide with Lignin Concentration at 70°C and 6328Å.

FIGURE 6.3.3-6 Determination of Weight Average Molecular Weight of Lignin by Light Scattering in DMF at 70°C and 6328Å; Effect of Prefilter Temperature.

We are in the process of eliminating or compensating for these effects. If there are effects due to absorbency or florescence, the value of M_w should be dependent upon the incident beam. We determined the M_w for another lignin in DMF at 70°C at two different light intensities. These results are shown in Figure 6.3.3-7. The curve labelled "without attenuator" is at the same intensity used for the measurements presented in Figure 6.3.3-6. The curve labelled "with attenuator" is for measurements at half that intensity. As can be seen, light intensity has an effect on the measurement; the M_w values differ by 9+%. The effects of florescence and polarization will be corrected for by installing filters in the KMX-6. Absorbency will be determined by an auxiliary measurement and results corrected for this effect.

At this point, we have an instrument and method to determine M_w of lignins when the filters have been installed on the KMX-6. A unit for preconditioning solution filters is being prepared, because solution filters must be bathed in solvent for 2-3 days and are reliable for only 2-3 determinations.

6.3.4 Lignin Glass Transition

A Perkin-Elmer DSC-2 has been used to determine the glass transition temperature (T_g) for lignins purified from the St. Regis test liquors. The instrument was first tested for accuracy and precision by using polystyrenes.

Polystyrenes of known molecular weights were studied. The sample (5 to 15 mg) contained in an aluminum pan was placed in the instrument and heated at a constant rate. The T_g was determined as the mid-point temperature of the transition. A typical result for polystyrene is shown in Figure 6.3.4-1.

T_g is a function of M_n . T_g was measured at a heating rate of 10°C/minute and compared with accepted literature values, as shown in Figure 6.3.4-2. Agreement is excellent.

DSC is a dynamic method while T_g is a thermodynamic function; therefore, T_g is dependent on heating rate. The true value of T_g should be more closely determined by measuring T_g as a function of heating rate and extrapolating to zero heating rate (infinite heating time). This has been done for polystyrenes, as shown in Figure 6.3.4-3. These results show that T_g is a function of M_n , but that the values are displaced above those determined at 10°C/minute, as shown in Figure 6.3.4-4.

T_g values have been determined for lignins separated from each test liquor and wash (eight in all) from St. Regis. All values were in the range 144-148°C for a heating rate of 10°C/minute. The precision of the method is estimated to be $\pm 2^\circ\text{C}$. Therefore, there appears to be no significant difference in T_g for the lignins. We suspect that the lignins are quite pure and of high molecular weight.

6.4 THERMAL ANALYSES RESEARCH METHODS

6.4.1 Heat Capacity

The Perkin-Elmer DSC-2 has been calibrated and used to determine heat capacity of black liquors as a function of temperature and solids content. The instrument that is being used is shown in Figure 6.4.1-1.

FIGURE 6.3.3-7 Determination of Weight Average Molecular Weight of Lignin by Light Scattering in DMF at 70°C and 6328Å; Effect of Light Intensity.

FIGURE 6.3.4-1 Typical DSC Scan for Polystyrene to Determine the Glass Transition Temperature. Heating Rate = $10^\circ\text{C}/\text{min}$.

FIGURE 6.3.4-2 Comparison of Glass Transition of Polystyrene as Determined on Perkin-Elmer DSC with Literature Values. Heating Rate = 10°C/min.

FIGURE 6.3.4-3 Determination of Glass Transition Temperatures of Polystyrene by Extrapolation of DSC Results to Zero Heating Rate.

FIGURE 6.3.4-4 Effect of Extrapolation to Zero Heating Rate of Glass Transition Temperatures of Polystyrenes as Determined by DSC.

FIGURE 6.4.1-1 Perkin-Elmer DSC-2

Differential scanning calorimetry is based on the principle of measuring the differential power input required to maintain sample and reference substances at the same temperature while scanning at a constant rate over a temperature range. The power required to do this is directly proportional to the energy absorbed (or released) by the sample with respect to the reference. This is given by:

$$d(\text{power}) = d(\text{voltage} \times \text{amp}) = d\left(\frac{J}{C} \times \frac{C}{S}\right) = d\left(\frac{J}{S}\right) \quad (6.4.1-1)$$

and

$$d(J/S) = d\left(\frac{\text{energy}}{\text{time}}\right) = dM/dt$$

The specific heat of the sample is related to the ordinate scale on a time vs. power curve as:

$$dH = MC_p dT \quad (6.4.1-2)$$

where:

H = enthalpy
M = mass of sample
C_p = specific heat of the sample
T = temperature

If we divide both sides by the differential time, dt:

$$\frac{dH}{dt} = MC_p \frac{dT}{dt} \quad (6.4.1-3)$$

where:

dH/dt = the output value of the DSC
dT/dt = the rate of the temperature scan.

In practice, the specific heat of a sample is not determined by measurement of an absolute ordinate value, but rather is determined by comparison to a standard. We use pure sapphire as a standard, because the specific heat of sapphire is known within 0.2% over the entire range of interest (-40 to 200°C). The specific heat of the sample is determined by comparison to the standard as follows:

$$C_p(\text{sample}) = \left(\frac{\text{sample deflection @ } T}{\text{standard deflection @ } T} \right) \left(\frac{\text{standard mass}}{\text{sample mass}} \right) C_p(\text{standard}) \quad (6.4.1-4)$$

The absolute temperature has been calibrated for the instrument by using the temperatures of fusion of deionized water, indium, lead, and zinc. The differences between measured and accepted fusion points for these materials ranged from -0.09°C to -0.73°C , which is within the range of accuracy expected for thermal devices. A calibration curve is used to correct measured values of absolute temperature.

The precision and accuracy of the instrument for specific heat measurements were checked in two ways. Firstly, the specific heat of the sapphire standard was determined by an absolute measurement. The specific heat determined was within 1% of the accepted value for sapphire. Secondly, the specific heats of four polystyrene standards were determined by comparison with sapphire at 50°C and 125°C . The results are shown in Figure 6.4.1-2. The average values determined at 50°C and 125°C are within 1% of the values reported in the literature for static polystyrene. We have also demonstrated that most of this error is due to uncertainties in weighing. Weights must be precise to ± 0.02 mg. or better, or several samples must be measured and results averaged.

The specific heats of a black liquor at different solids contents from 15 to above 70% solids have been determined from about 35 to 117°C . These results are shown in Figure 6.4.1-3. There appear to be no difficulties in this determination, and we hope to extend the DSC measurement to temperatures that are well above the normal boiling point.

6.4.2 Densities

Densities of black liquors at solids contents below 60% are being determined by normal pynometry methods for temperatures at 25°C . Sample results for a black liquor are shown in Figure 6.4.2-1. Our pynometers have been modified for direct measurements at temperatures from 25 to about 60°C . Densities at higher temperatures will be calculated from measurements of thermal expansion of the liquors from 50 to above 100°C in dilatometers.

Densities of black liquors at 25°C and at solids contents above about 60% solids will be determined by weighing precision-molded samples. Densities of these liquors at higher temperatures will be calculated from measurements of thermal expansion in glass dilatometers or in a dilatometer attachment used in the Perkin-Elmer TMS-2 that is shown in Figure 6.4.2-2.

Measurements of density, while tedious, present no real difficulties and density does not appear to be sensitive to differences in lignin characteristics in the liquor.

6.4.3 Thermal Stability

Thermal stability is determined in several ways. TGA is used to determine the stability of black liquors and lignins to pyrolysis reactions that produce volatile components. A DuPont 951 TGA system, shown in Figure 6.4.3-1, is used. Work done with this instrument has been reported [Snow, 1982].

Black liquors, when heated in nitrogen, show three main intervals of activity, as shown in Figure 2.3-8. The first is loss of water primarily and the second is either pyrolysis or loss of high boiling organics. The black liquor is stable after drying, however, If liquor is heated to 140°C and held, it will

FIGURE 6.4.1-2 Specific Heats of Polystyrenes at 50°C and 125°C as Determined by DSC; Comparison to Literature Results.

FIGURE 6.4.1-3 Specific Heat of a Trial Kraft Black Liquor as Determined by DSC.

FIGURE 6.4.2-1 Effect of Solids Content on Density of Trial Kraft Black Liquors at 25°C.

FIGURE 6.4.2-2 Perkin Elmer TMS-2 Thermal Mechanical Analyzer for Dilatometry Studies.

FIGURE 6.4.3-1 DuPont 951 TGA Thermal Gravimetric Analyzer with Computer Interface.

come to a constant weight after about two hours, as shown in Figure 2.3-9. Upon reheating after cooling, the liquor will remain at constant weight until heated to temperatures above 140°C. Similar behavior has been noted with respect to the second interval of activity, i.e., at about 180-230°C.

Lignin behaves in a similar manner. A typical TGA curve for a purified lignin from one of the test liquors from St. Regis is shown in Figure 6.4.3-2. The first temperature interval for activity corresponds to evolution of residual hexane used in the purification. Aside from this, there is only very minor activity below about 250°C. We will continue to perform TGA experiments with black liquors and lignins on a routine basis.

Not all reactions need evolve gases or volatile liquids. Reactions of the lignin in the black liquors may involve bond scission or addition reactions. Such reactions will be reflected, if they occur, in changes in viscosity of the system with time.

Liquors can presently be held for long periods (100 hours or more) in the Haake viscometer at temperatures up to 250°C and the viscosity determined periodically during the holding period. Modifications are being made to permit testing at temperatures up to 300°C. Changes in liquor that affect physical properties should be indicated by a change in viscosity.

As an example, suppose that only one type of scission reaction occurs. The viscosity will be a function of molecular weight. Since a scission reaction is first order, the viscosity should decrease in a manner consistent with first order kinetics in this case. Thus, it very likely may be possible to use viscosity as a sensitive, albeit indirect, method of following reactions.

Tests to date at 120°C for short periods (less than 3 hours) indicate no significant changes. However, one test run at 130°C for 48 hours on a sample containing more than 70% solids indicates significant decrease in viscosity, and the viscosity decrease correlates as first order kinetics. Further tests of this type are planned.

FIGURE 6.4.3-2 Typical Thermal Gravimetric Analysis (TGA) and Derivative Analysis (DA) of Lignin Isolated from a Trial Kraft Black Liquor. Analysis Performed in Nitrogen at 10°C per Minute.

7. UNSOLVED PROBLEMS

7.1 Lignin UV-VIS Absorption

Not only is it important to resolve the question of UV-visible absorption vs. concentration of lignin as an analytical method to provide a means for quantitatively determining lignin in liquors, but it is important to determine absorption at 632.8 nm for lignin to correct light scattering readings for MW determinations.

Effort is directed toward determining absorption at 205 and 280 nm of lignin solutions prepared by various methods to evaluate the best method of analysis. The lignin solutions are also being checked for drift in absorption with time.

Initial measurements at 632.8 nm indicate that absorption by lignin in solution in such solvents as DMF is significant. Absorption as a function of concentration of lignin has been determined at 25°C. Measurements at 50-90°C will be made so that light scattering at higher temperatures can be corrected for absorption.

7.2 Refractive Index of Solvents

Molecular weight analyses of lignin in organic solvents must be performed at elevated temperatures (50-90°C). For light scattering, the refractive index of the solvent at the temperature of measurement must be known. Amazingly, these data do not exist for our solvents. Values of refractive index for DMF, DM50 and pyridine are being determined for us for temperatures from 25 to 90°C.

7.3 Thermal Conductivity

We originally intended to determine thermal conductivity of black liquors by a comparative method using a DSC; however, we find that this is not applicable to our materials. We now plan to determine thermal conductivity directly by using a coaxial cylinder cell similar to that used by Lohe (1965) or a guarded hot plate cell similar to that used by Thompson (1982) for polymer melts and viscous liquids. We will select the geometry in December and have made arrangements for construction.

7.4 Saccharidic Acid Analysis

This analysis will be performed by using a Water HPLC. Techniques have been developed by the Chemistry Department at UMO; however, analyses have not yet been run on our liquors. While we foresee no problems, we cannot be certain until analyses have been performed.

7.5 Digester

We have not yet selected a digester design. We have reviewed three basic types and will select one soon. The best type would appear to be a circulating digester. We believe that the digester should be designed to hold about 27 pounds oven dry chips per cook and that the liquor should be circulated.

We have reviewed one design that will permit us to handle cooks of this size with liquor circulation at liquor-to-wood ratios as low as 3.5/1. A local fabricator has been identified and delivery on long lead time components determined. We believe that fabrication and assembly can be completed by July, 1984. if design is completed by January, 1984.

Our design will permit us, if we wish, to blow the digester without exposing the liquor to air and to sample the liquor stream for analysis during cooking. If possible, the digester will be designed to permit us to vary the wood charge by a factor of two.

7.6 Surface Tension

No work will be done on surface tension until the degree of viscoelastic behavior of the liquors has been determined, since this affects the choice of method.

Also, we must have more confidence in our ability to control the level of soap in the liquor before making measurements, since soap is expected to have a significant effect on surface tension.

8. TIME SCHEDULE AND STAFFING

8.1 Time Schedule

This program has grown to be extremely complex with several interlocking studies. Therefore, timing of each element of the program becomes important.

8.1.1 Pulping Experiment

The first phase of the pulping experiment in which we will conduct cooks 1 through 8 of the pulping experiment for slash pine (the first $\frac{1}{2}$ factorial experiment) will begin November 14 with first delivery of liquors to UMO on about November 25. Two runs will be conducted for each cook; therefore, the $\frac{1}{2}$ factorial will be run in duplicate. In addition, cooks 22, 18, 17, and 13 will be run this time to provide additional information. Cooking will be complete by early December.

The second phase of the designed experiment, at least cooks 7 through 17 (the second $\frac{1}{2}$ factorial experiment) will be conducted in January, 1984 with the final cooks to follow.

All cooks for the designed experiment should be completed by April, 1984 or earlier.

8.1.2 Liquor Storage and Evaporation

All arrangements necessary for liquor evaporation, skimming, and liquor storage have been made. Necessary facilities will be available and ready by late November.

8.1.3 Revisions of Rheological Equipment

Revisions on the Haake, Rheometrics, and dual chamber capillary devices necessary for high precision and accuracy have been developed. In most cases, revisions are complete and have been tested.

Final revisions on the dual chamber include digitizing variable outputs. This will not be completed until January. However, the unit can be used with analog recorders in the meantime.

We will be able to operate the Haake pressurized cell without temperature variations, since we have installed a temperature bath in which the cell is immersed. We have redesigned the cell and a new cell is under construction. This will be available in late December.

8.1.4 Lignin Characterization

Final refinements for light scattering and VPO are being made. We will be in a position to determine $\bar{M}_w$ and $\bar{M}_n$ routinely and accurately by late November.

8.1.5 Chemical Analyses

Analyses run during the trial tests have been reviewed and refined. These are ready. We are prepared to conduct TAPPI T-625 analyses. Total elemental analyses and saccharinic acid analyses cannot be performed until the CDS TEA unit and the Water HPLC have been put into operation. We plan to begin this in December.

8.1.6 UMO Digester

Design will begin on a UMO digester in December. We expect to start fabrication in April, 1984 for installation in July, 1984.

8.1.7 Other Experimental Units

Work will begin on a thermal conductivity cell in December, 1983. We will select a method for surface tension studies in March, 1984 and should begin work during 1984. Measurement of heating values will begin in 1984.

8.2 Staffing

Staffing with graduate students and faculty is now complete. Dr. Fricke, Dr. Hill, and Mr. Farrington will continue as faculty or research associates. Five graduate students will continue through early 1984. As M.S. students complete their work, they will be replaced to maintain a staff of five graduate students.

Technicians have not yet been employed. We plan to use two undergraduates part-time for some routine work. This will amount to a total of about 20 man-hours/week of effort. One technician will be hired for full-time work in late December. The technician will be used principally to collect rheological and thermal data. A laboratory technician currently employed in the department will be used part-time for some liquor analyses. In general, technicians and undergraduates will not be employed until routine methods have been established and the skills necessary have been defined sufficiently to enable us to formulate job descriptions.

9. TECHNOLOGY TRANSFER

This report serves as a description of progress during Phase I and will be made available through DOE. Other reporting is planned.

Project review meetings of representatives from supporting companies and DOE with the UMO project group, such as have been held during Phase I, will continue during Phase II. At least two will be held. These have been useful in guiding and evaluating the work, and these will undoubtedly serve as the most efficient means for transfer of information to supporting companies and DOE. Periodic progress reports will be issued at a rate of about one every month to six weeks.

Presentations at Technical Meetings (AIChE and TAPPI) on our results from Phase I are planned for 1984. At least two papers will be presented. We plan to make at least five presentations on various aspects of our work during the first experiment in 1985.

An Annual Report will be issued in 1984 and a Final Report in 1985. These will be made available through DOE.

10. ENERGY SAVINGS

It is difficult at this point to specify exactly the energy savings to be expected from this program. However, there is no reason at present to revise our original estimate. Based on net savings in stack losses alone, we had estimated that if our program results in capability to fire liquors at 75% solids rather than 65% solids, the energy savings for the average 1000 ton/day mill would be 1.5×10^{11} Btu/yr (equivalent to 26,000 bbl/yr of fuel oil). This is an estimated total savings in the U.S. and Canada of 7.2×10^{12} Btu/yr (1.24×10^6 bbl/yr of fuel oil), if the developments are utilized by 80% of the industry.

Also, since recovery systems are usually the limiting unit in a mill, the ability to fire at 75% solids could increase capacity at levels estimated at 3-15% without major new capital investment.

Finally, our work during Phase I has given rise to several possible approaches to lowering viscosity so that even higher solids liquors could be handled. If these prove successful, our original estimates on energy saving could prove to be quite conservative.

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