

**A COMPREHENSIVE PROGRAM TO DEVELOP CORRELATIONS
FOR THE PHYSICAL PROPERTIES OF KRAFT BLACK LIQUOR**

Interim Report No. 3

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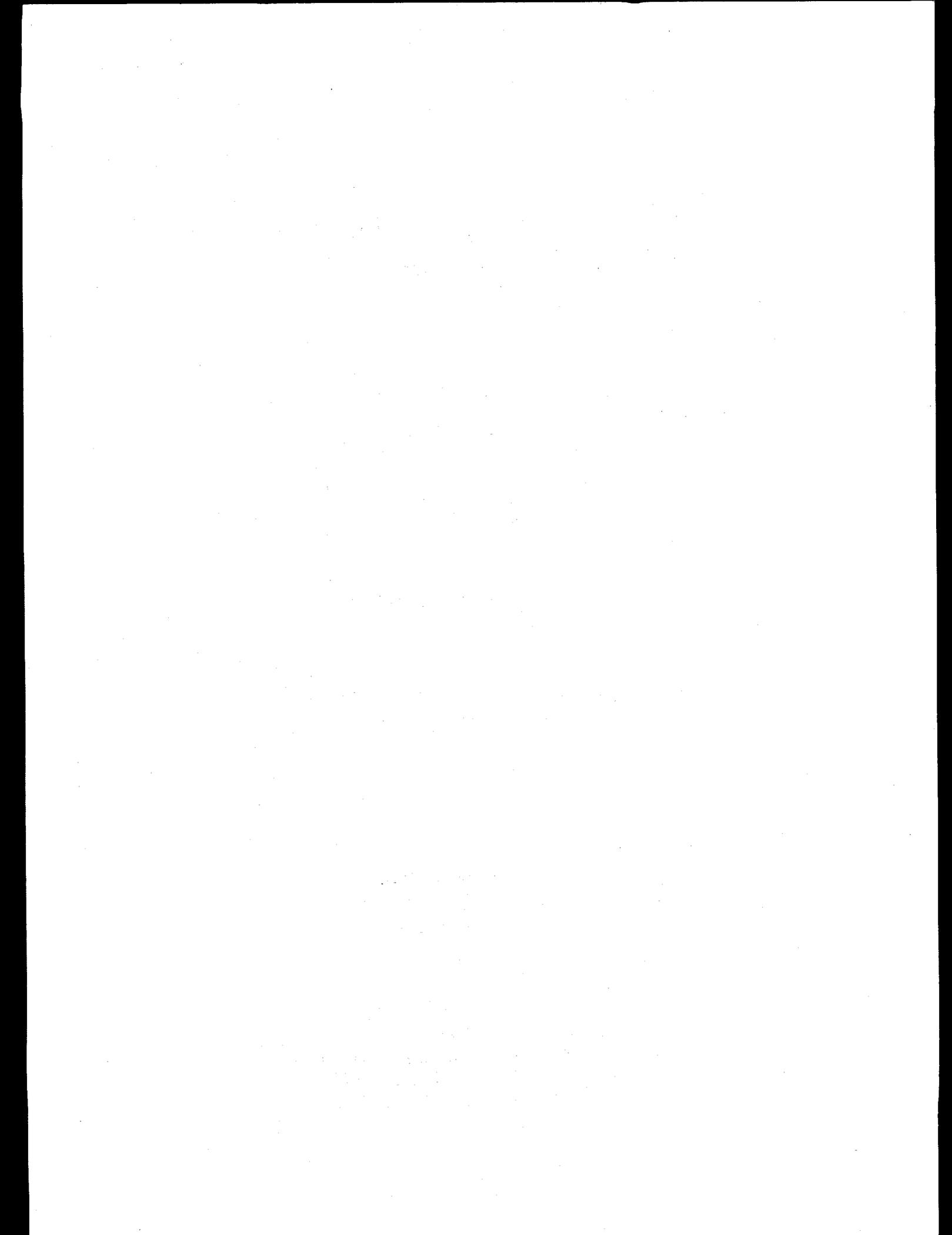
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SEPTEMBER 1993

**Work Performed Under Grant DE-FG02-85CE40740
The University of Florida**

**Prepared For:
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**Office of Industrial Technologies
U.S. Department of Energy
Energy Efficiency and Renewable Energy
Washington, DC 20585**



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INTRODUCTION

The kraft black liquor properties program has been conducted in a manner such that correlations relating liquor properties to liquor composition can be developed ultimately, particularly with respect to the composition of the solids in black liquor. The philosophical approach that has always been followed is shown simply in Figure 1. We recognized in the beginning that, if properties and liquor composition were to be related, liquors made from pulping chips of a known species at known pulping conditions would have to be available. Properties and composition of these liquors could be determined and correlations developed to relate them to pulping conditions. Finally, correlations relating properties to composition could be developed. Conducting the program in this manner has led to a number of developments.

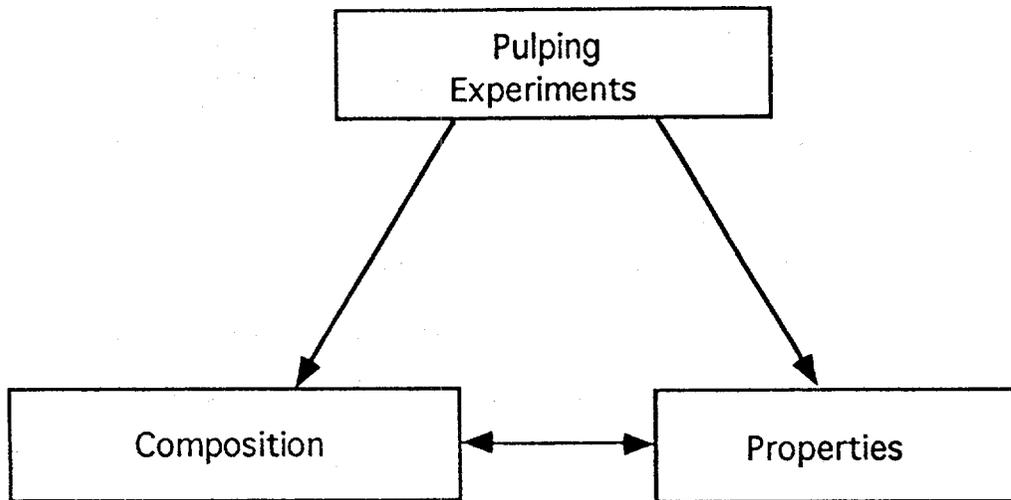
We have designed, constructed, and operated a batch digester that can be used in several modes of operation. This digester has been described in our earlier reports. Statistically designed pulping experiments have been conducted using this digester.

Since we do not know a priori which components of the black liquor solids affect properties, the composition of the solids must be determined as completely as possible. Some analyses have been performed using procedures already developed. However, a great deal of effort has been devoted to development of new analytical procedures as well as to improvements of other procedures. With the exception of some saccharinic derivatives, the composition of the liquor solids is fully determined.

Characterization of the lignin contained in the liquor solids has been considered to be of special interest for properties evaluation, particularly rheological properties evaluation. A great deal of research effort has been devoted to lignin analysis, lignin purification, and lignin molecular weight

Figure 1

Approach to Black Liquor Studies



determination. This has proven to be a most difficult task, but characterization methods have been developed that have been proven to be correct.

Properties that have been determined are vapor pressure equilibria as a function of solids; density as a function of solids and temperature; viscosity as a function of solids, temperature, and shear rate; normal stress as a function of solids, temperature, and shear rate for selected liquors; heat capacity as a function of solids and temperature; heat of solution as a function of solids; and heat of combustion. Many of these properties measurements required development of new instruments and development of experimental procedures. Some of these have been described in earlier reports or publications or both. Some pertinent details are given in this report, but full details will not be given. Complete descriptions of instruments, procedures, and data treatment used in this program will be included in our final report.

The general approach used in properties measurements has been to determine the property at constant solids concentration as precisely as possible. The property is measured as a function of temperature, or temperature and shear rate in the case of viscosity or normal stress, at constant solids. This is repeated at different solids concentration to determine the property over as wide a range of solids concentration as possible. In many cases, properties can be measured at up to 100% solids. This constitutes data for one liquor, and the procedure is repeated for each liquor.

Data reduction and correlation involves a number of steps. The first step is to consider data for the property for one liquor. Data reduction schemes, based as much as possible on theories that have proven to be successful for other fluids, are tested. These are modified as necessary for our use. A data reduction scheme is sought that will partition the effects of temperature, solids concentration, solids composition, and shear rate in the case of rheological properties. Where possible,

results are checked for thermodynamic or theoretical consistency. To be considered successful, the data reduction method must be applicable to all liquors made in our study and to liquors obtained from mills. As an example, consider correlation of heat capacity. Black liquor is not an ideal fluid. As reported earlier, the heat capacity of a black liquor can be defined as:

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

where:

C_{p_w}	=	heat capacity of water
x	=	mass fraction of liquor solids
C_{p_s}	=	$a + bT$ = heat capacity of liquor solids
$A(1-x)x^m$	=	excess heat capacity
A	=	$c + dT$
m	=	constant

This has been found to be applicable to all liquors. Note that the effects of solids concentration, temperature, and solids composition are clearly partitioned. The constants a , b , c , d , and m depend only upon solids composition. In addition to development of a generally applicable correlation, this leads to a large reduction in the amount of experimental work needed to define the constants required to describe a new liquor. In our studies, we normally have run fifteen to twenty differential scanning calorimeter (DSC) experiments on a liquor. This can now be reduced to three or four.

After data reduction is completed, the constants for a property that are dependent only upon liquor solids composition are correlated empirically to pulping conditions, since solids composition is dependent upon pulping conditions. Simultaneously, each component of the liquor solids is being

correlated empirically to pulping conditions. The correlations developed are used to provide sets of smoothed results for liquor solids composition and constants for properties relations. The final step is to develop correlations between constants for properties relations and solids composition.

At this point, development of methods for properties measurements, except for thermal conductivity, has been completed successfully, and these methods have been applied to many liquors. Methods for solids composition analysis and for lignin characterization, except for saccharinic derivatives, have been developed and applied. Data reduction correlations have been developed for the properties studied, except for density and thermal expansion at high solids concentration. Complete pulping experiments with slash pine have been conducted. All properties data on these liquors and on a few mill liquors have been collected, except for density at high solids for some liquors. Empirical correlations relating composition, lignin characterization, and constants for correlating properties to pulping conditions are in progress. Some initial work on correlating properties correlation constants to liquor solids composition has begun. More than 80 experimental pulping cooks have been made with slash pine. These are to be the primary basis for final correlations. While the correlation methods are generally applicable, the data for other species that is necessary for correlations for these species is not available. It has not been possible to include this in our work, because there has not been sufficient time. However, the methods developed and the trends identified should make it possible to extend the work in future studies with much less effort. We estimate that repetition of our work for a new wood species would require less than one-fifth of the effort of this study.

PULPING AND LIQUOR TREATMENT

As reported in our progress summaries and in our interim reports of July, 1989 and December, 1990, our batch digester system operates very well. Full details of the digester system, process schematic, and process control systems were given in the July, 1989 interim report. These will be included in the final report for this program. Only the most pertinent details on pulping and liquor treatment will be presented in this report.

The digester itself is a 3.5 ft³ reactor with a basket and filter system designed to contain chips and pulp with negligible flow resistance due to the filtering screens. The digester is presently heated indirectly with 250 psig steam which permits digestion at temperatures up to 400°F. The system is equipped with a white liquor tank, wash water tank, and liquor receiver with internal heat exchanger for cooling the liquor. Liquor and wash water are metered into the digester at up to 220°F and 200°F, respectively. The liquor or wash can be discharged to the liquor tank within 10 seconds or less after digestion or washing. The digester is equipped for liquor or wash circulation through the chip bed. The digester can be operated as a closed reactor with no liquor circulation, as a closed reactor operated as a tumbling autoclave, or as a closed reactor with liquor circulation through the digester at up to 30 gallons per minute. When operating the digester without tumbling (rotation), we measure the temperature within the chip bed at four points along the axis of the digester. The system is designed so as to virtually eliminate contact of the liquor and wash with air and to condense and retain all volatile components in the liquor. The chip load can be varied from about 30 to 70 lbs of wet chips. The liquor-to-wood ratio can be varied from about 3.6/1 to about 8/1 when operating the digester with no liquor circulation and from about 2.8/1 to 8/1 when operating the digester with circulation. Normally, two washes with water have been done after cooking is completed with each wash

volume approximately equal to the liquor volume. The combined liquor and two washes are cooled in the liquor receiver and then transferred into a portable tank. The liquor is filtered through a cartridge filter during transfer to remove fiber that has passed through the chip screens in the digester. The pulp is then washed in place in the digester with a large amount of water after which the digester is opened and the pulp removed. Yield and Kappa number for the pulp are determined.

Cooks have been run in duplicate for each cooking condition. If results do not agree, cooking is repeated. Except in the early work, cooking results for duplicate cooks agree very well. This is primarily due to the development of good control of the cooking process. Most cooking has been done with liquor circulation. Figure 2 is an example of the time-temperature within the chip bed during cooking with circulation. Temperature within the bed can be maintained within $\pm 1^\circ\text{C}$ when controls are tuned properly. A total of approximately 95 cooks with slash pine have been conducted at 25 different pulping conditions to give 17 duplicated conditions with no liquor circulation and 25 duplicated conditions with liquor circulation. These liquors form the primary basis for the properties studies.

Some modifications have been made to our earlier procedures. The most important is the reduction in volume of the first two washes. We have found that, with circulation, effective washing can be done with wash water equivalent to about one-half of the liquor volume for each of the first two washes. This decreases the total volume of liquor that must be concentrated by about one-third. We have also modified our handling procedures to improve labor efficiency.

The pulping variables were sulfidity, effective alkali, temperature, and time at temperature. These were varied over broad ranges. Yield and Kappa number were determined and H-factor was calculated from the time-temperature

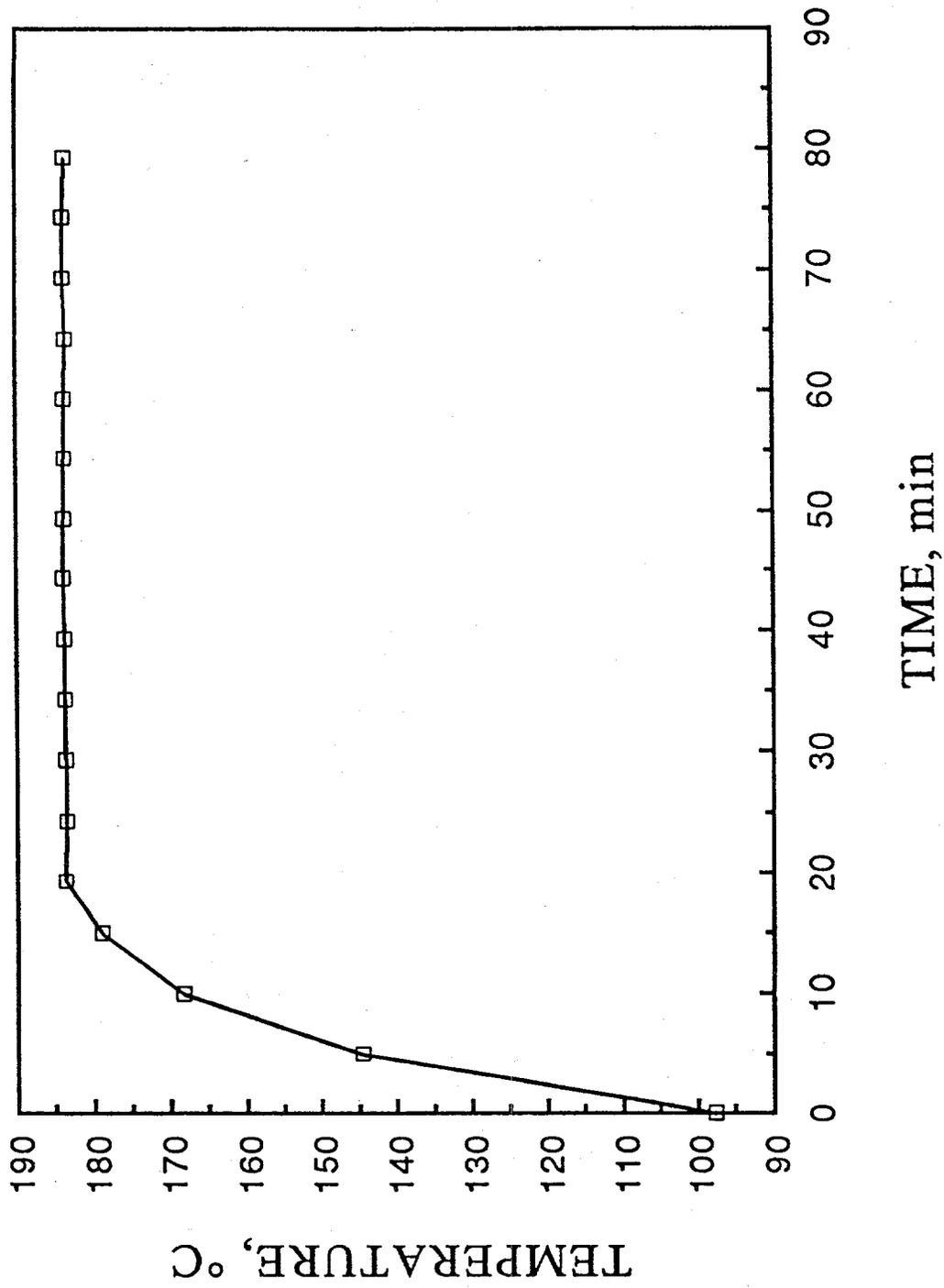


Figure (2): Pulping Time-Temperature Record for Cook ABAFX051.

record. The exact procedure specified by TAPPI was used to determine Kappa number, except that the reaction time during the Kappa test was extended for pulps with Kappa number above about 60, since this yielded more reproducible and possibly more accurate results. H-factor was calculated from the time-temperature record by using the relative rate equation developed by Vroom:

$$H - \text{factor} = \int_0^t \exp[43.2 - 16,113/T] dt \quad (1)$$

where:

T = temperature, °K

t = time, hrs

Yield, based on oven dry wood, as a function of Kappa number for rotational cooks done in this work is given by:

$$Y = 43.41 + 0.1107K + 4.871 \times 10^{-6} K^2 \quad (2)$$

where:

Y = Yield, % of oven dry wood

K = Kappa number

with a correlation coefficient of almost 0.98. Yield vs. Kappa number for circulation cooks done in this work is given by:

$$Y = 41.32 + 0.210K + 2.980 \times 10^{-6} K^2 \quad (3)$$

with a correlation coefficient of 0.92. There are two points concerning these results. The lower correlation coefficient for the circulation cooks is thought to

result primarily from the much broader range of cooking variables used; however, some of the difference is probably attributable to less control of the uniformity of chips used in the circulation cooks. Also, the results show that circulation affects the rate of cooking, particularly in the early stages. Therefore, one could expect this to affect the liquor solids composition and properties of liquors supposedly made at the same pulping conditions.

The data for circulation and rotational cooking have been fitted by the following equations for circulation and rotational cooking respectively:

$$Y = 118.3 - 2.315[\log_e H][EA]^{0.438} [S]^{0.06} \quad (4)$$

and:

$$Y = 112.5 - 3.135[\log_e H][EA]^{0.316} [S]^{0.056} \quad (5)$$

where:

H	=	H-factor
EA	=	effective alkali
S	=	sulfidity

with correlation coefficients of 0.998+. Similarly, Kappa numbers for circulation and rotational cooking have been fitted by the following equations for circulation and rotational cooking respectively:

$$K = 303.8 - 6.53[\log_e H][EA]^{0.492} [S]^{0.11} \quad (6)$$

and:

Figure 3 Statistics for Kappa Number Correlation with Pulping Conditions for Circulation Cooks---Slash Pine

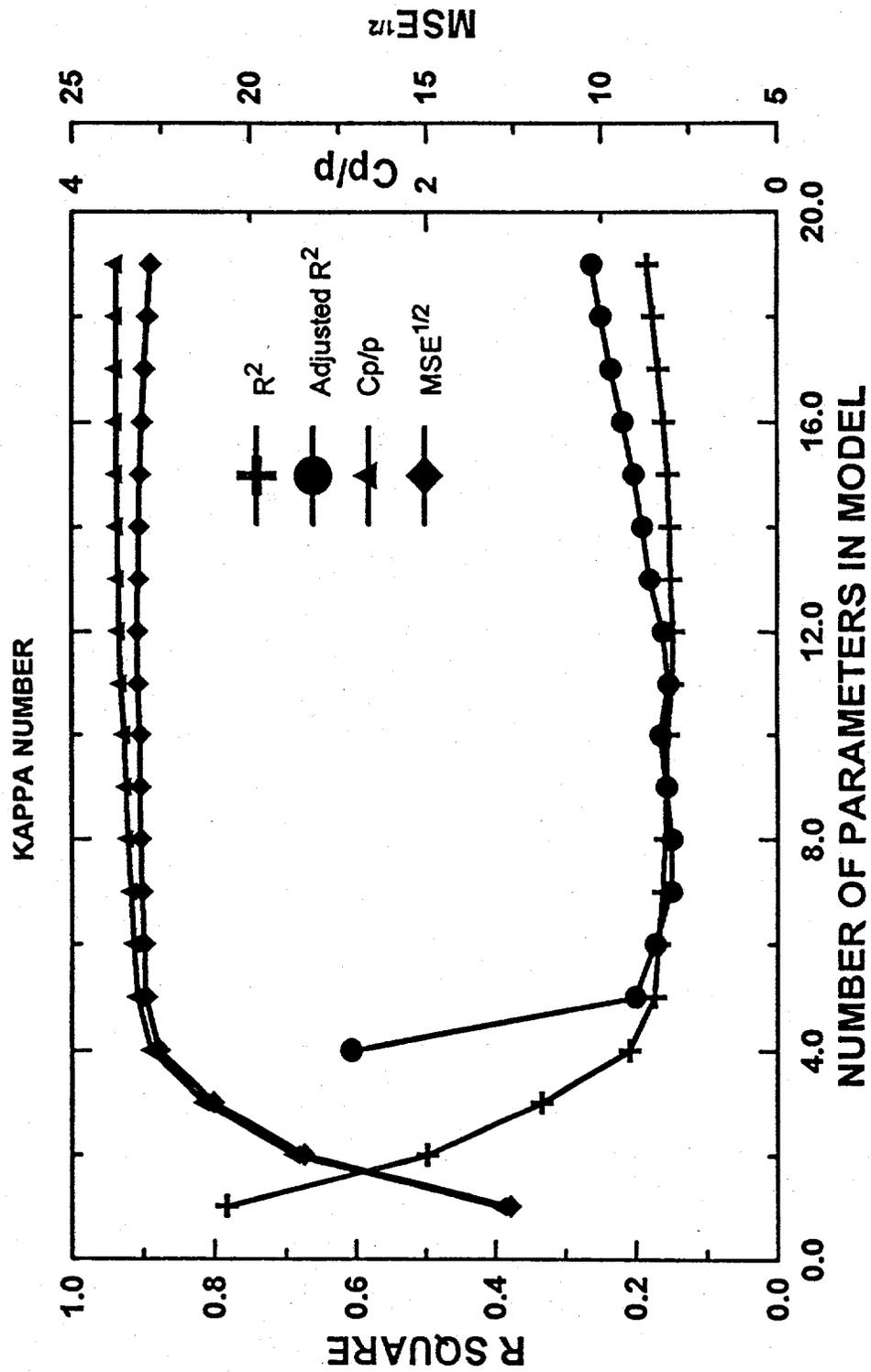
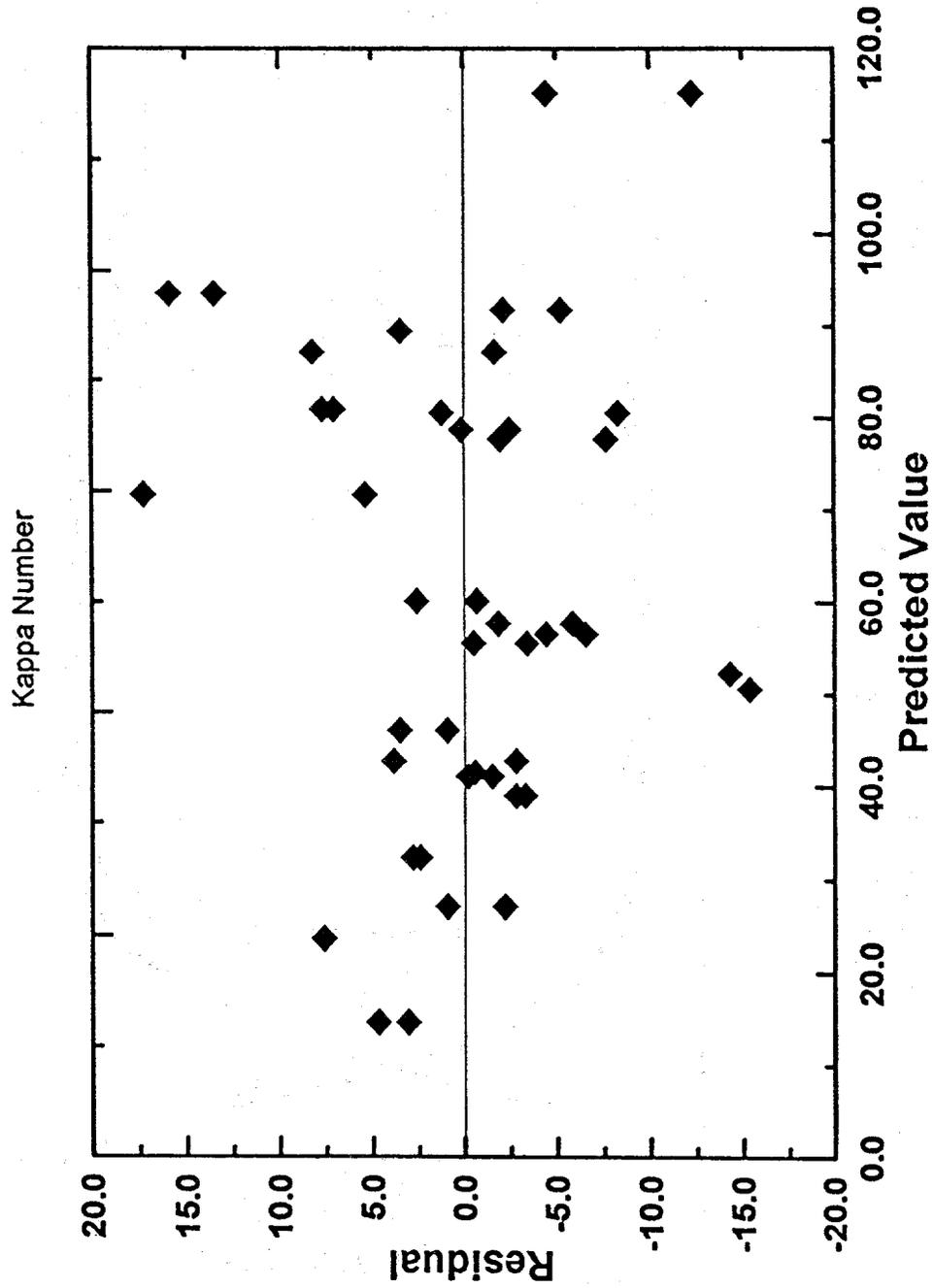


Figure 4 Residuals of Correlation for Kappa Number vs. Cooking Conditions for Circulation Cooking of Slash Pine



$$K = 463.56 - 18.24[\log_e H][EA]^{0.337}[S]^{0.087} \quad (7)$$

with correlation coefficients of 0.991+.

More recently, empirical analyses of results using statistical methods have been used to identify the main variables and interactions. The general form of equation used is:

$$y = a_0 + \sum b_i x_i + \sum c_i x_i^2 + \sum_{i \neq j} d_i x_i x_j + \sum_{i \neq j, \neq k} e_i x_i x_j x_k \quad (8)$$

where:

- y = the response variable
- x_i = cooking variables
- a₀, b_i, c_i, d_i, e_i = regression constants

Statistical tests are applied to obtain the simplest equation that fits the data by dropping terms one at a time until there is a statistical difference between equations. In this manner, the significant responses to cooking variables and cooking variable responses can be identified. This type of procedure is being used on all results of this work. Review of the statistics and residuals is important when data are treated in this manner. Figure 3 shows the statistics plotted as a function of the number of terms (parameters) retained in the model for the response of Kappa number to pulping conditions. It can be seen that the best fit results when 6 to 12 parameters are retained, but that there is little statistical difference for 6 to 12 parameters. Figure 4 shows residuals for a 6 parameter model. These are clearly random. The regression equations can then be used to prepare contour and three-dimensional plots of the response vs. any two selected variables to illustrate trends. An example for Kappa number as a function of

sulfidity and active alkali at 340°F and 60 minutes at temperature is shown in Figure 5. Similar types of analyses are being applied to liquor solids components and to constants developed for properties relations to correlate these to pulping conditions.

Liquor treatment is very important. Figure 6 is a schematic of the path of liquor treatment and handling. Liquor exposure to air is minimized. The liquor is sampled for analysis after filtering, but before evaporation. The final product is stored at 4°C to eliminate or minimize changes with time. Our pilot scale evaporator runs extremely well with a minimum of operator attention. Mill liquors are treated in a similar manner. Liquors are received in drums. The liquor is filtered, sampled and transferred to the evaporator feed tank. Thence, the treatment path is the same as for experimental liquors.

LIQUOR ANALYSIS

The liquors are analyzed as completely as possible. We determine:

1. solids content
2. inorganic positive ions—Na, K, Ca, Mg
3. inorganic negative ions—sulfide, sulfite, thiosulfate, sulfate, carbonate, and chloride
4. organic ions—oxalate, formate, acetate, lactate/glycolate
5. sulfated ash
6. lignin content

These analyses are costly and time consuming. One should note that organic components of molecular weights greater than that for lactates, other than lignin, are not determined. The methods used have been previously reported, but some modifications have been made.

Figure 5 Contour Plots of the Effect of Sulfidity and Effective Alkali on Kappa Number at Constant Cooking Time and Temperature for Circulation Cooking of Slash Pine

KAPPA NUMBER
Time=60 minutes, Temperature=340F

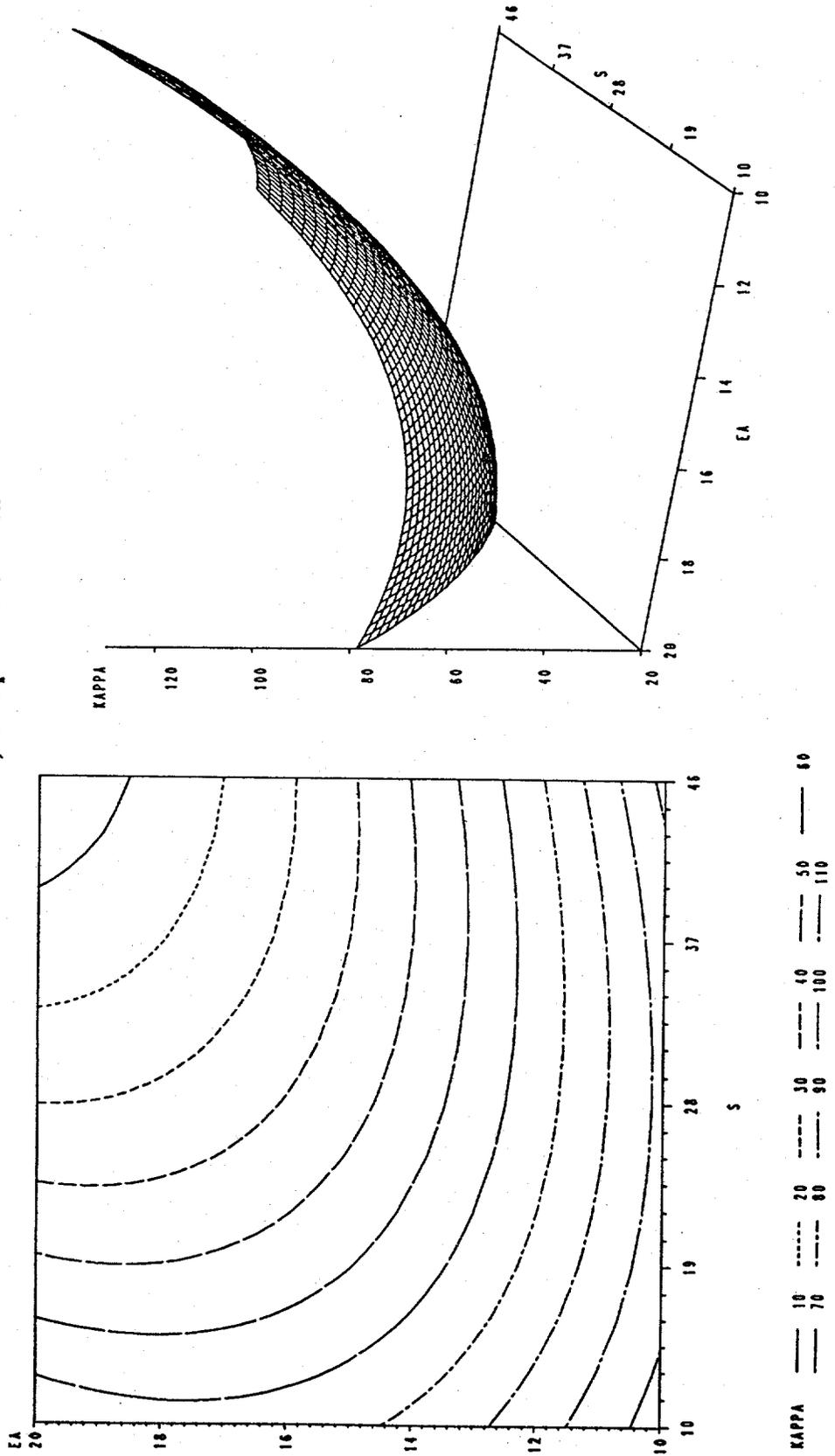
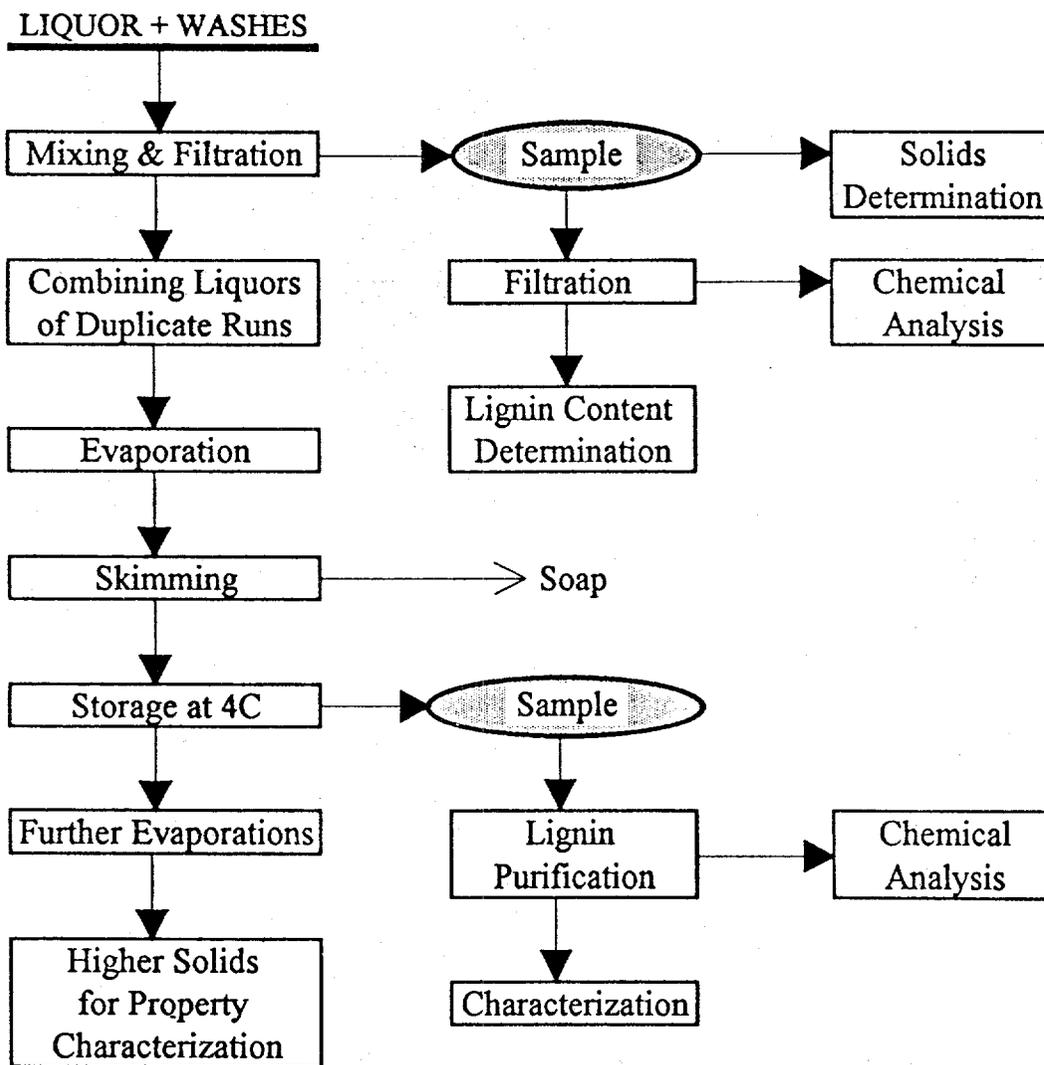


Figure 6 Schematic of Path for Black Liquor Treatment and Handling



Sodium concentration and sulfide ion concentration are determined by ion selective electrode methods that have been found to be more reliable, accurate, and easier than the atomic absorption or ion chromatographic methods used formerly. Details on these procedures will be reported. It is to be suggested that they be adopted as standard methods.

Lignin analysis has received a great deal of attention in this study. Using lignins purified and characterized as described later, the effects of concentration, solution temperature and pH, and lignin molecular weight and source on UV-visible response has been investigated. Figure 7 shows the UV-visible spectra of a purified lignin in NaOH solution and several black liquors with pH adjusted to 13 or higher at 25°C. The softwoods all show a definite plateau at 280 nm, but the hardwood does not. Figure 8 shows the absorbance as a function of lignin concentration in NaOH at two different pH levels. It has been determined that absorbance at 280 nm for hardwood or softwood lignins in NaOH or in black liquors is not affected by pH at levels above 13, that absorbance of lignins at 280 nm is a linear function of lignin concentration, and that absorbance is not affected by lignin molecular weight. Finally, analyses performed periodically over as much as a four day period on the same solution show no effect of time on results. Analysis of lignins in black liquors used in this work have been performed by using this technique and extinction coefficients determined from lignin solutions.

A summary of typical analysis results for four liquors used in this study is given in Table 1. Complete results for analyses of all liquors will be presented in the final report. As discussed earlier, the results are being analyzed to develop the simplest empirical relations between the component in the liquor and the pulping conditions. In all cases, the concentration of the component is expressed as mass fraction or mass percent of liquor solids, not as mass fraction or mass percent of the liquor. Figure 9 shows the effect of number of model parameters for

Figure 7 UV-visible Spectra for Selected Kraft Black Liquors and Purified Softwood Lignin in NaOH Solution

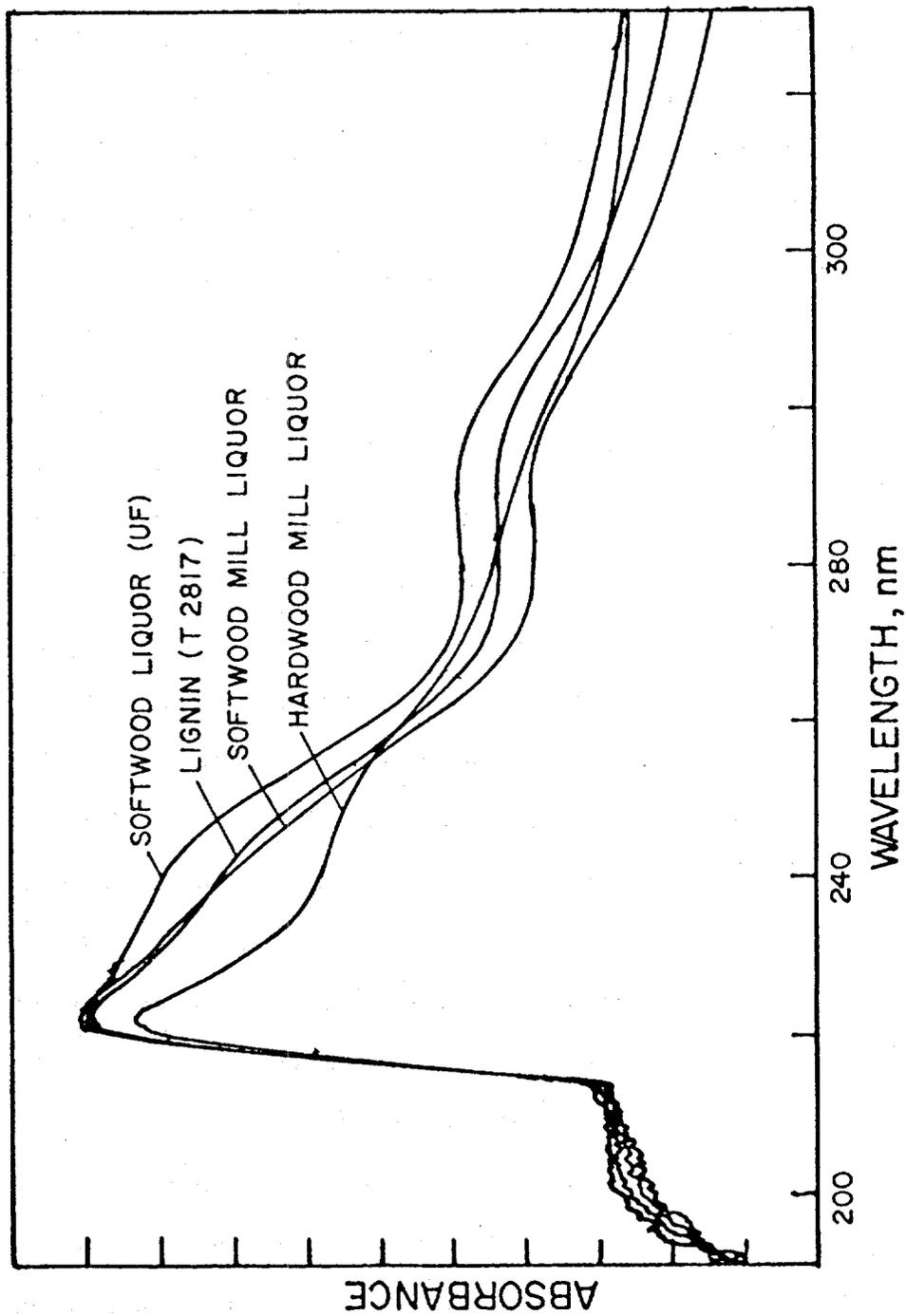


Figure 9 Statistics for Correlations of Lignin Content of Black Liquor from Circulation Cooking of Slash Pine

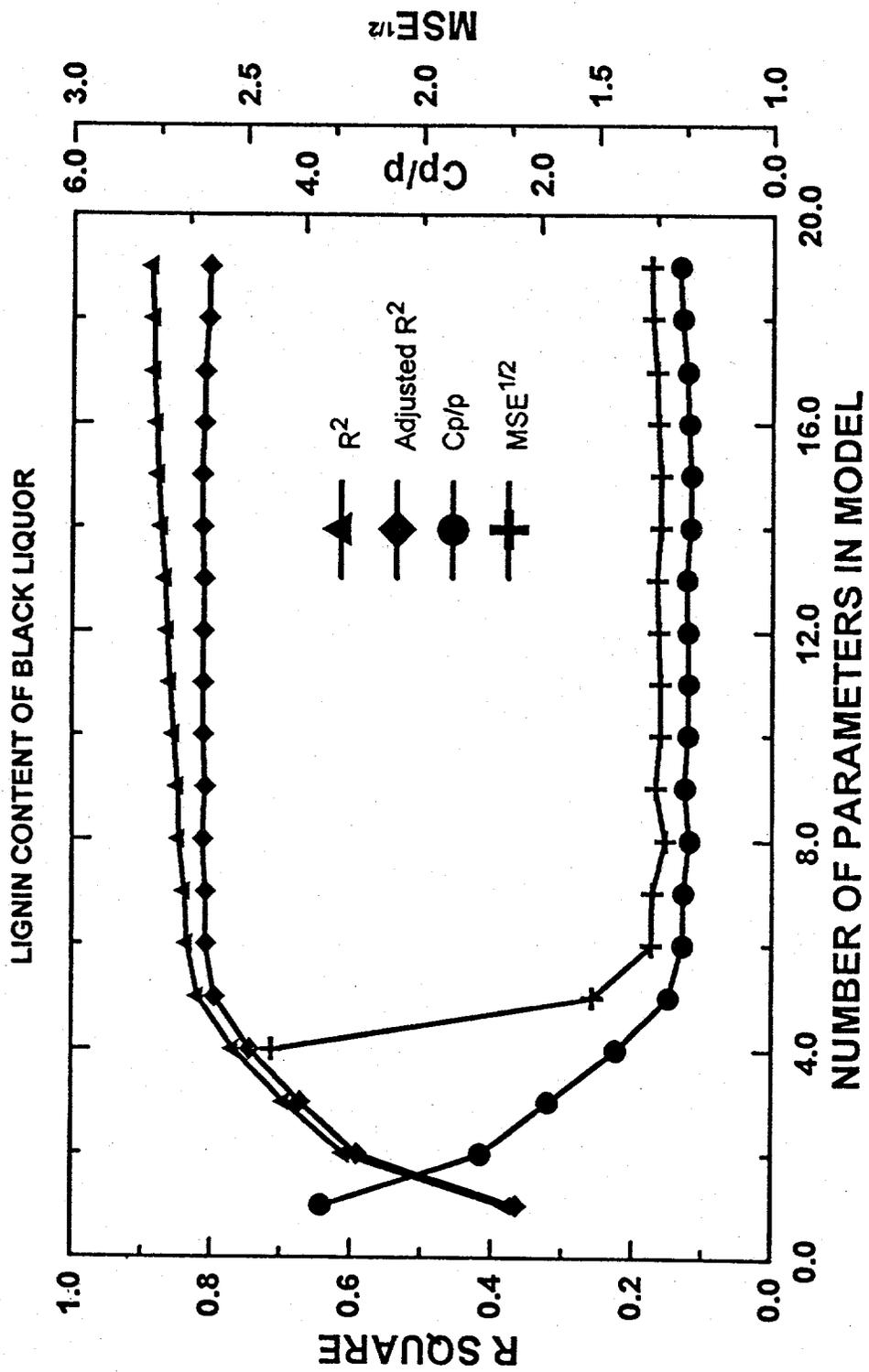
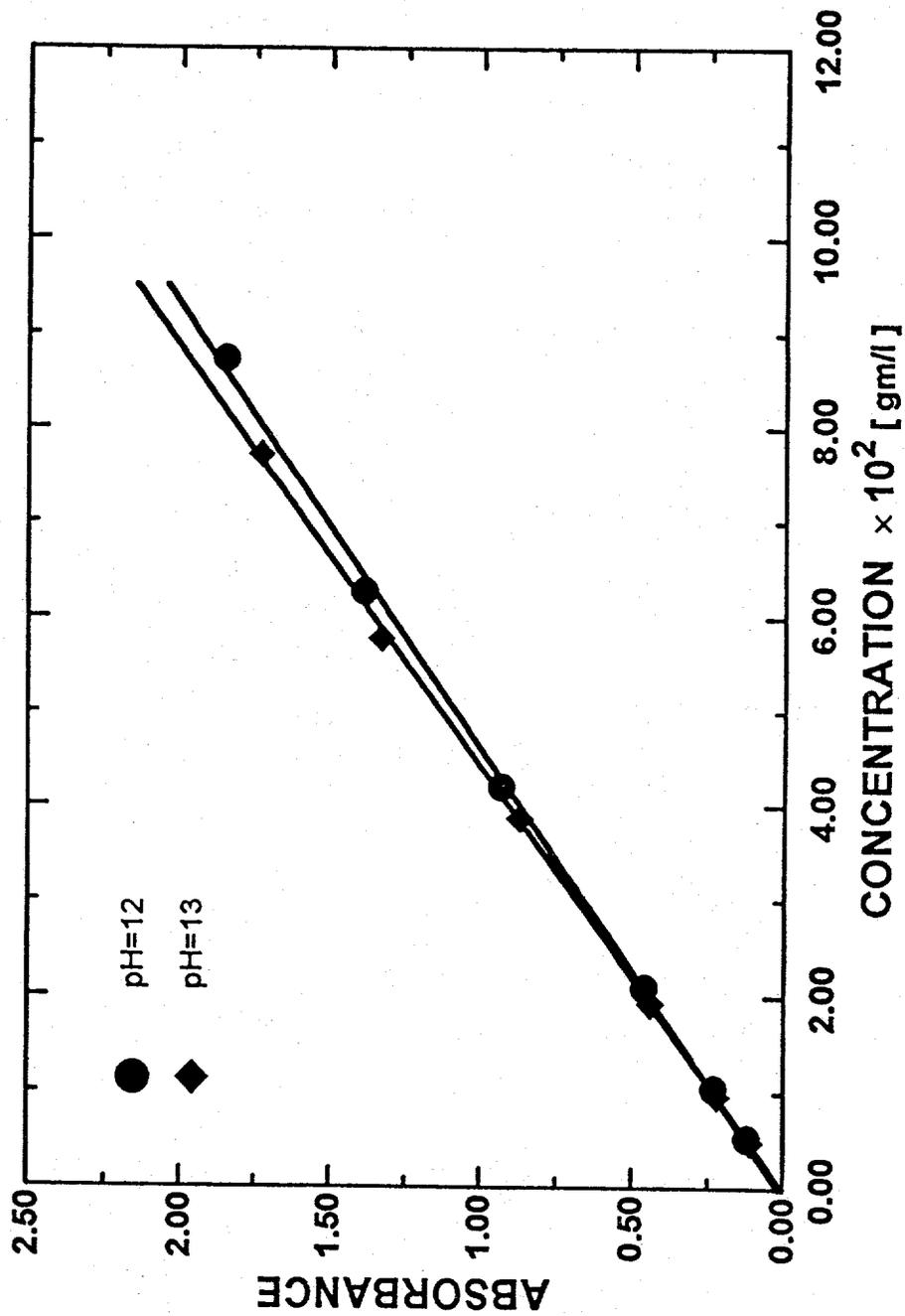


Table 1. Results of Solids Analyses for Selected Liquors.

Components, g/g solids	ABAFX011,12	ABAFX025,26	ABAFX043,44
chloride	2.52×10^{-3}	3.10×10^{-3}	3.47×10^{-3}
sulfite	2.78×10^{-3}	3.15×10^{-3}	2.94×10^{-3}
sulfate	1.42×10^{-2}	2.08×10^{-2}	2.44×10^{-2}
oxalate	6.39×10^{-3}	5.18×10^{-3}	6.22×10^{-3}
thiosulfate	3.28×10^{-2}	6.32×10^{-2}	4.70×10^{-2}
carbonate	2.89×10^{-2}	6.56×10^{-2}	6.02×10^{-2}
lactate/glycolate	6.58×10^{-2}	9.41×10^{-2}	8.06×10^{-2}
formate	6.96×10^{-2}	7.77×10^{-2}	7.08×10^{-2}
acetate	5.19×10^{-2}	4.94×10^{-2}	5.49×10^{-2}
sodium, pre-evap	0.152	0.207	0.153
sodium, post-evap	0.209	0.218	0.21
sulfide, pre-evap	4.85×10^{-3}	2.27×10^{-2}	1.87×10^{-2}
lignin	0.35	0.3928	0.4178
calcium	1.88×10^{-3}	1.81×10^{-3}	2.22×10^{-3}
magnesium	6.73×10^{-4}	6.33×10^{-3}	7.77×10^{-4}
potassium	1.15×10^{-3}	6.85×10^{-4}	7.17×10^{-4}
sulfated ash %NaOH	31.6	36.1	33.2
PH	12.59	12.98	12.83
organic-to-inorganic ratio	2.12	2.051	2.227

Figure 8 UV-visible Absorbance of Softwood Kraft Lignin at 280nm in NaOH Solutions at pH 12 and pH 13.



correlating lignin content on statistical measurements. The best fit is obtained with models containing 6 to about 14 parameters. With these results, contour and three dimensional plots of lignin content of black liquor solids as a function of two pulping conditions can be prepared. Figure 10 is such a plot for lignin content as a function of effective alkali and sulfidity at constant temperature and time. Figure 11 is a plot of lignin content as a function of time and temperature at constant effective alkali and sulfidity.

All analyses that are to be performed have been completed on all of the liquors to be included in this study.

LIGNIN CHARACTERIZATION

The characterization of the lignin in black liquor is very important for our properties studies, and we have devoted a great deal of research effort to developing methods as well as to applying these methods for characterization, since prior studies were not very definitive. Polymer characterization of the lignin that is acid precipitable, the high molecular weight portion, has been extensive. The lignin is isolated from the black liquor and purified as much as possible by the sequence shown in Figure 12. The purified lignin sample is then analyzed for inorganic ion and low molecular weight organic ion content by the same methods used for black liquors. The fraction of the lignin contained in the black liquor that is recovered as purified lignin is 59 to 69% of the lignin. The unrecovered lignin appears to be very low molecular weight degradation products.

Vapor pressure osmometry (VPO) is used to determine the apparent number average molecular weight (M_n) of the purified lignins. The standard condition used is lignin dissolved in DMF at 80°C. The instrument constant is determined using monodisperse polymers of known molecular weight or high molecular weight compounds of high purity dissolved in DMF. Figure 13 shows

Figure 10 Contour Plots of the Effect of Sulfidity and Effective Alkali on Lignin Content of Black Liquor at Constant Cooking Time and Temperature for Circulation Cooking of Slash Pine

LIGNIN CONTENT OF BLACK LIQUOR

Time=60 minutes, Temperature=340F

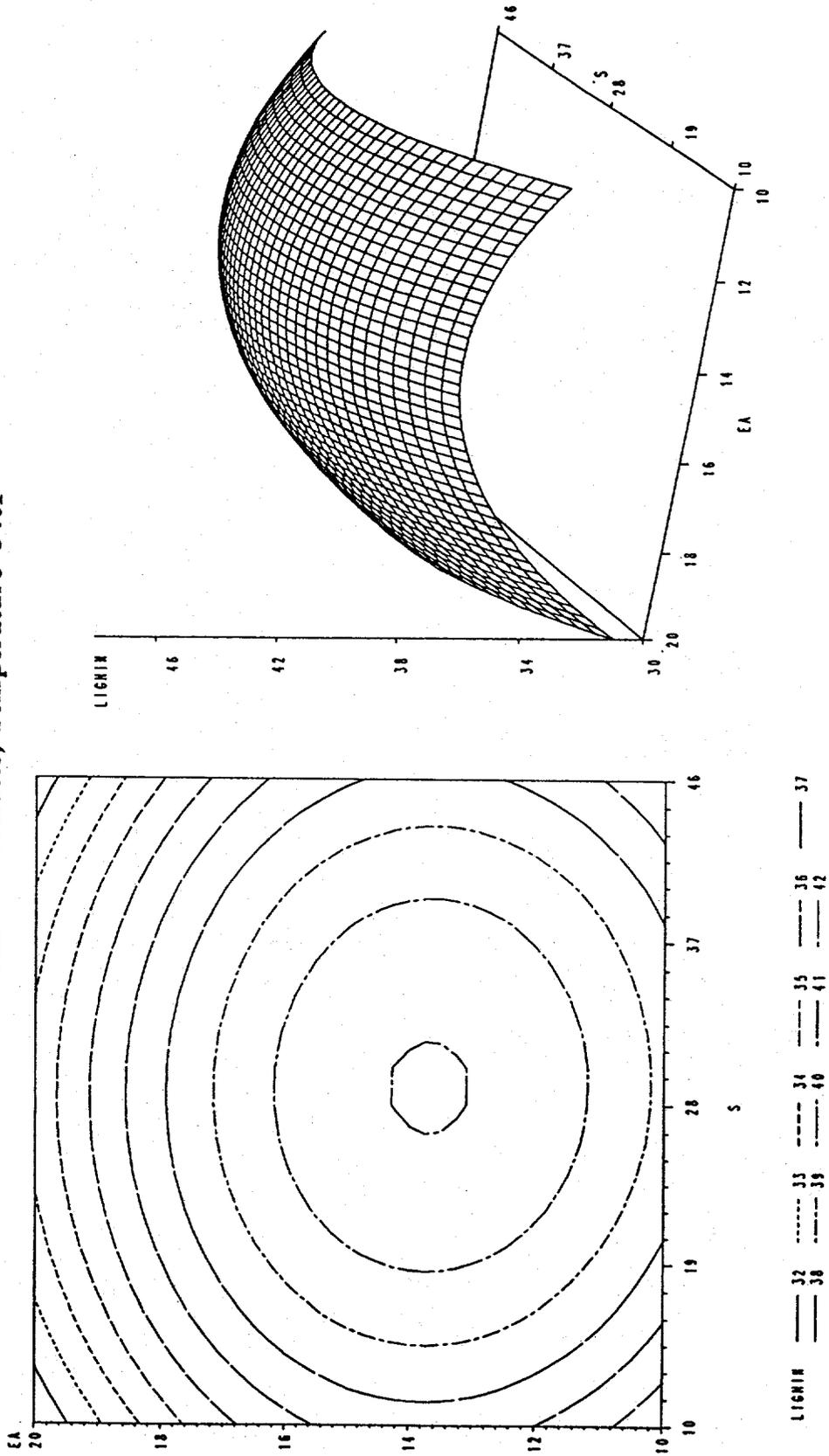


Figure 11 Contour Plots of the Effects of the Cooking Time and Temperature on the Lignin Content of Black Liquor at constant Effective Alkali and Sulfidity for Circulation Cooking of Slash Pine

LIGNIN CONTENT OF BLACK LIQUOR
 Effective Alkali=14.5%, Sulfidity=27.5%

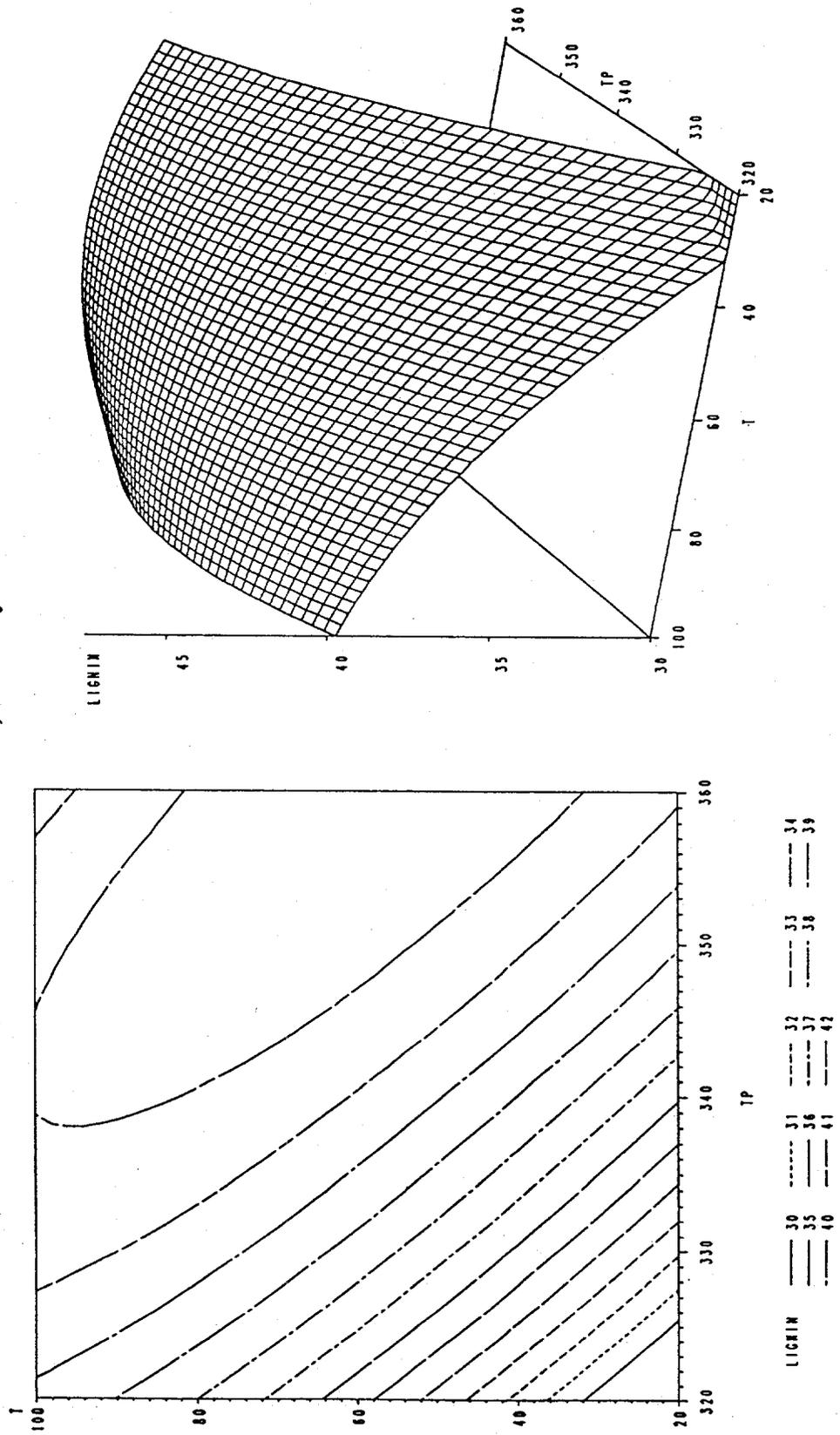


Figure 12 Sequence for Purification and Preparation of Kraft Lignin

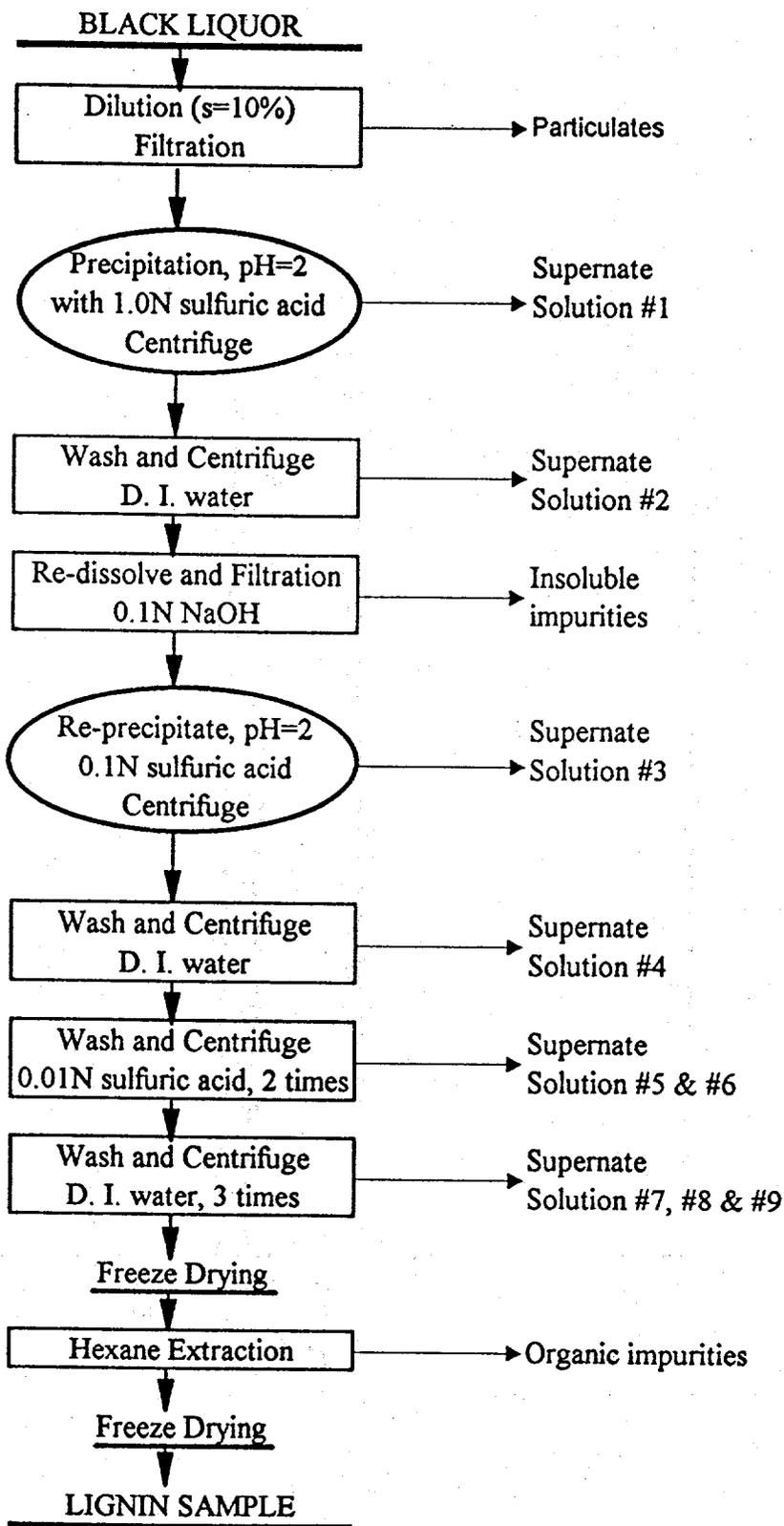
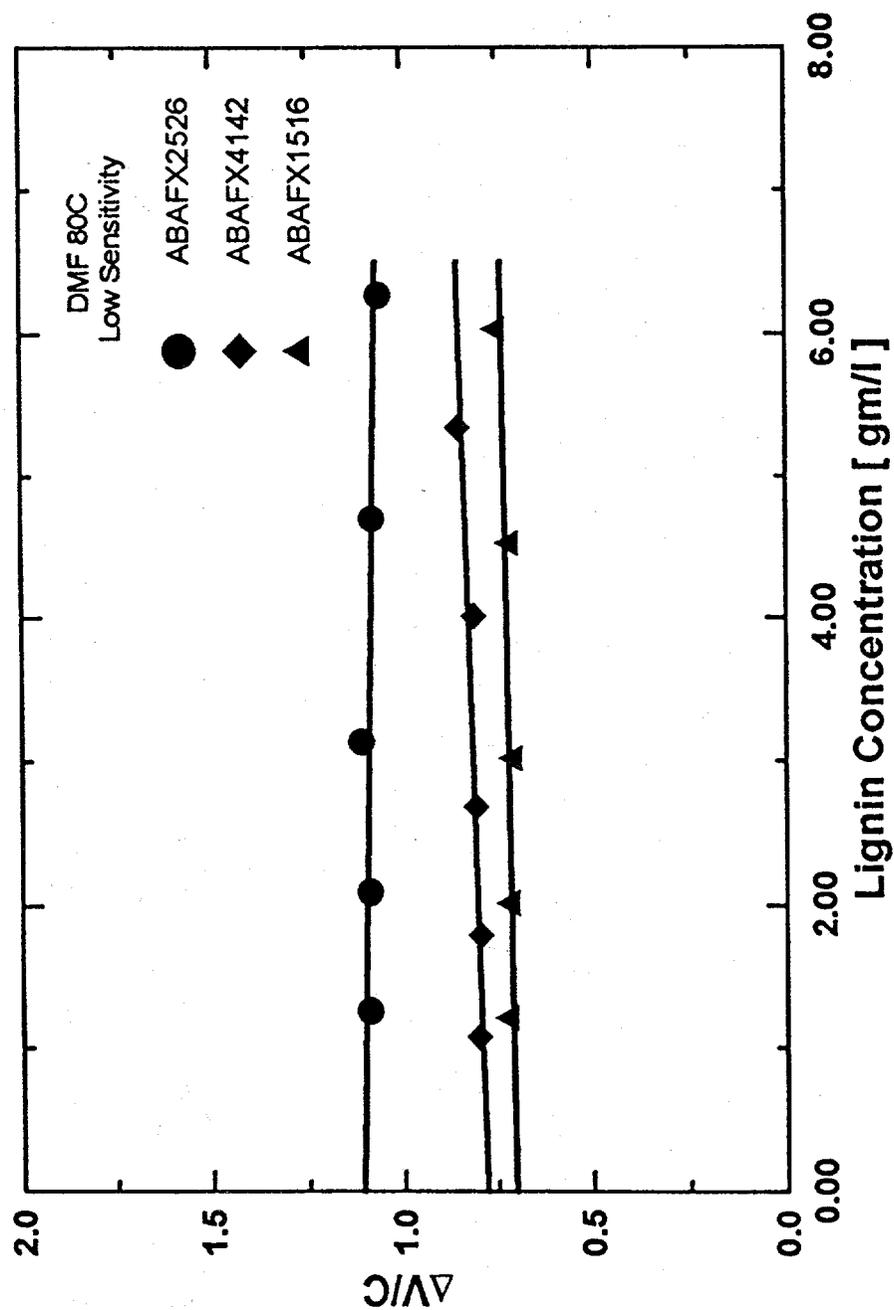


Figure 13 Typical VPO Results for Kraft Lignins from Circulation Cooks of Slash Pine



VPO results for three lignins. The M_n values are corrected to account for impurities contained in the lignins. M_n values have been determined for all lignins. Regression analyses have been performed to relate M_n to pulping conditions. Figure 14 is a contour plot of M_n as a function of effective alkali and sulfidity at constant temperature and time, which is an example of results of these analyses.

Weight average molecular weight (M_w) analysis by light scattering has received even more attention. We have performed analyses in different solvents in order to demonstrate that the molecular weights determined are true values of M_w , and to determine the effects of different optical effects. DMF, pyridine, and 0.1 N NaOH have been used at conditions known to be at or above the theta condition for lignin polymer.

Figure 15 shows the refractive index difference as a function of lignin concentration for the three solvents at a wave length of 6328 Å. The relations are all linear and well defined.

At a wave length of 6328 Å, lignin shows fluorescence, polarization, and absorption effects. The relative impact of these effects is illustrated in Figure 16, which shows Rayleigh factor vs. concentration for one lignin with different corrections applied for a measurement in DMF at 80°C. The large difference between the relation as normally measured (apparent) and as fully corrected is substantial.

Figure 17 shows refractive index difference vs. concentration for different lignins of various molecular weights obtained from liquors from circulation and rotational digestion. Relations for DMF and 0.1 N NaOH solutions are shown. For lignin from one wood species, it is obvious that neither the process variation nor lignin molecular weight affects these relations. Similar checks of the effects on fluorescence, absorption, and polarization have been made.

Figure 14 Contour Plots of the Effects of Sulfidity and Effective Alkali on Lignin Number Average Molecular Weight at Constant Cooking Time and Temperature for Circulation Cooking of Slash Pine

NUMBER AVERAGE MOLECULAR WEIGHT OF LIGNIN
 Time=60 minutes, Temperature=340F

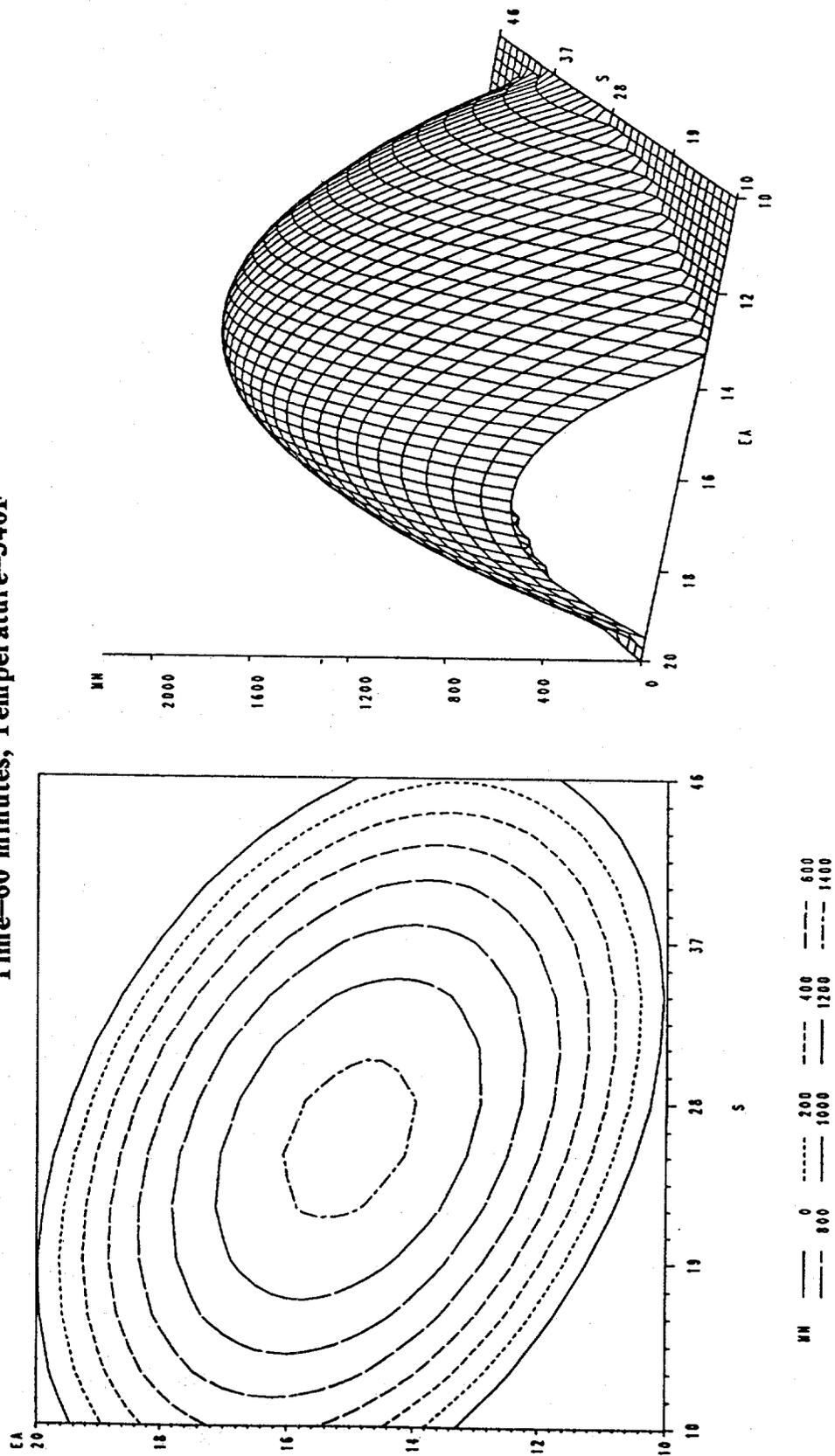


Figure 15 Refractive Index Difference at 632.8nm for Slash Pine Lignin in Different Solvents

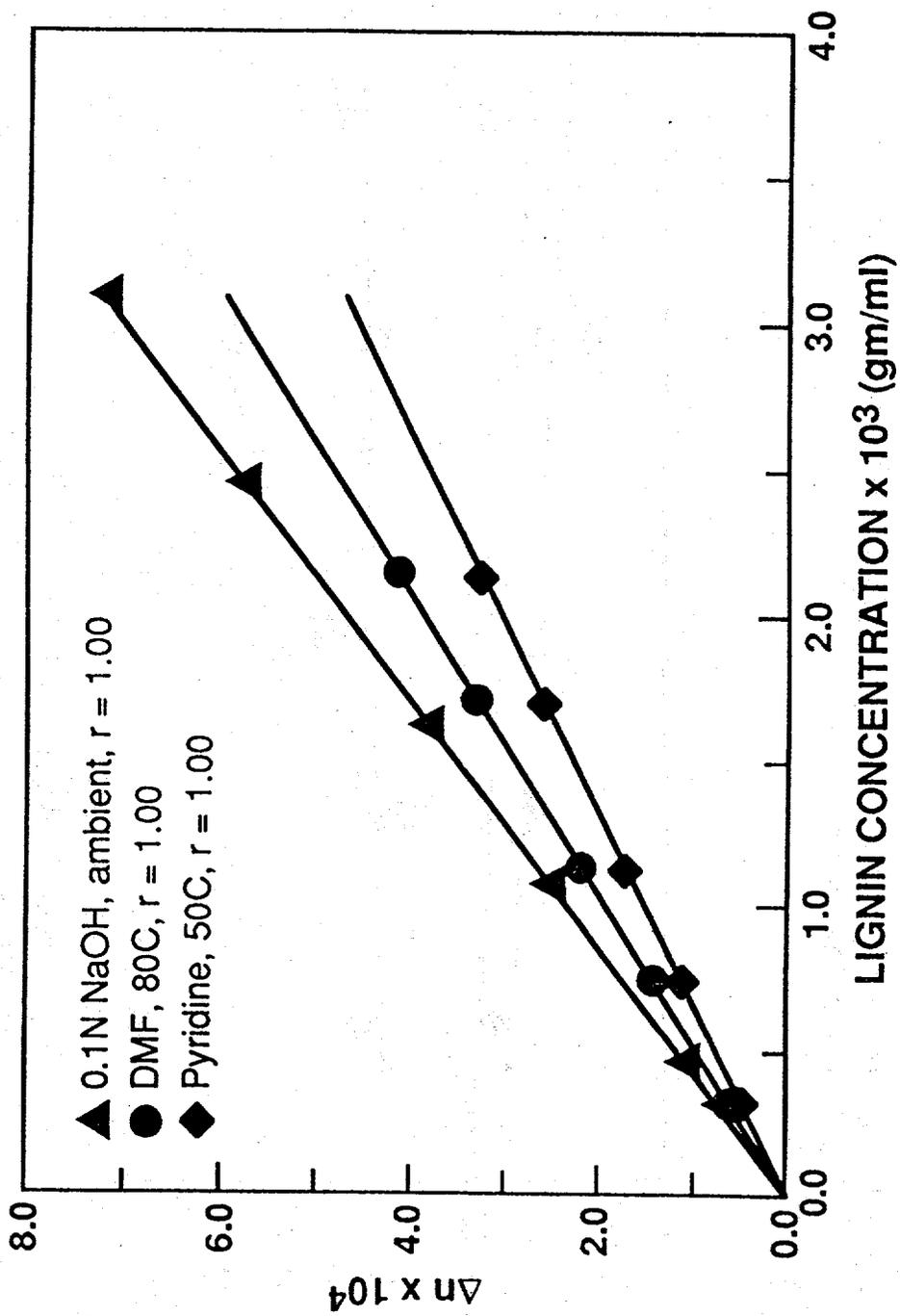


Figure 16 Apparent and Corrected Low Angle Light Scattering Plots for a Softwood Lignin in DMF at 80C

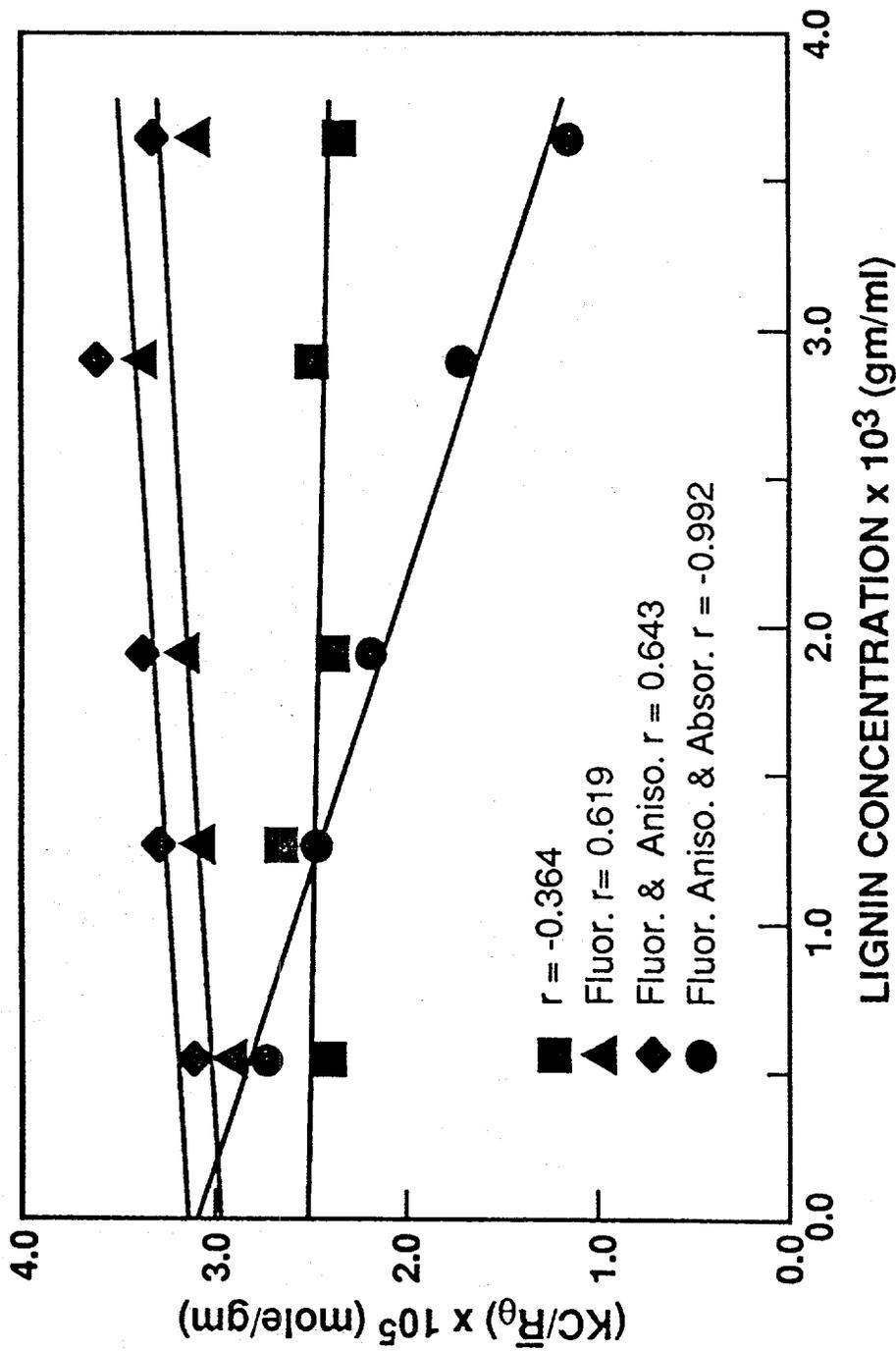


Figure 17 Refractive Index Difference for Slash Pine Lignins of Different Molecular Weight at 632.8nm in Different Solvents

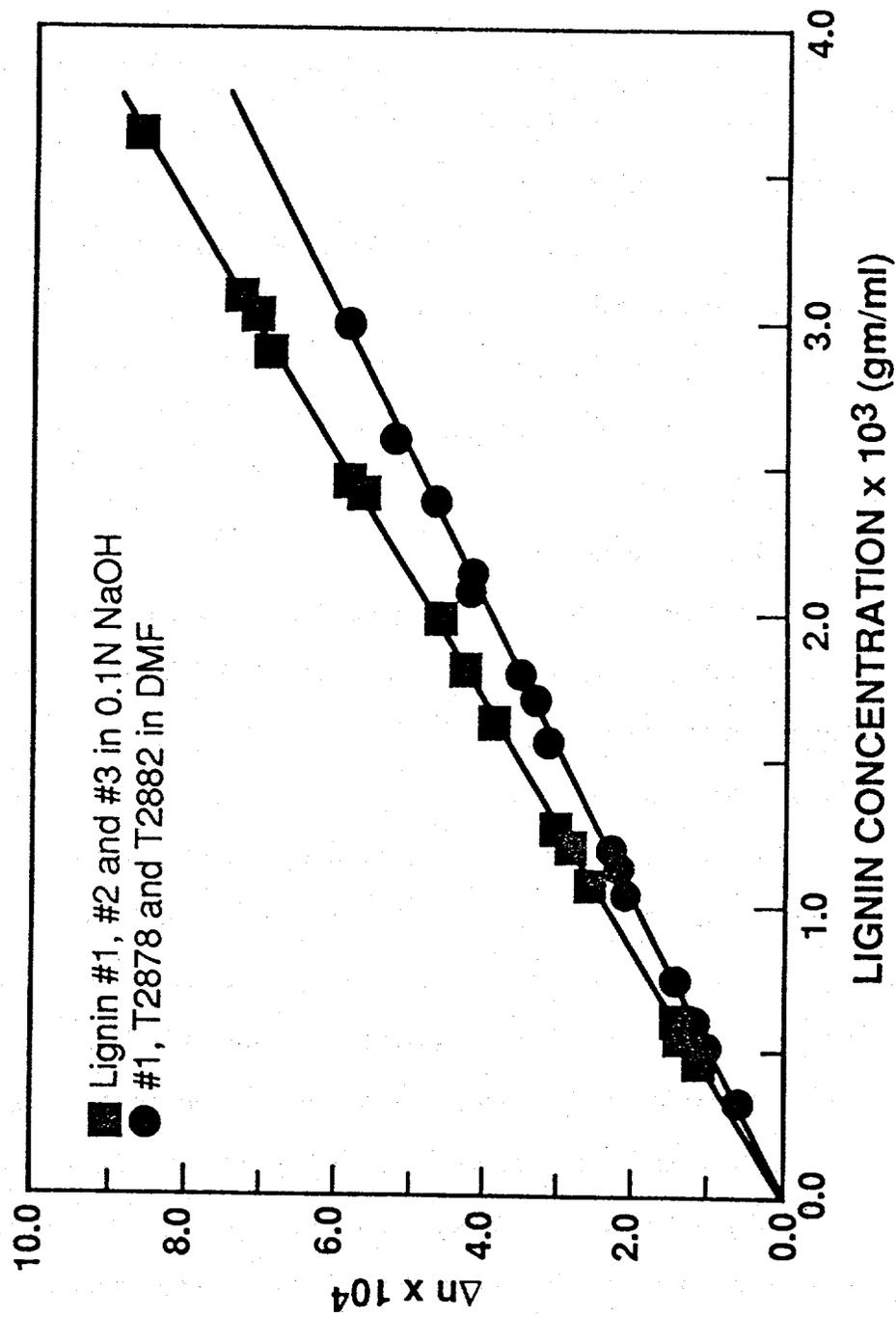


Figure 18 shows the variation of Cabannes factor with lignin concentration for the different solutions. The Cabannes factor is a quantitative measure of the light polarization by the solution for light scattering. It is worth noting that nearly all of the polarization is due to the organic solvents; there is virtually no polarization in 0.1 N NaOH solution. Figure 19 shows that the effect is virtually independent of lignin molecular weight; it is primarily an effect produced by polymer-solvent interaction.

A single M_w determination has required four sets of measurements as a function of concentration. These are:

1. light absorption
2. refractive index difference
3. polarization
4. fluorescence

Studies of these have now shown that absorption, refractive index difference, and polarization can be determined for one lignin-solvent pair and the results used for determinations for other lignins derived from the same source. This is a considerable reduction of work.

Theoretically, M_w values determined for the same lignin in different solvents should be identical, if there are no experimental artifacts. This test has been performed a number of times using three solvents. Values of M_w determined for a lignin in three solvents agree within 10% or less. Considering the complexities of the determination, we believe that this is very good confirmation that M_w determined for lignin by light scattering is correct.

Figure 20 shows light scattering results for lignins from several of our experimental softwood liquors and for a lignin obtained from a mill black liquor from pulping sugar maple. M_w is the reciprocal of the intercept. It is worth

Figure 18 Cabannes Factors for Softwood Kraft Lignin in Different Solvents for Scattering at 632.8nm

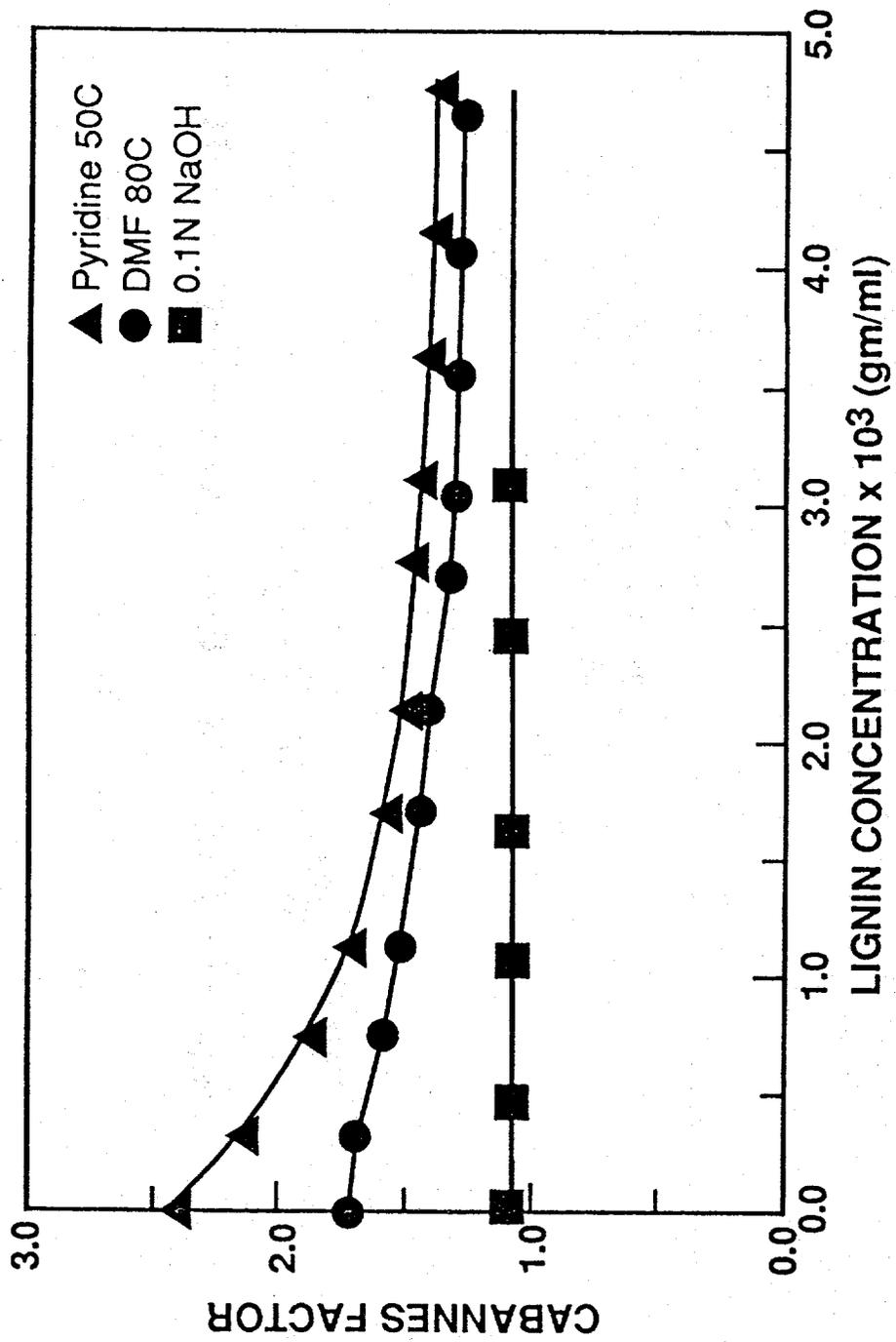


Figure 19 Cabannes Factors for Softwood Kraft Lignins of Different Molecular Weights in Different Solvents for Scattering at 632.8nm

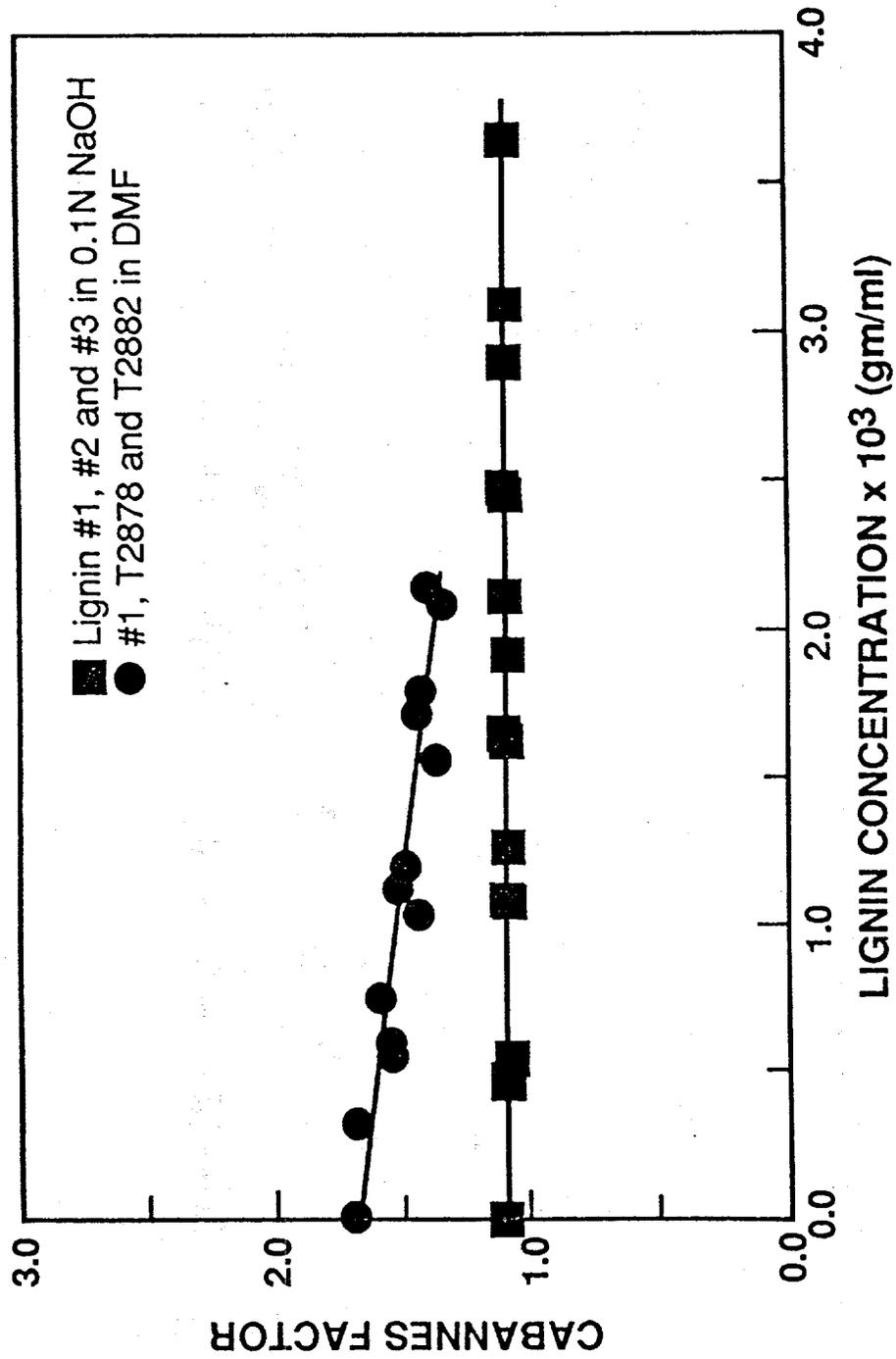
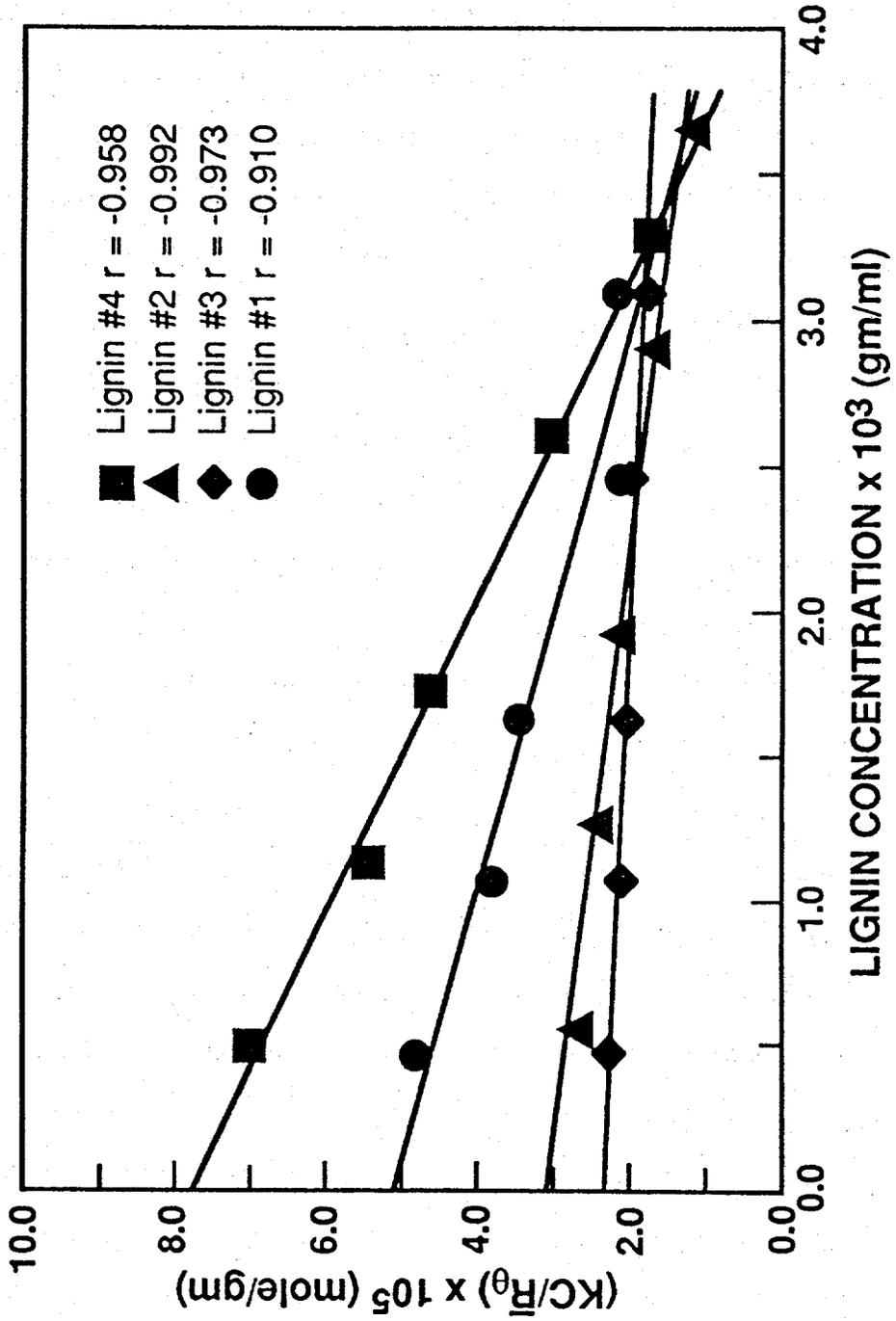


Figure 20 Corrected Light Scattering Curves for Three Softwood and One Hardwood Kraft Lignins



noting that M_w for the sugar maple lignin is much lower than M_w for the softwood lignins shown.

Regression analyses have been performed to relate M_w to pulping conditions, and the empirical relations developed can be used for preparing contour plots. Figure 21 is a contour plot of M_w as a function of effective alkali and sulfidity at constant time and temperature. Figure 22 is a contour plot of M_w as a function of time and temperature at constant effective alkali and sulfidity. The implications of the effects shown in these plots on such properties as viscosity is immediately obvious to a rheologist.

Molecular weight dispersion, as expressed by the M_w/M_n ratio, is also of interest. Regression of this quantity has been performed, and the contour plots shown in Figures 23 and 24 are examples of results. The dispersion varies considerably and shows differences in functional shape, depending upon the pulping variables considered.

High performance liquid chromatography at high temperature has also been studied. Almost eighty different combinations of temperature, solvent, column packings, and detectors were tried. Most failed, usually because of lack of reproducibility. The study illustrated that most work on molecular weight distribution (MWD) of lignin by gel permeation chromatography is erroneous. Three systems were found that were stable and gave reproducible size exclusion results. One of these, however, was demonstrated not to be able to partition the lignin by molecular weight sufficiently to be useful. The other two show that lignin recovered from black liquors exhibits a low molecular weight tail and is probably bimodal. However, when the columns were calibrated with any of a number of polymer standards, the values of M_w calculated from GPC results did not agree with light scattering results. The values differed often by a factor of ten. Lignin is obviously a very compact molecular that behaves much differently than

Figure 21 Contour Plots of the Effects of Sulfidity and Effective Alkali on Lignin Weight Average Molecular Weight at Constant Cooking Time and Temperature for Circulation Cooking of Slash Pine

WEIGHT AVERAGE MOLECULAR WEIGHT OF LIGNIN
 Time=60 minutes, Temperature=340F

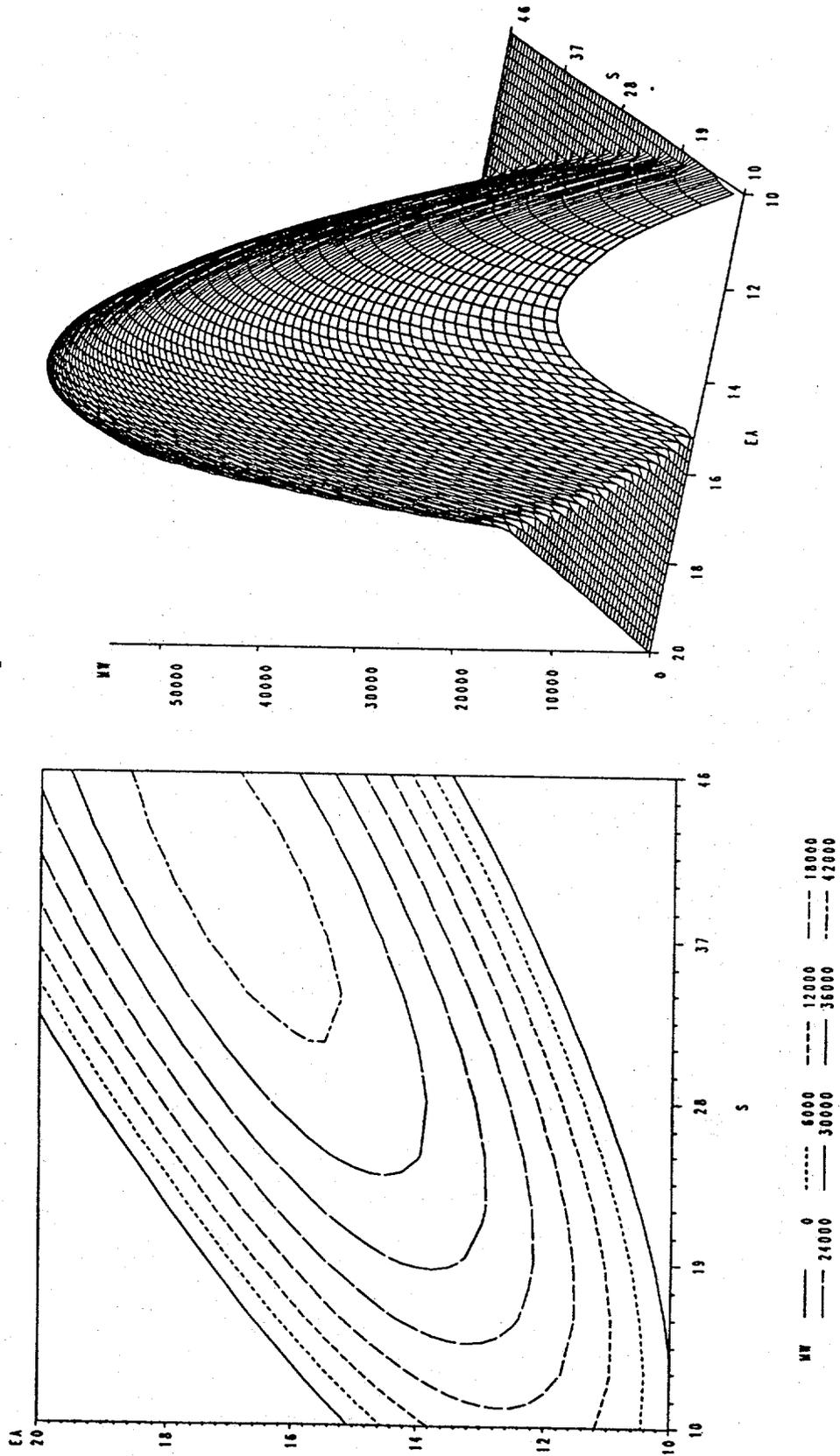


Figure 22 Contour Plots of the Effects of the Cooking Time and Temperature on Lignin Weight Average Molecular Weight at Constant Effective Alkali and Sulfidity for Circulation Cooking of Slash Pine

WEIGHT AVERAGE MOLECULAR WEIGHT OF LIGNIN
 Effective Alkali=14.5%, Sulfidity=27.5%

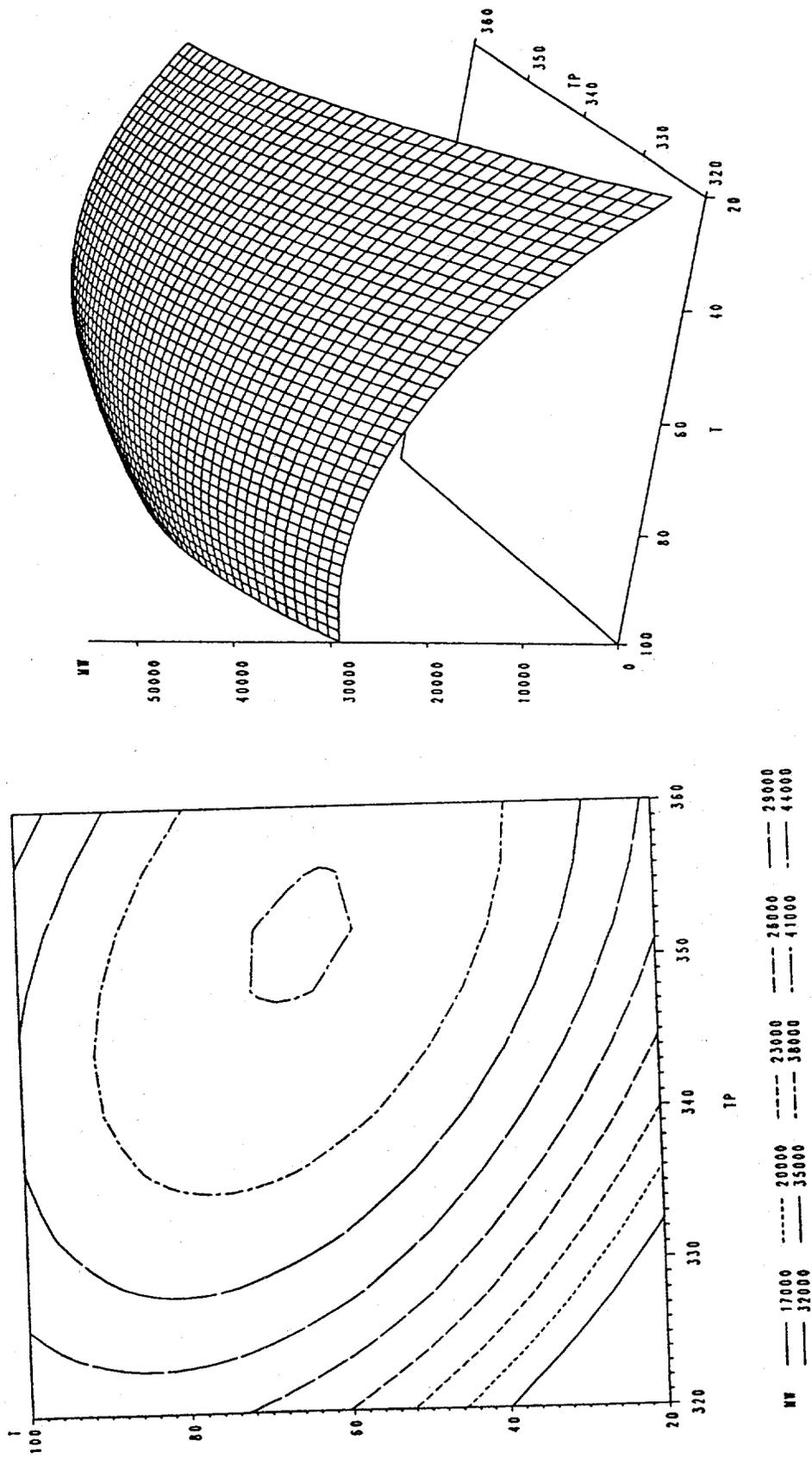


Figure 23 Contour Plots of the Effects of the Cooking Time and Temperature on the Mw/Mn Ratio of Lignin at constant Effective Alkali and Sulfidity for Circulation Cooking of Slash Pine

Mw/Mn RATIO OF LIGNIN
 Effective Alkali=14.5%, Sulfidity=27.5%

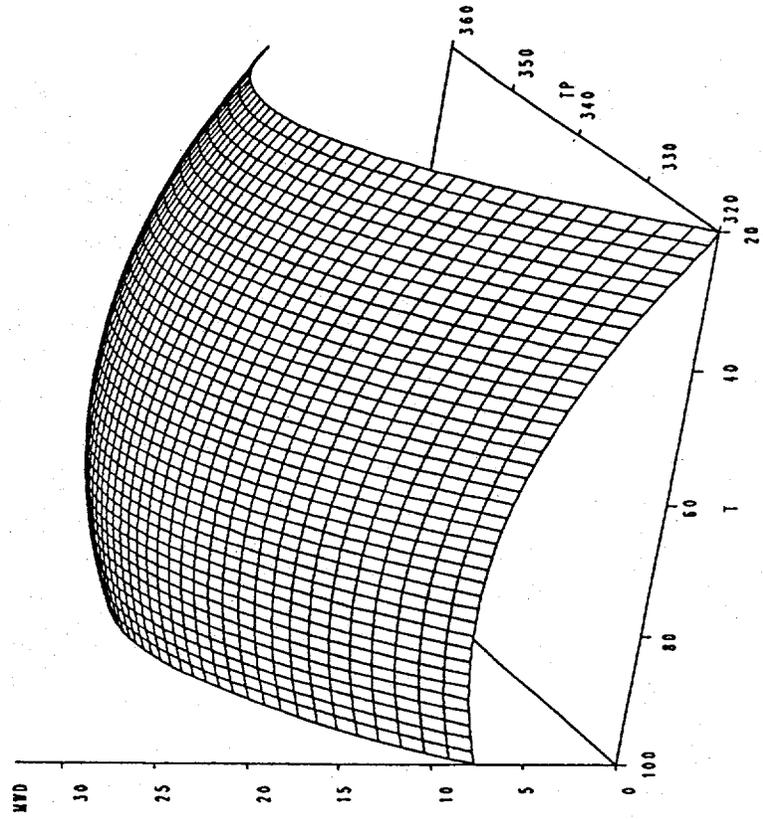
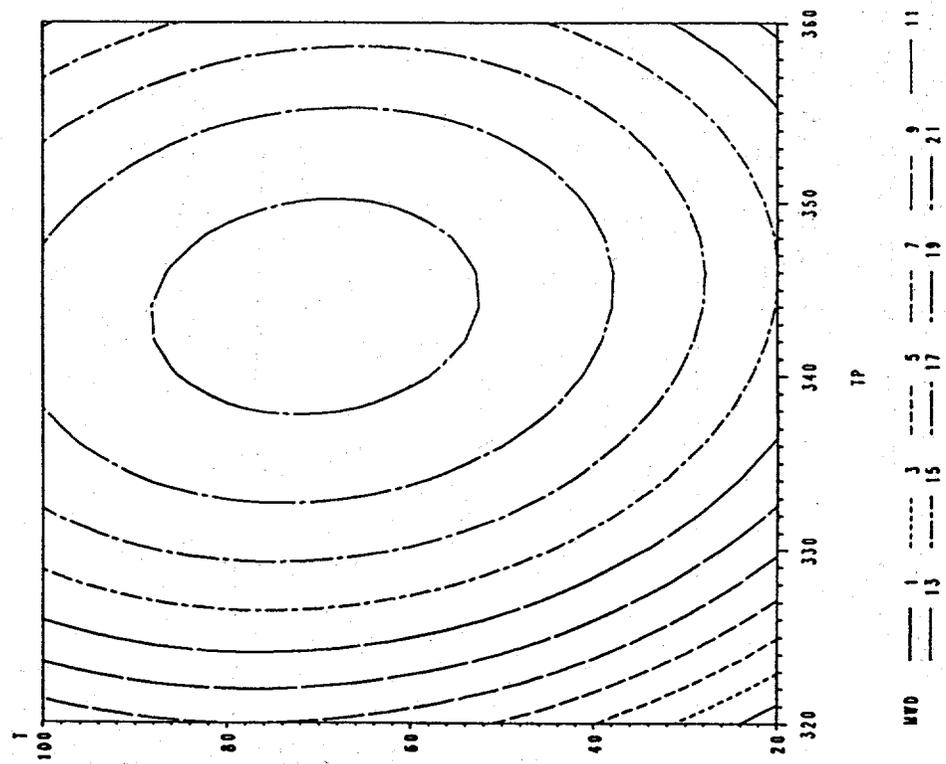
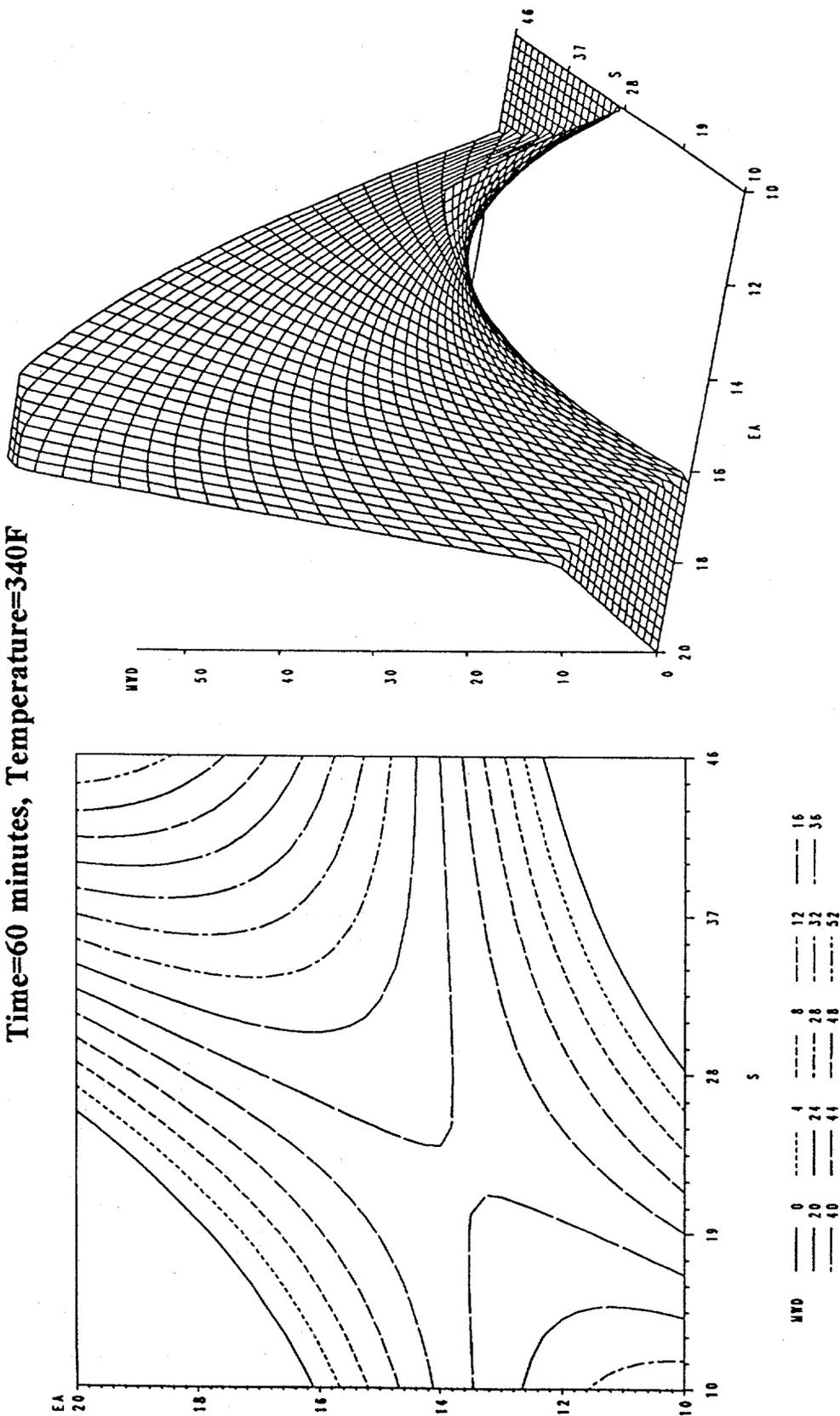


Figure 24 Contour Plot of the Effects of Sulfidity and Effective Alkali on Lignin Mw/Mn Ratio at constant Cooking Time and Temperature for Circulation Cooking of Slash Pine

Mw/Mn RATIO OF LIGNIN
Time=60 minutes, Temperature=340F



any calibration polymer now available. We are now using M_n and M_w results from light scattering and VPO to attempt to calibrate the GPC results by method of moments resolution. This work is in progress.

Except for method of moments analyses of the GPC results, all work on lignin characterization for liquors used in this program has been completed.

VAPOR PRESSURE EQUILIBRIA

A direct method has been developed to determine boiling temperatures of black liquors as a function of solids concentration and pressure at up to 85% solids. The apparatus has been described in an earlier progress summary. Boiling temperatures can be determined at pressures ranging from 125 to 760 mm Hg pressure. The apparatus can be operated in either of two ways. The pressure can be held constant while the liquor is slowly concentrated at a constant, low rate of evaporation. The condensate is collected in an accumulator mounted on an electronic balance. The liquid temperature in the still is continuously recorded. The concentration in the still at any time can be calculated by material balance. Thus, a curve of boiling point vs. solids concentration at constant pressure can be determined. Alternatively, the liquor can be concentrated to the desired concentration at low pressure and a moderate evaporation rate, and then the apparatus can be operated with total reflux at a low constant rate of evaporation. The pressure is increased stepwise to a new pressure, steady state is established, and the boiling temperature recorded. This is repeated a number of times to determine the vapor pressure-temperature relation for the liquor at constant solids concentration. The procedure is repeated at different concentrations to determine the effect of solids concentration.

The second procedure described is the procedure used most frequently. Not only does this procedure involve less high temperature exposure of the liquor,

but it is useful in also providing samples at high solids concentration for other experimental work with a minimum loss of experimental liquor. Using this procedure, we have determined the vapor pressure equilibria for our experimental liquors and for some mill liquors. All show similar characteristics. Only typical results will be presented here.

Figure 25 shows results for an experimental liquor made from slash pine, along with the vapor pressure for water. The equation:

$$\ell n P = a + b/T + c/T^2 \quad (9)$$

where:

- P = absolute pressure
- T = absolute temperature
- a,b,c = constants

fits the data extremely well. Since there is virtually no curvature over this range, c is extremely small and can be ignored. Therefore, the simple expression:

$$\ell n P = a + b/T \quad (10)$$

can be used to represent the data. Also, the lines for vapor pressure at various solids concentrations are very nearly parallel, indicating that the heat of vaporization of water from black liquor is constant. Even though the data are limited to sub-atmospheric pressure, the data can be extrapolated to 2-3 atmospheres with reasonable accuracy.

Figure 26 shows the boiling point elevation as a function of solids at two pressures, as determined from the data presented in Figure 25. This behavior is

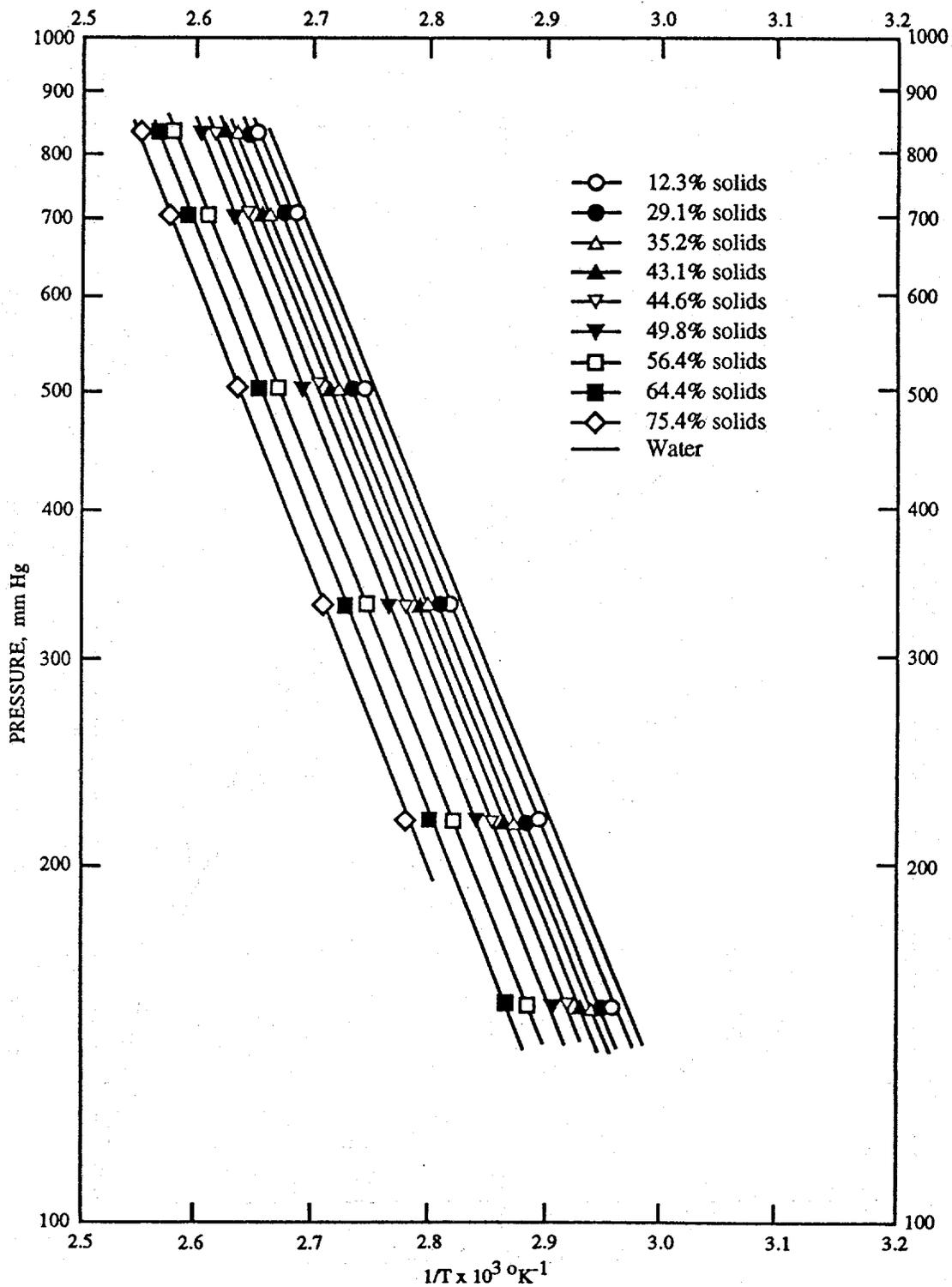


FIGURE 25. Vapor Pressure Equilibria for slash Pine Draft Black Liquor

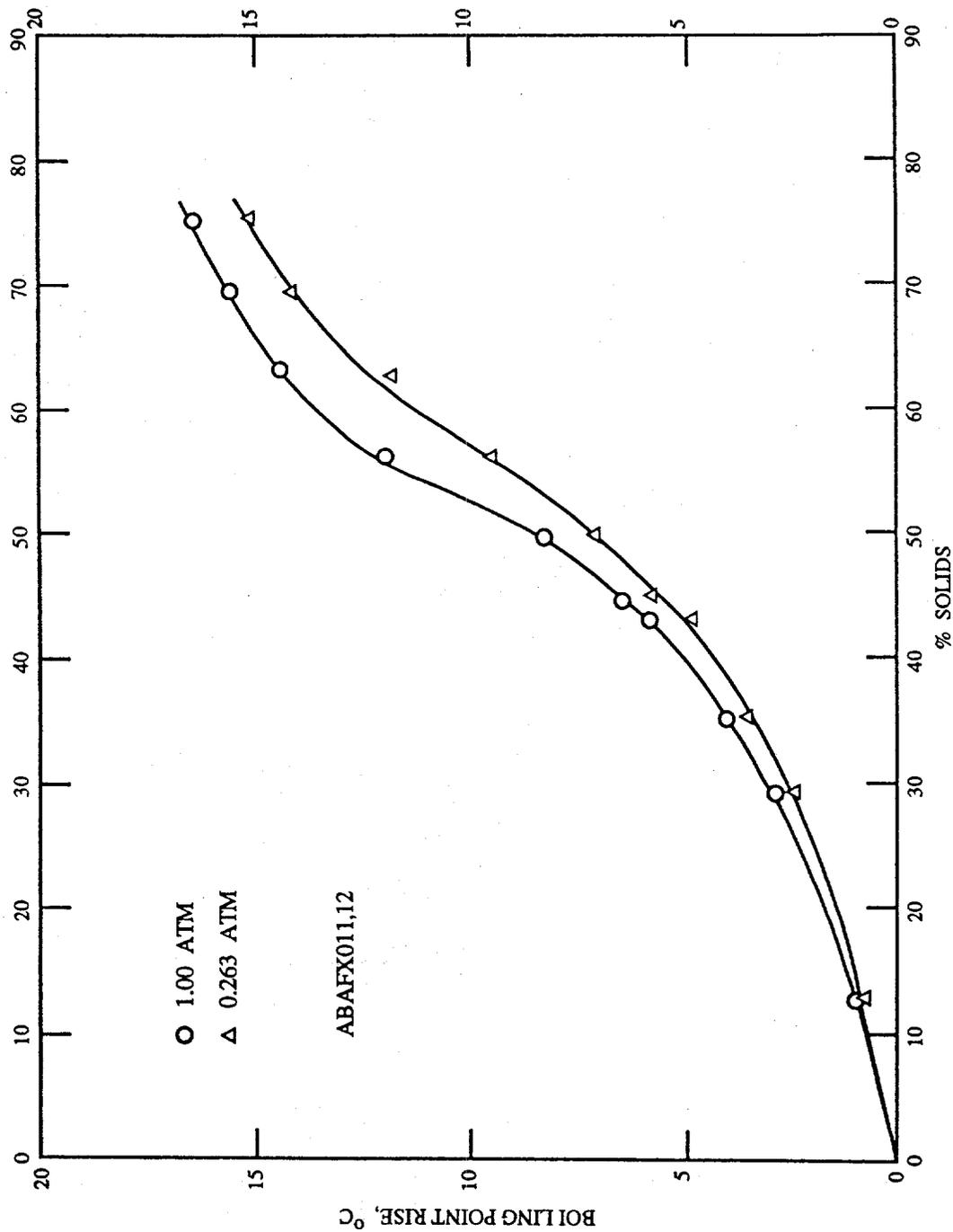


FIGURE 26. Effect of Pressure and Solids Concentration on Boiling Point Elevation of a Slash Pine Kraft Black Liquor

typical for softwood liquors. Figure 27 shows the boiling point elevation for this liquor presented as a Duhring plot.

There are variations in boiling point elevation from liquor to liquor, even for liquors originating from the same species, at solids concentrations above about 20-25% solids. However, the general behavior has been the same for all liquors.

Data reduction is a problem. Data at constant solids for any liquor can be fitted exactly by equation (9) as expected, and can be fitted nearly as well by equation (10). Results from application of equation (10) to the data show that the constant, b , in equation (10) is virtually the same at all solids concentrations for one liquor, and varies only slightly from liquor to liquor. Therefore, only the constant, a , in equation (10) varies significantly with solids concentration and from liquor to liquor. The relation between the constant, a , and the solids concentration is an S shaped function, and we have no theoretical basis for reducing this function. Thus, we have to describe this relation as a power series as:

$$a = \sum_{i=0}^n d_i s^i \quad (11)$$

where:

- a = constant for equation (10)
- d_i = empirical constants
- s = solids concentration

The constants, d_i , are functions of the pulping conditions or liquor composition only. We are searching for a simple expression to relate the constant, a , to solids concentration.

The work on vapor pressure equilibria of black liquors that we have done is the most comprehensive available to date and appears to be the most reliable.

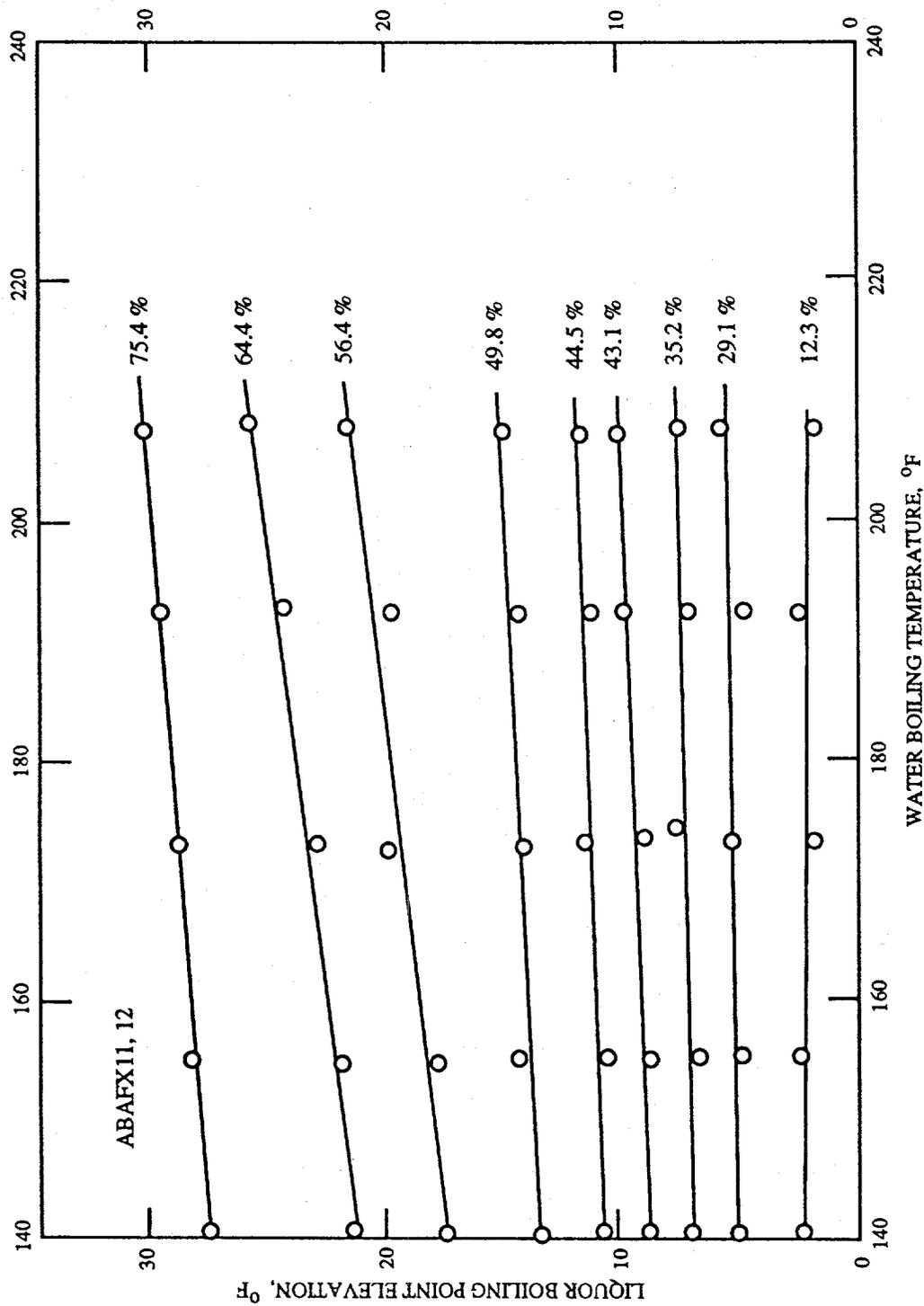


FIGURE 27. Duhring Plot of Boiling Point Elevation of a Slash Pine Kraft Black Liquor

In future work, we believe that vapor pressure equilibria for a liquor could be determined with about 25% of the effort that we have commonly used to this point.

HEATS OF COMBUSTION

Heats of combustion have been determined for all black liquors by using a Parr Automatic Combustion Calorimeter. Heats of combustion have been determined for 100% black liquor solids where the samples for combustion have been obtained by freeze drying black liquor rather than evaporating to constant weight in a vacuum oven as is normally done. As we have reported earlier, drying to constant weight in a vacuum oven to obtain a 100% solids sample appears to lead to results that are dependent upon drying history. Freeze drying does not. Therefore, we have used freeze drying to obtain 100% solids black liquor samples for combustion, heat capacity, and density studies.

Heats of combustion have been determined for all black liquor samples at 65% solids as well as at 100% solids to check that heats of combustion at other solids concentrations could be predicted from data for 100% solids. For one of the liquors, heat of combustion has been determined as a function of solids from 62% to 100% solids.

Regression analyses of the data are being performed. The empirical relation between heat of combustion and pulping conditions appears to be relatively simple; however, pulping conditions do have a large effect on heat of combustion. Figure 28 is a contour plot of the effect of sulfidity and effective alkali on heat of combustion at constant cooking time and temperature. Figure 29 is a contour plot of the effect of cooking time and temperature on heat of combustion at constant effective alkali and sulfidity. Further work is in progress to relate heat of combustion to solids composition.

Figure 28. Contour Plot of the Effects of Sulfidity and Effective Alkali on Heat of Combustion of Black Liquor Solids at Constant Cooking Time and Temperature for Circulation Cooking of Slash Pine

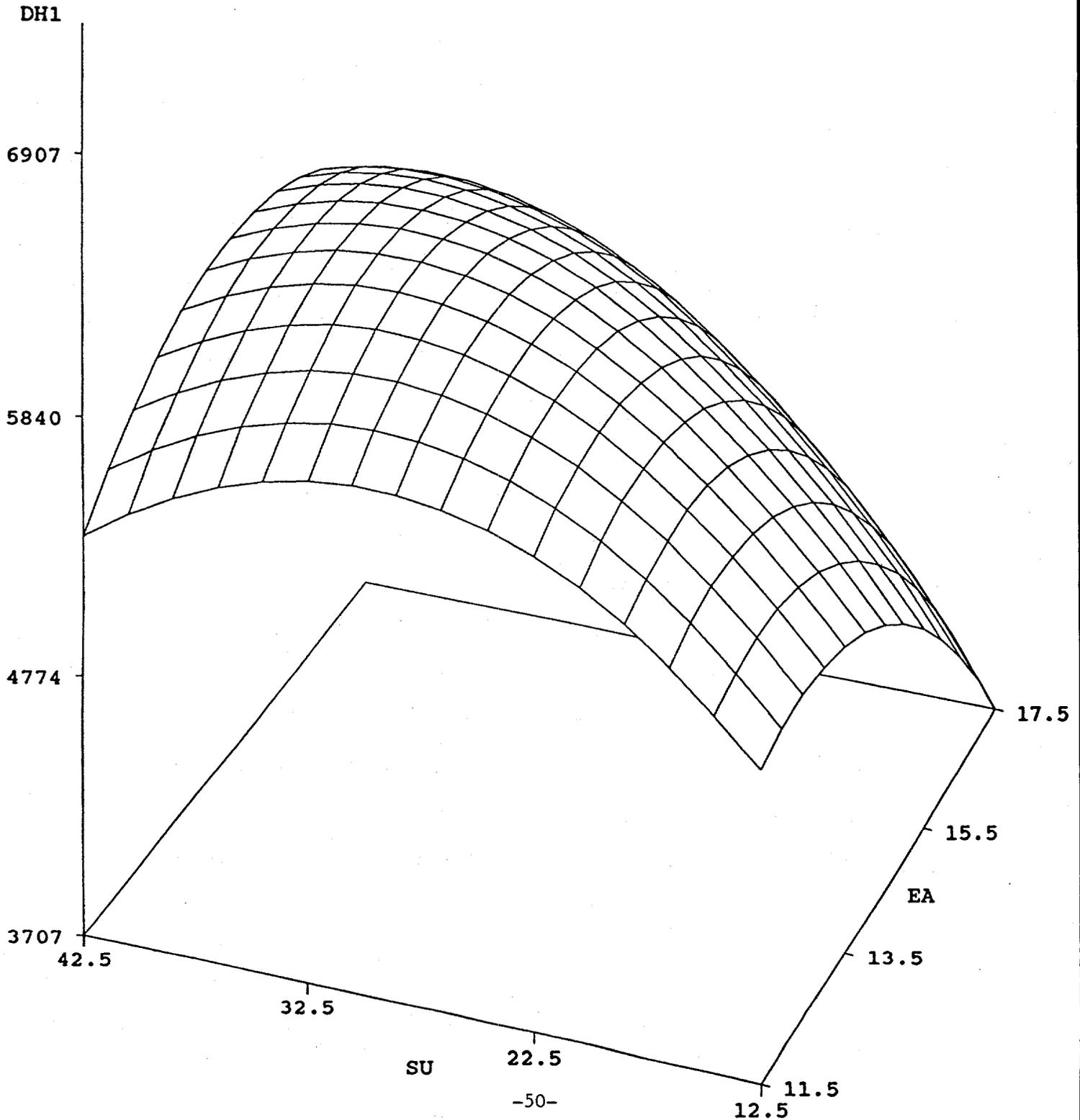
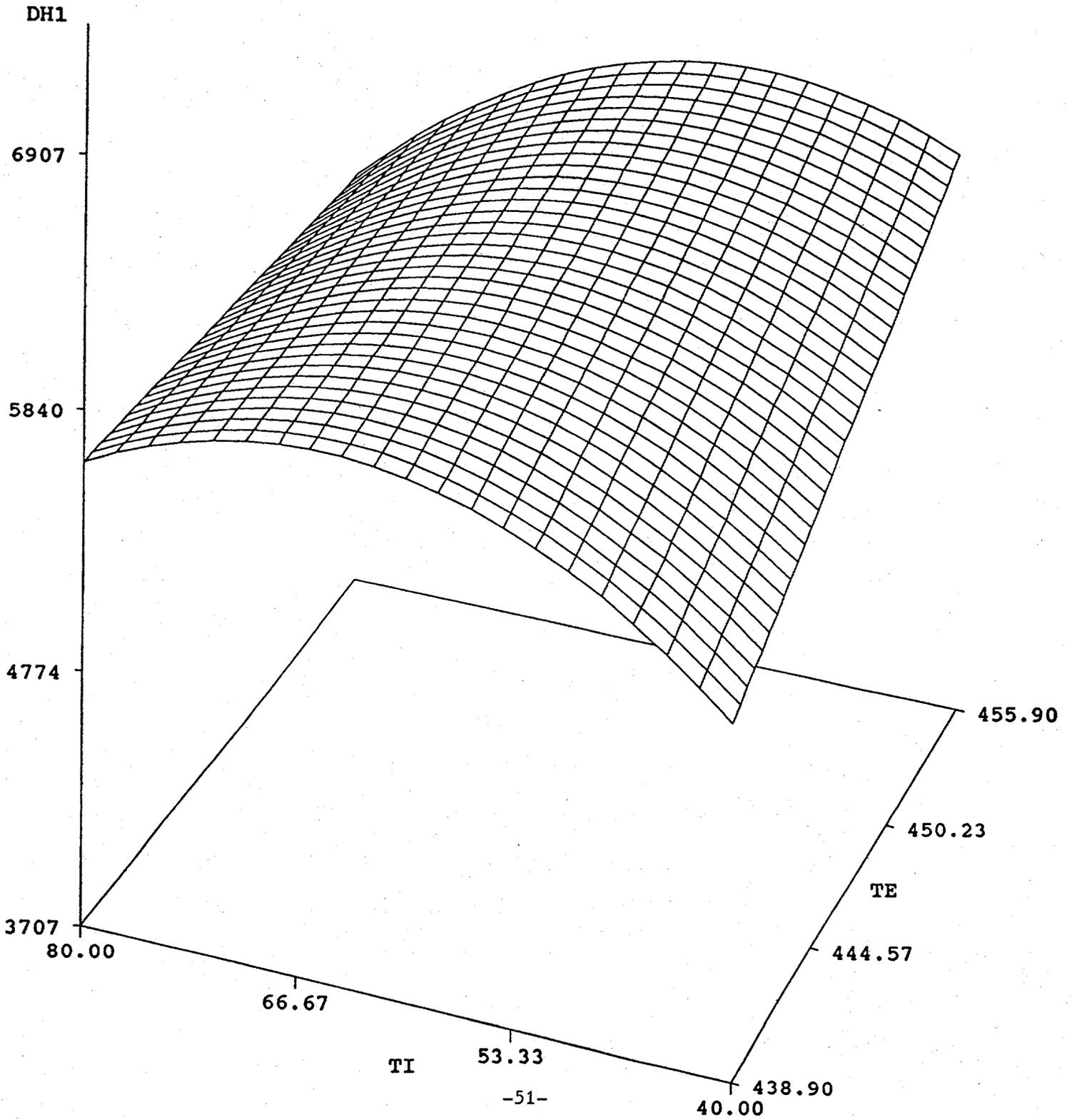


Figure 29. Contour Plot of the Effects of Cooking Time and Temperature on the Heat of Combustion of Black Liquor Solids at Constant Sulfidity and Effective Alkali for Circulation Cooking of Slash Pine



RHEOLOGY

The rheological behavior of black liquors is extremely important, and the study of rheological behavior has received major attention. In the course of this work, we have developed new methods of measurement, developed a general understanding of the regimes of rheological behavior of black liquors, developed very good methods of data reduction, and are now developing generalized correlations for black liquor rheology. We have defined three regimes for black liquor rheology, and we have conducted studies in each regime. The first regime is one in which black liquor always behaves as a Newtonian fluid, and this generally occurs at low solids or very high temperatures. The second regime is one in which black liquor behaves as a non-Newtonian fluid with little or no elastic effects. The third regime is one in which black liquor behaves as a viscoelastic fluid. The first two regimes have received the most attention, since these are the most important from a processing point of view.

Early in this work, it was recognized that black liquor behaves as a Newtonian fluid at low solids ($\sim < 50\%$), and that this limit could probably be extended to as high as about 60% solids at elevated temperature ($> 100^\circ\text{C}$). Extensive data on dynamic viscosity at low solids ($\leq 50\%$) have been taken for all liquors in this study. Figure 30 shows typical results for a black liquor. Figure 31 shows these data as Arrhenius plots. Several approaches have been taken to reduce these data.

The concept of reduced variables for dilute polymer solutions has been used to reduce viscosity data for black liquors at low solids concentrations ($\leq 50\%$), as reported earlier in this study. This method has been successfully applied to all black liquors, by using the combined concentration-temperature variable as:

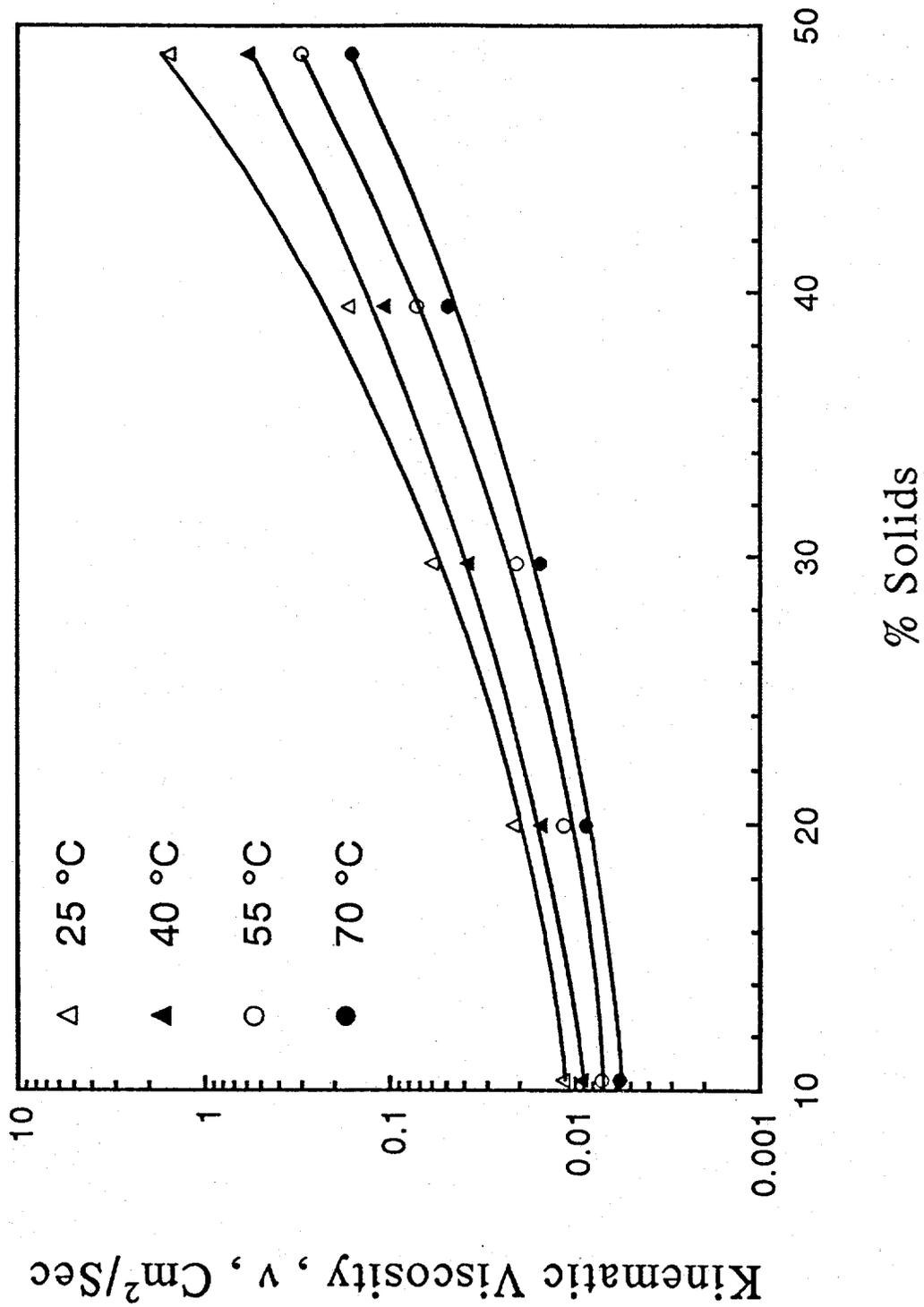


Figure (30): Low Solids (< 50%) Viscosity Data for a Mill Softwood Kraft Black Liquor.

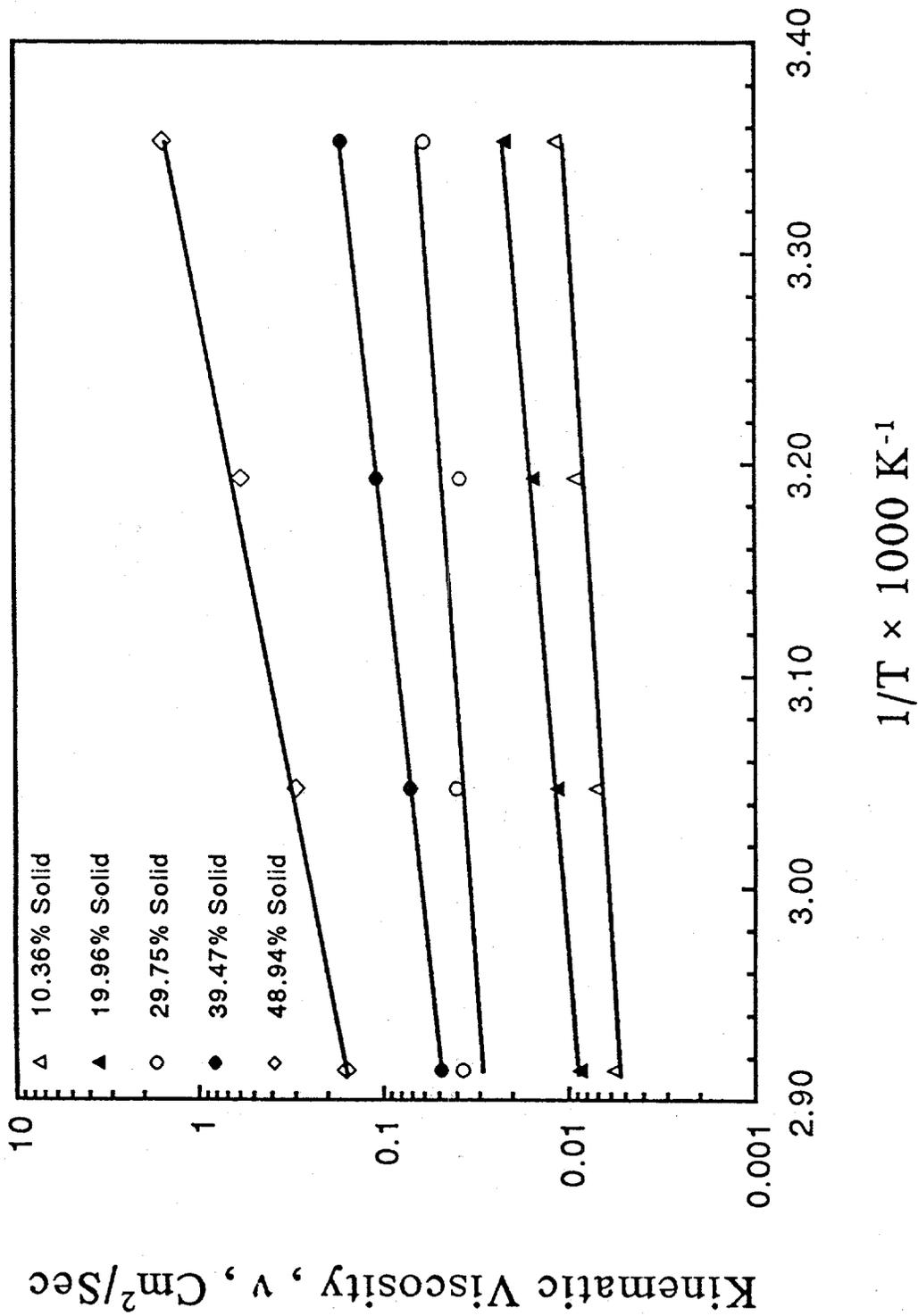


Figure (31): Arrhenius Plots of Low Solids (< 50%) Kinematic Viscosity of a Mill Softwood Kraft Black Liquor.

$$\log(\mu_R) = a_1 \left(\frac{ST_0}{T} \right) + a_2 \left(\frac{ST_0}{T} \right)^2 \quad (12)$$

where:

S = solids concentration, %

T = absolute temperature

T₀ = reference temperature

and a reduced kinematic viscosity as:

$$\mu_R = \mu / \mu_w \quad (13)$$

where:

μ_R = reduced kinematic viscosity

μ = kinematic viscosity of the black liquor

μ_w = kinematic viscosity of water at the same temperature

The relations:

$$\log(\mu_R) = \sum_{i=1}^n a_i \left(\frac{S}{T} \right)^i \quad (14)$$

or:

$$\log(\mu_R) = \sum_{i=1}^n a_i \left(\frac{ST_0}{T} \right)^i \quad (15)$$

where a_i are constants can reduce the data for a single liquor, as shown in Figure 32. This relation has been applied successfully to every liquor studied, and an

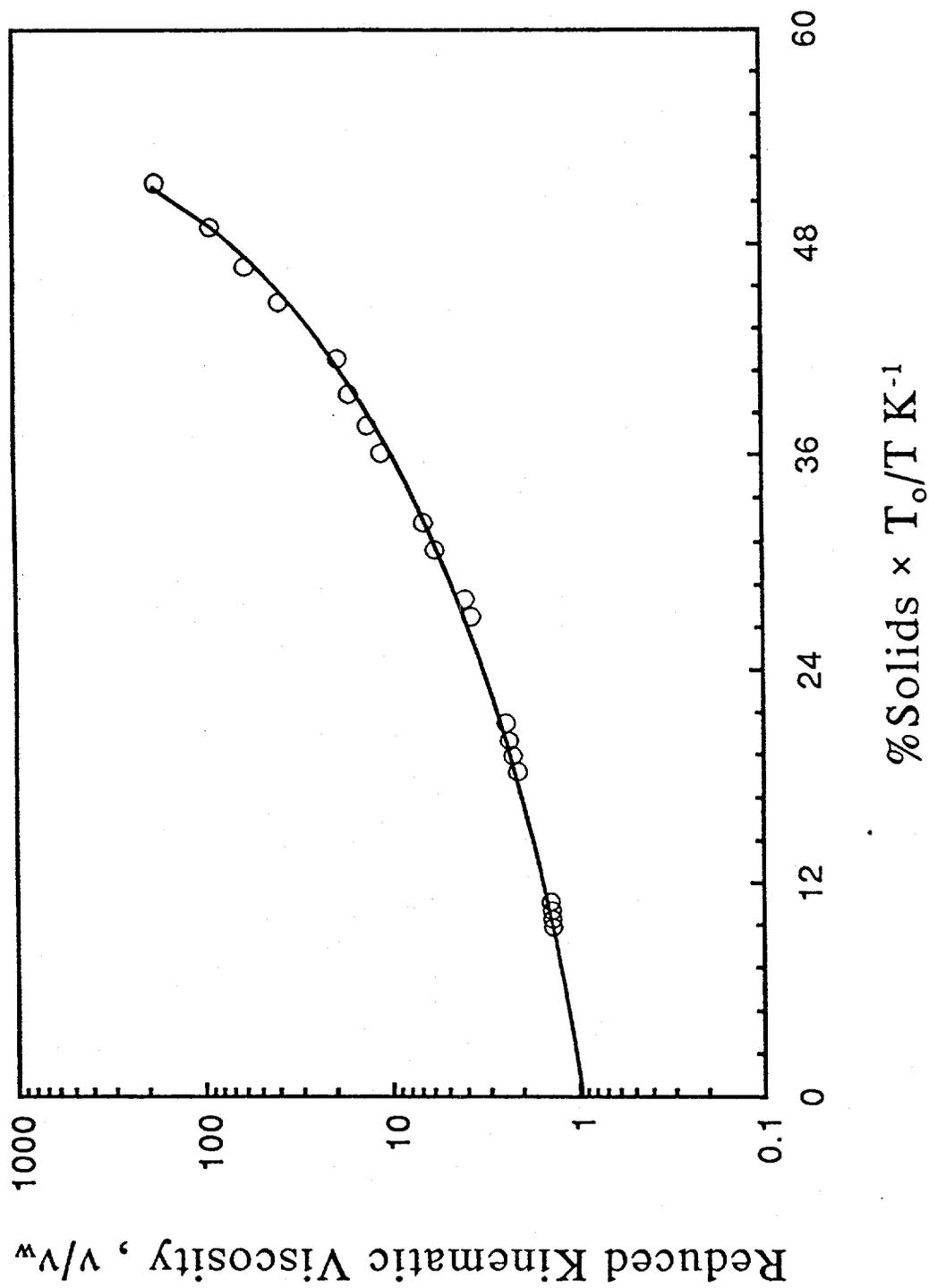


Figure (32): Low Solids (< 50%) Reduced Kinematic Viscosity Relation for a Mill Softwood Kraft Black Liquor.

accurate description of the relation can be obtained with two constants for equation (14) or (15) as:

$$\log(\mu_R) = a_1 \left(\frac{ST_0}{T} \right) + a_2 \left(\frac{ST_0}{T} \right)^2 \quad (16)$$

a_1 and a_2 are functions of the solids composition and vary from liquor to liquor. One should not use a single relation to describe all liquors as has been recommended by some workers who have adopted this method. At present, we are correlating a_1 and a_2 to pulping conditions and solids composition.

A thorough review of theories and relations for viscosity of Newtonian fluids has been made. As a result, relations based upon absolute reaction rate and free volume theories have been developed and applied to black liquors. The relation based upon absolute reaction rate theory is:

$$\mu = A_1 T^{0.5} \exp \left[\frac{B_1}{T} \right] \quad (17)$$

where:

- μ = dynamic viscosity
- T = absolute temperature
- A_1, B_1 = constants

and the relation based upon free volume theories is:

$$\mu = A_2 T^{0.5} \exp \left(\frac{B_2 T_0}{T - T_0} \right) \quad (18)$$

where:

μ	=	dynamic viscosity
T	=	absolute temperature
T_0	=	temperature at which free volume = 0
A_2, B_2	=	constants

T_0 has been taken as a fixed value of 220°K, which is very close to the average freezing point of black liquors at low solids. Both of these relations have been applied successfully to low solids viscosity data. The constants, A_1 , A_2 , B_1 , and B_2 , are solids concentration dependent.

A_1 and B_1 values derived from applying equation (17) to the data could not be correlated to the solids concentrations; therefore, this relation is not recommended for these fluids. The free volume based model was more successful. A_2 and B_2 derived from applying equation (18) to the data could be correlated to the solids composition as:

$$A_2 = a_1 + a_2S \quad (19)$$

and:

$$B_2 = b_1 + b_2S + b_3S^2 \quad (20)$$

where:

A_2, B_2	=	constants for equation (18)
S	=	solids concentration
a_1, a_2, b_1, b_2, b_3	=	constants

According to the free volume theory, A_2 should not vary for the system, i.e., A_2 should be the same for all liquors from the same source. Equation (18) has been

used to fit data for 23 different black liquors made from slash pine. For these liquors, there is one relation for A_2 as a function of solids concentration, which is:

$$A_2 = 2.75 \times 10^{-3} + 3.18 \times 10^{-4} S \quad (21)$$

One should expect, if the theory is applicable, that relations of B_2 from equation (20) will vary from liquor to liquor, but that the relations will form a family, and this has been found to be true. Therefore, given the species one can correlate three constants (b_1 , b_2 , and b_3) vs. liquor composition to completely describe all low solids viscosity behavior.

At this time, we have two methods for data reduction that combine or partition the effects of temperature and solids concentration, and that yield two or three correlating constants that are a function only of pulping conditions or solids composition. Correlations of the constants for both models are being developed.

The second regime, which lies roughly between 50% and 85% solids, is extremely important, because it is in this range that difficult concentration and liquor firing is done. In general, black liquors in this regime behave as non-Newtonian fluids with little or no elastic behavior. Also, black liquor viscosity may be time dependent due to degradation of the lignin in this region and the effect of change in temperature on viscosity is high. Therefore, techniques had to be developed to collect the data within very short time periods and instruments had to be modified to permit very precise temperature control. Finally, since the fluids are non-Newtonian, a number of instruments had to be used to cover a wide range of shear rates. Complete data has been taken for all liquors; however, only examples will be presented here. These will be sufficient to explain the data reduction and correlation methods developed thusfar. Complete results will be given in our final report.

Figure 33 illustrates capillary flow curves for a liquor at 95°C. These are typical, and these illustrate the rapid change in viscosity with solids concentration that is normally observed in this region. Figures 34 through 38 present viscosity data for an experimental liquor as a function of shear rate and temperature at 55.8%, 63.5%, 72.7%, 75.4%, and 84.1%, respectively. Inspection of these figures shows that non-Newtonian behavior begins at about 63% and is present even at 110°C for 84.1% solids. The very large temperature effect on viscosity is also evident. At 63.5% solids, a 50°C temperature change results in an order of magnitude change in viscosity. At 84.1% solids, a 20-25°C temperature change results in an order of magnitude change in viscosity for this liquor.

In the non-Newtonian region, as the shear rate is lowered, the apparent viscosity will approach a constant value that is called the limiting viscosity or the zero shear rate viscosity, which is usually denoted as η_0 . Values of η_0 can be obtained by direct measurement at very low shear rates or by extrapolation. Extrapolation has been used for much of our data; however, the validity of extrapolation has been checked by comparing values of η_0 obtained by direct measurement with values obtained by extrapolation in many cases. These were found to agree quite closely; therefore, extrapolated values have been used in many cases where direct measurement of η_0 would be very difficult and time consuming.

The zero shear rate viscosity, η_0 , is important for two reasons. Firstly, many commercial operations will be carried out under conditions such that the viscosity experienced in processing is the zero shear rate viscosity. Secondly, the zero shear rate viscosity is an important normalizing factor for nearly all rheological data reduction and correlation methods. Therefore, the first step in treatment of rheological data in this region is to determine the zero shear rate viscosity at all conditions of concentration and temperature. Zero shear rate

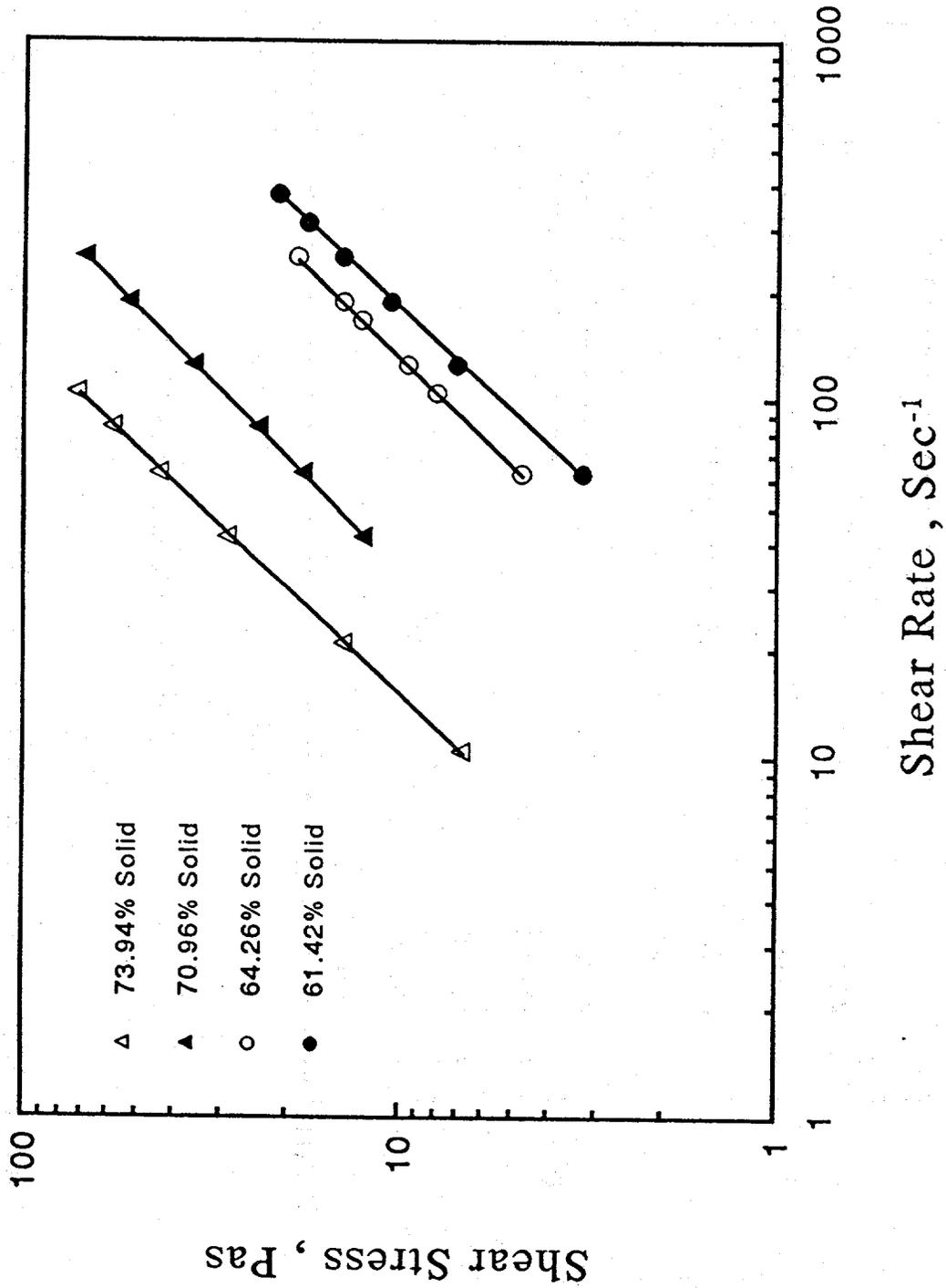


Figure (33): Shear Stress - Shear Rate Curves for a Mill Softwood Kraft Black Liquor at 95 °C.

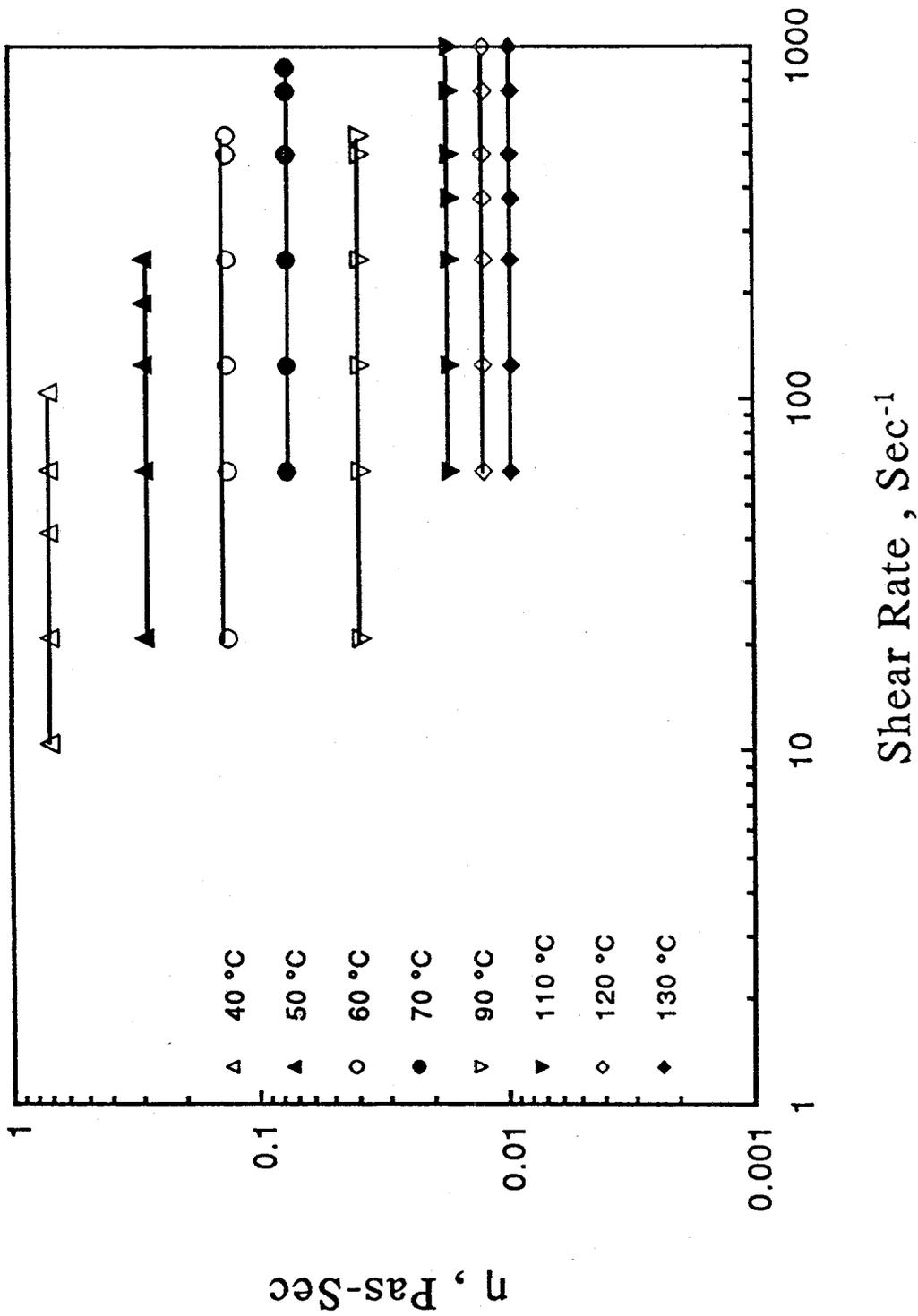


Figure (34): Viscosity of an Experimental Slash Pine Kraft Black Liquor at 55.8% Solids.

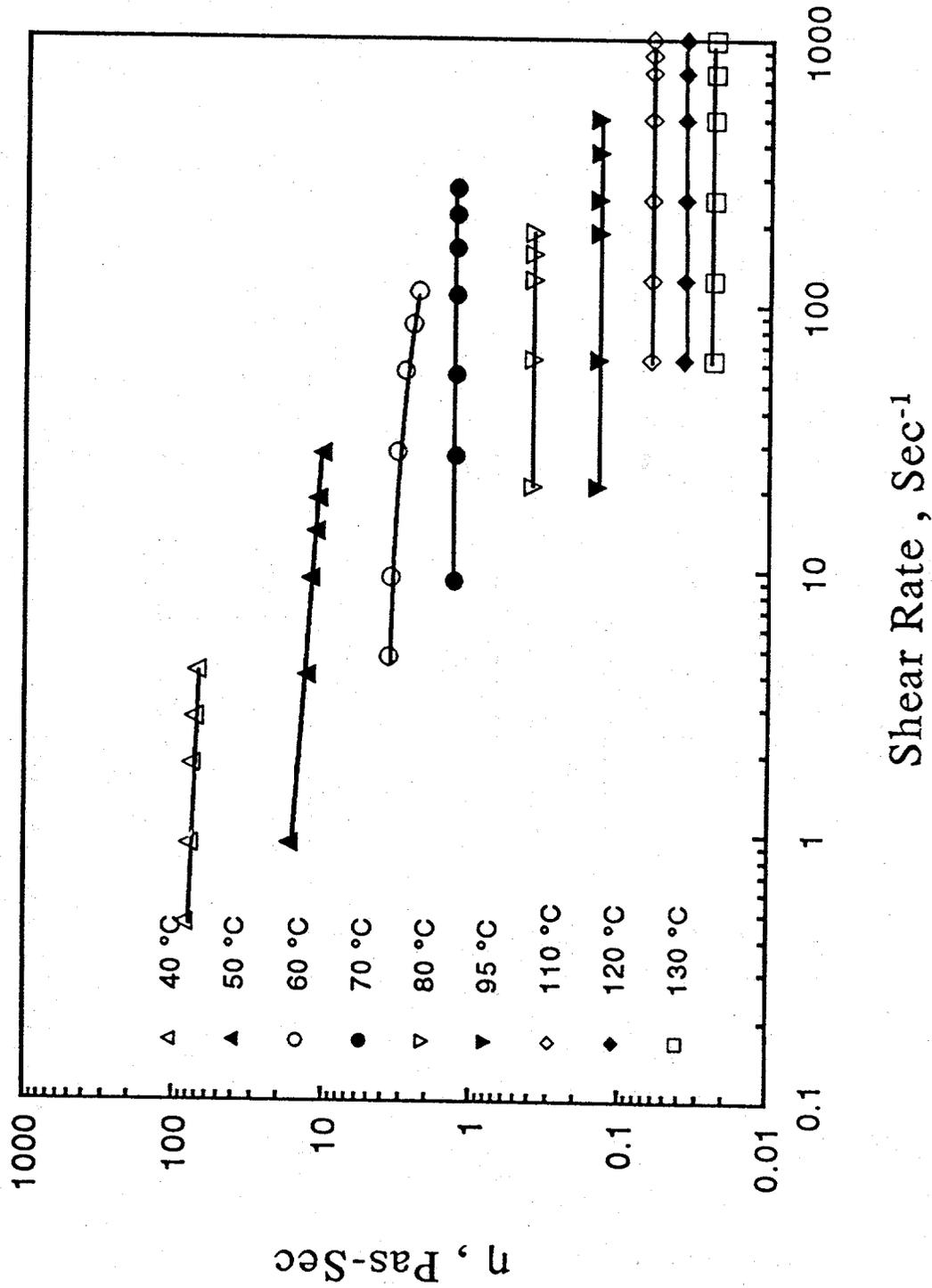


Figure (35): Viscosity of an Experimental Slash Pine Kraft Black Liquor at 63.5% Solids.

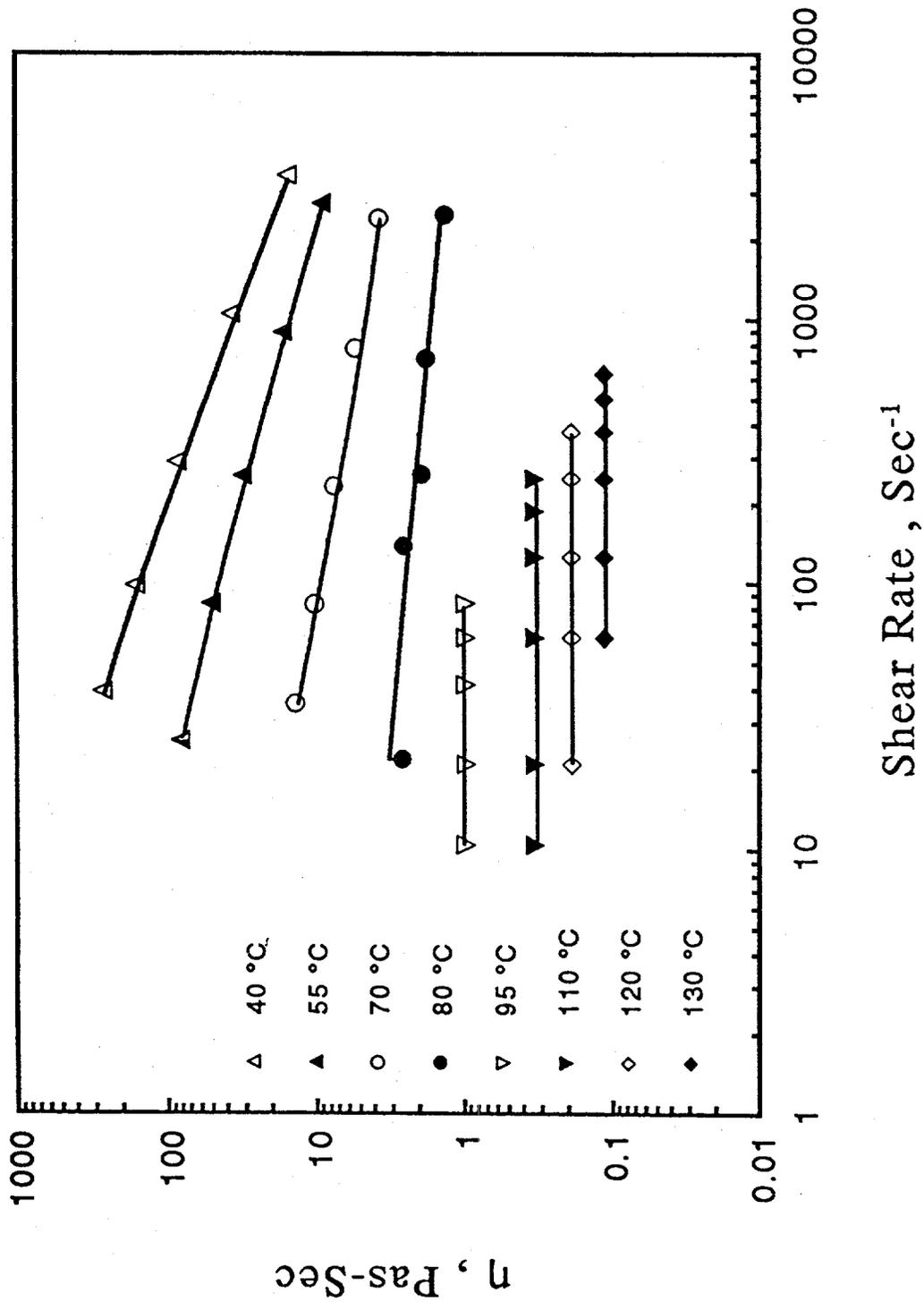


Figure (36): Viscosity of an Experimental Slash Pine Kraft Black Liquor at 72.7% Solids.

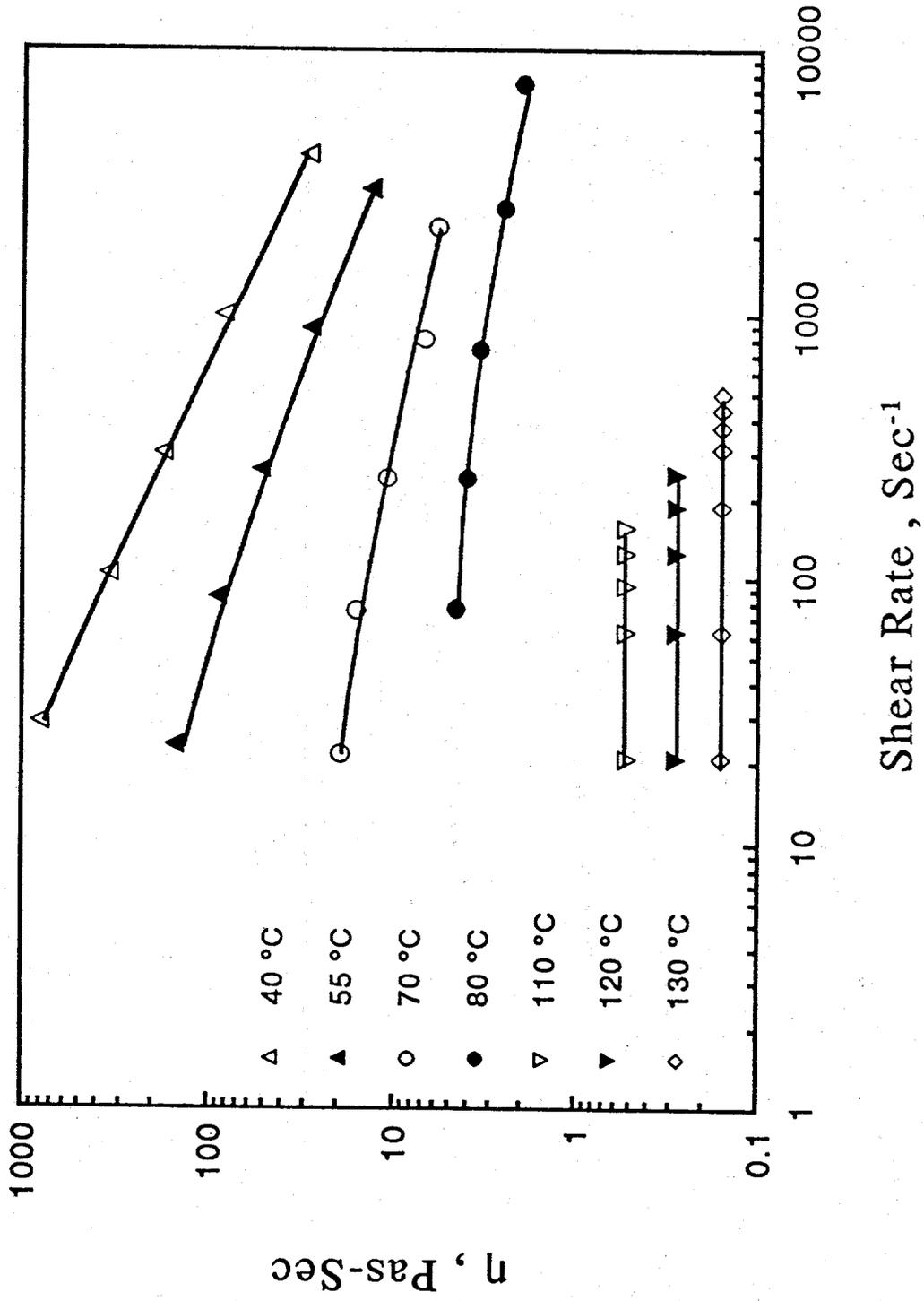


Figure (37): Viscosity of an Experimental Slash Pine Kraft Black Liquor at 75.4% Solids.

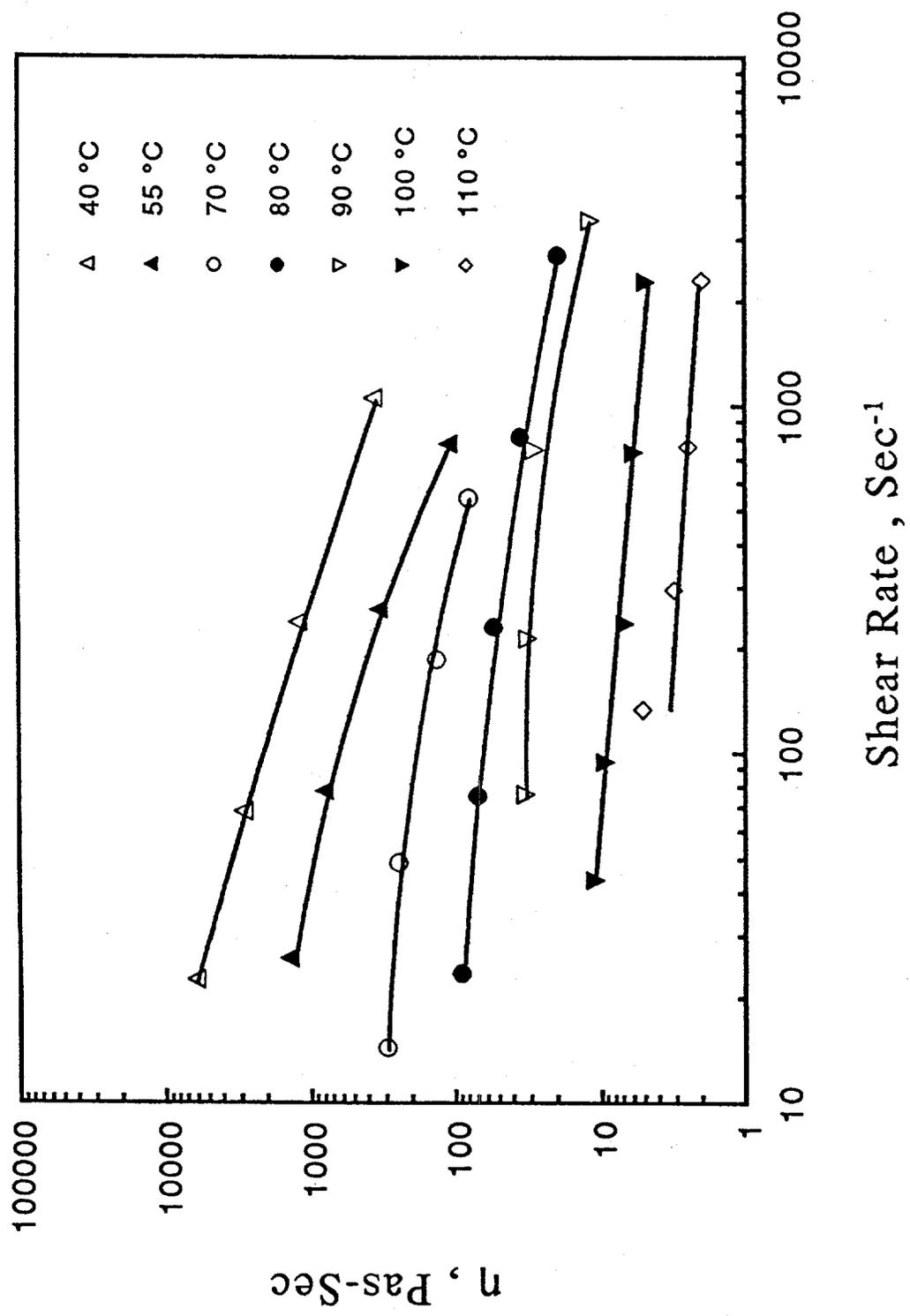


Figure (38): Viscosity of an Experimental Slash Pine Kraft Black Liquor at 84.1% Solids.

viscosities at various solids levels between 55.8 and 84.1% are presented in Figure 39 as an Arrhenius plot. The large change in temperature response that occurs between 55.8 and 63.5% solids at lower temperatures is evident.

A great deal of effort was expended in searching for a function to relate zero shear rate viscosity to temperature and solids concentration. An empirical function roughly based on corresponding states was found to reduce the data surprisingly well. This function is:

$$\log_e \eta_o = \sum_{i=0}^n a_i \left[\left(\frac{S}{S+1} \right) \left(\frac{1}{T} \right) \right]^i \quad (22)$$

where:

- η_o = zero shear rate viscosity
- S = solids mass fraction
- T = absolute temperature

Data for one liquor can be correlated extremely well over six to seven orders of magnitude range of zero shear rate viscosity with three constants as:

$$\log_e \eta_o = a_o + a_1 \left[\left(\frac{S}{S+1} \right) \frac{1}{T} \right] + a_2 \left[\left(\frac{S}{S+1} \right) \frac{1}{T} \right]^2 \quad (23)$$

and this has been found to be applicable to all liquors tested. Figure 40 is an example of the correlation for one liquor. The constants, a_o , a_1 , and a_2 are functions only of the pulping conditions or solids composition. The utility of this function is obvious. The amount of experimental effort required to determine the relation is greatly reduced and the function permits one to predict the effect of increased solids on viscosity within this regime from data taken at lower solids

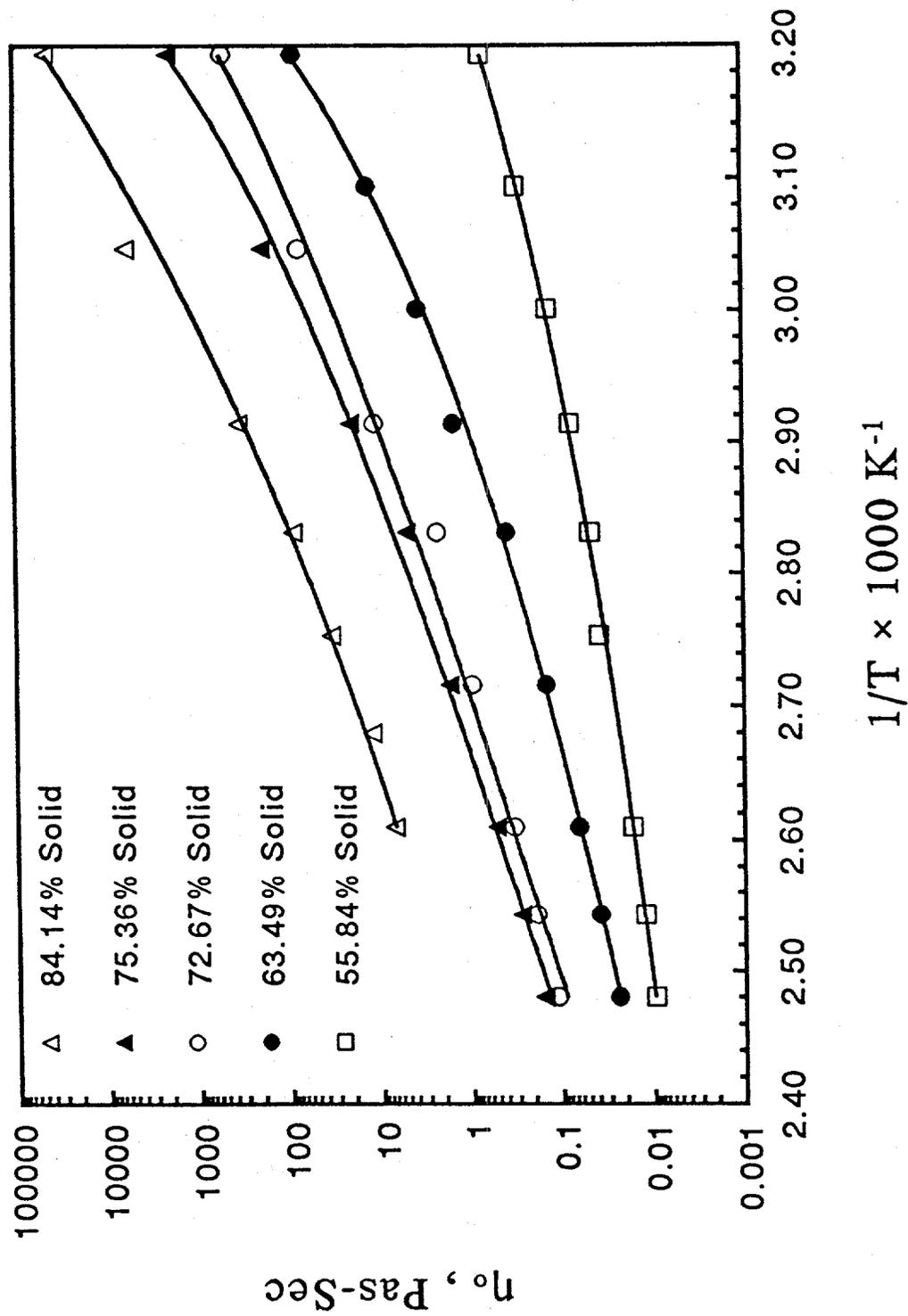


Figure (39): Arrhenius Plot of Zero Shear Rate Viscosities of an Experimental Slash Pine Kraft Black Liquor.

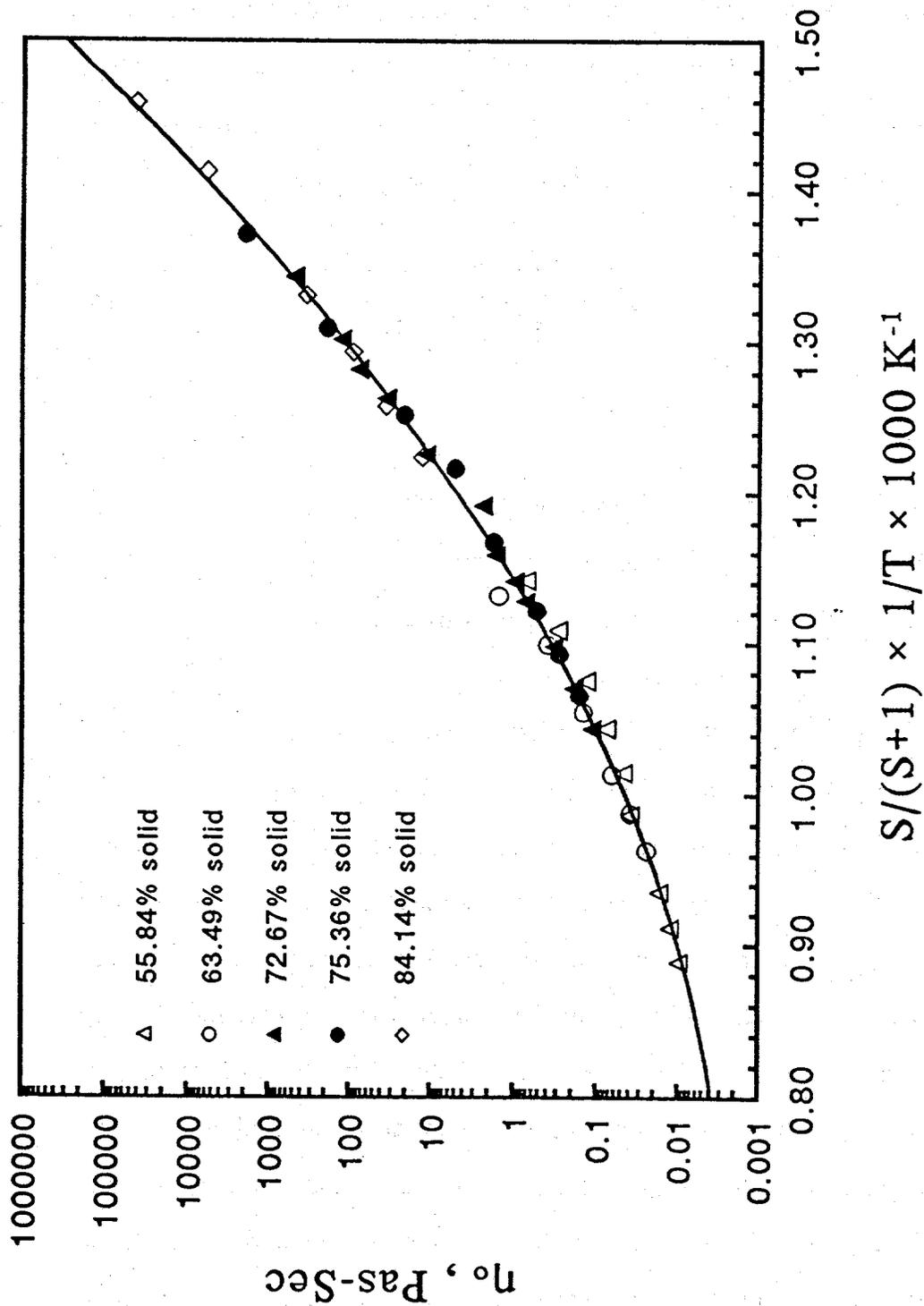


Figure (40): Correlation Curve for Zero Shear Rate Viscosity of an Experimental Slash Pine Kraft Black Liquor.

and lower temperature. Work is in progress to correlate the constants with solids composition and pulping conditions.

While equation 23 has been shown to be generally applicable and highly useful, it is quite empirical. Therefore, a more fundamentally based method of correlation was sought. Due to the success of free volume theory for correlating low solids viscosity and because this theory should apply here also, the use of free volume theory was explored. This leads to the following relation:

$$\eta_o = AT^{0.5} \exp \left[\frac{B}{T} + \frac{CT_s}{T - T_s} \right] \quad (24)$$

where:

- η_o = zero shear rate viscosity
- T = absolute temperature
- T_s = absolute temperature at which free volume = 0
- A, B, C = constants

Free volume theory predicts that T_s is related to the glass transition temperature. Most successful applications of this theory have led to $1.3 T_g < T_s < 1.4 T_g$. Since T_g can be determined directly for black liquor solutions and since T_g is a strong function of solids concentration, it was reasoned that this might be an applicable theory for relating zero shear rate viscosity to temperature and solids concentration. This was tried for a number of liquors and we were successful in fitting the data with $T_s = 1.3 T_g$. Data for a number of liquors made from slash pine were correlated with equation 24 and the constants evaluated. One should note that this is basically a four constant model with B related to the activation energy for flow and T_s related to the glass transition temperature. One should expect that the behavior of A and B would be independent (or nearly so) of solids

composition and that the variation in T_g with solids concentration should be negligibly affected by solids composition. This has proven to be the case. For slash pine liquors, the average value of T_g can be used to establish the relation between T_s and solids concentration for these liquors. Then, for the slash pine liquors:

$$A = \exp[11.824 - 52.456S] \quad (25)$$

and:

$$B = [-0.1382 + 3.013S] \times 10^4 \quad (26)$$

where:

S = solids mass fraction

are relations that apply for all of the liquors. We are left with the constant C . This is a parabolic function of solids mass fraction, but there is a separate function for each liquor. Values of C range from about 0.2 to 2.0 for the liquors studied.

One should note that, even though the relation is complex, it is applicable and that theoretical expectations are met. Finally, for liquors from one species, it yields a model that has at most three constants (the constants necessary to define C) that are solids composition dependent. Therefore, it should be no more difficult to generalize this relation to fit all liquors of one species than to generalize the empirical relation presented earlier. Work is now in progress to correlate the constants for both models to pulping conditions and to solids composition.

A second major effort on rheology in this solids concentration regime is to reduce the data for non-Newtonian behavior and to correlate the resulting model

constants to solids composition. the first step is to normalize all of the viscosity data to deal with reduced apparent viscosity as η/η_0 . When this is done, normal shifting principles can be applied to superimpose all data for one liquor at constant solids concentration on one curve. An example of such a curve is shown in Figure 41. Curves at different solids concentrations are similar, except that the point at which non-Newtonian behavior begins and the slopes of the pseudoplastic region are functions of the solids concentration. A second superposition with respect to solids can be done to give a relation for all solids, temperature, and shear rates. Figure 42 is an example of this for such a liquor. The result requires the definition of two shifting functions, a_T and a_S , as:

$$\log(a_T) = A + \frac{B}{T} + \frac{C}{T^2} \quad (27)$$

and

$$\log(a_S) = a + \frac{b}{S} + \frac{c}{S^2} \quad (28)$$

where:

a_T	=	temperature shift factor
a_S	=	solids shift factor
T	=	absolute temperature
S	=	solids concentration
A, B, C, a, b, c	=	constants

The constants are dependent only on the solids composition. However, there are six constants that must be related empirically to the solids composition and

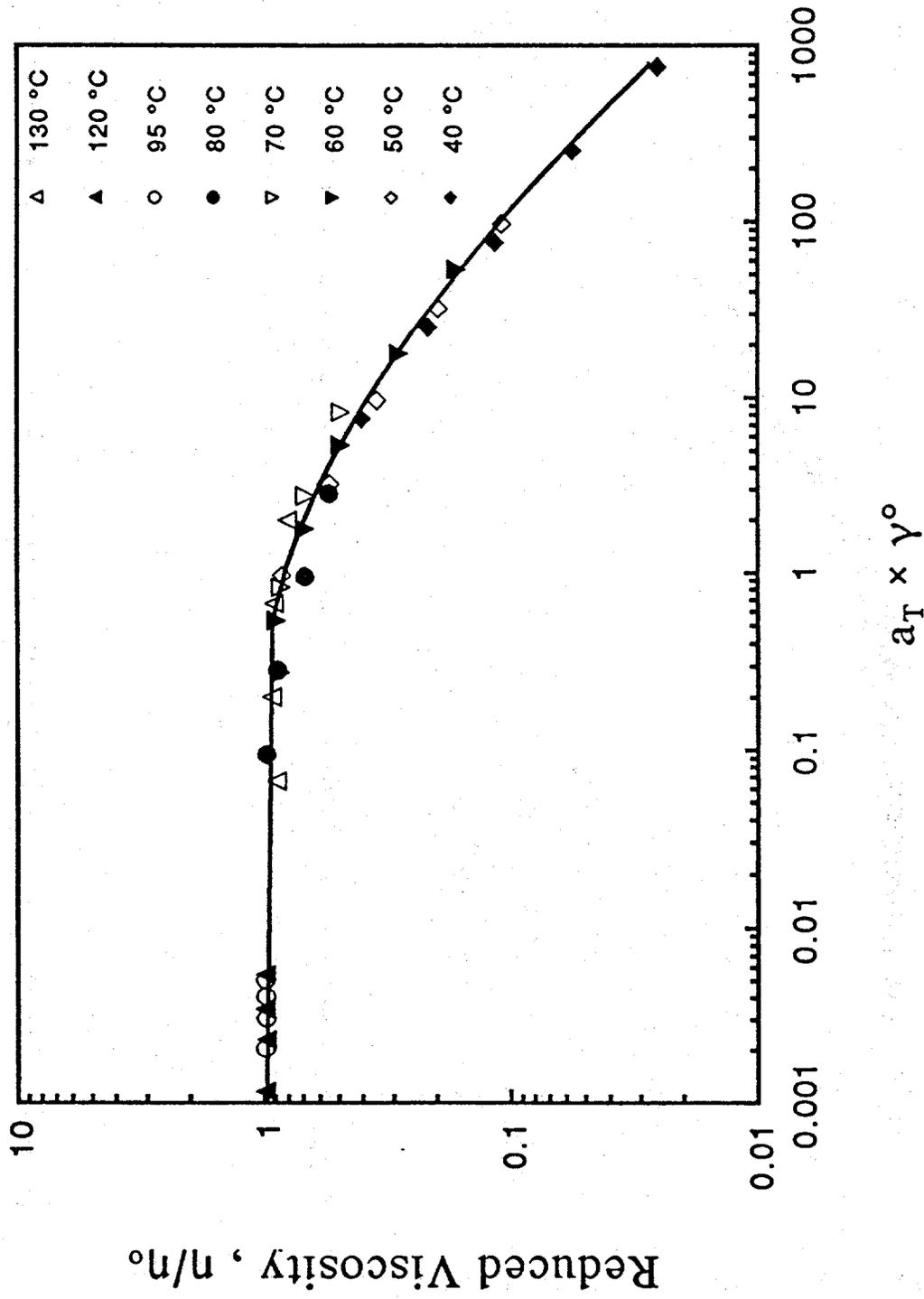


Figure (41): Temperature Superposition of Normalized Viscosity of a Mill Softwood Kraft Black Liquor at 77.87% Solids.

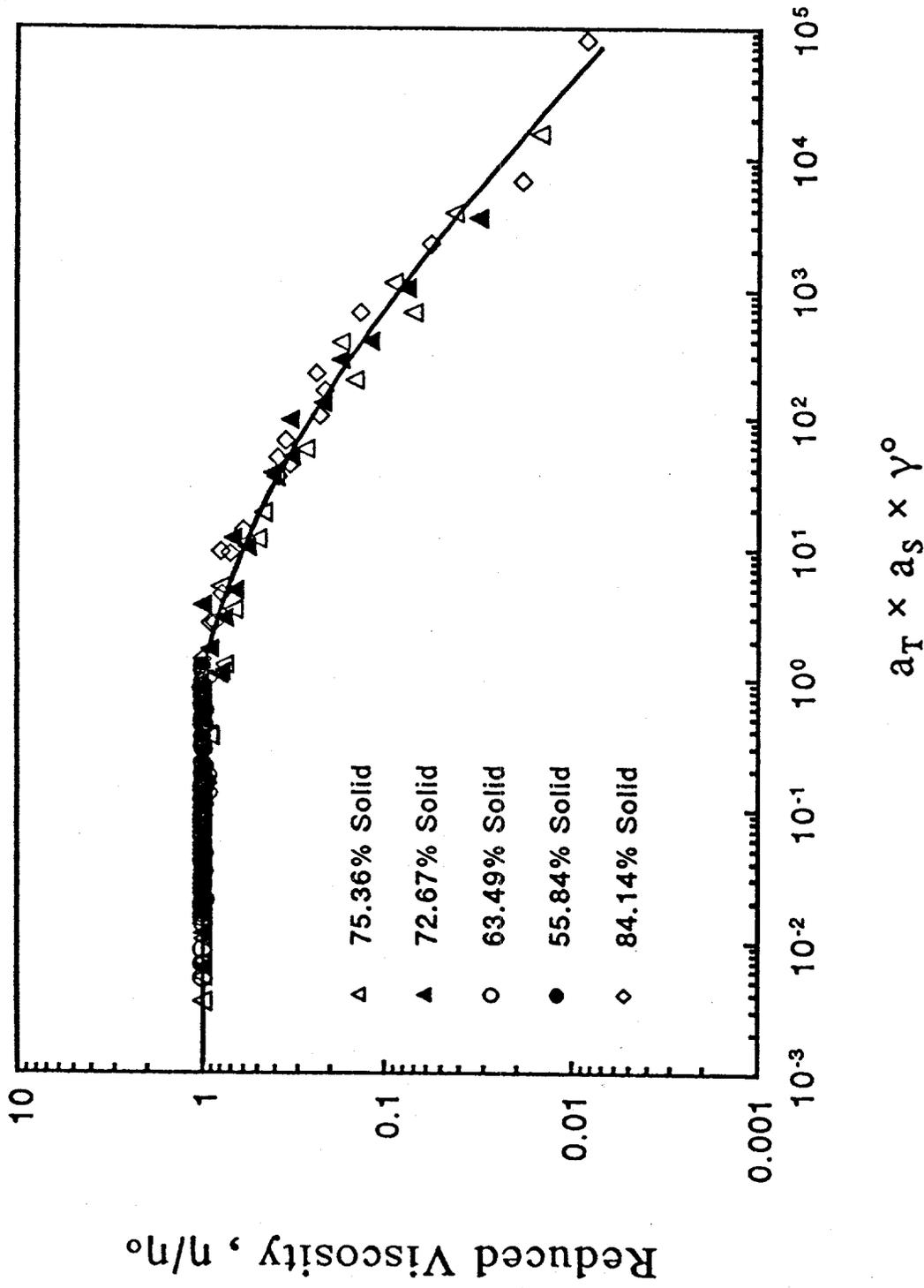


Figure (42): Superposition Curve for Viscosity of an Experimental Kraft Black Liquor with Successive Shift for Temperature and Solids.

application of a_S and a_T is cumbersome. One must remember that the master (superimposed) curve must still be modelled.

Due to the apparent success in applying free volume theories to low solids viscosity and to zero shear rate viscosity for high solids, a data reduction scheme based on free volume theories was sought. Past work by others for concentrated polymer solutions has shown that, if a reference temperature is suitably chosen, data for different temperatures and concentrations can be superimposed in one step. A shift factor, a_{ST} , can be defined as:

$$a_{ST} \approx \frac{\eta_0}{\eta_0^s} \frac{T_s}{T} \quad (29)$$

where:

- a_{ST} = shift factor
- η_0 = zero shear viscosity
- η_0^s = zero shear rate viscosity at the reference temperature, T_s
- T = absolute temperature
- T_s = reference temperature

In past work, it has been found that T_s lies about 50°K above the glass transition temperature, T_g . We have successfully superimposed data in this manner for different black liquors with $1.3 T_g \leq T_s \leq 1.4 T_g$. An example is shown in Figure 43. As expected, $[-1/\log a_{ST}]$ is a linear function of $[1/(T - T_s)]$ for black liquors. Therefore a Williams-Landel-Ferry (WLF) equation of the form:

$$\log_e a_{ST} = \frac{-C_1(T - T_s)}{(C_2 + T - T_s)} \quad (30)$$

where:

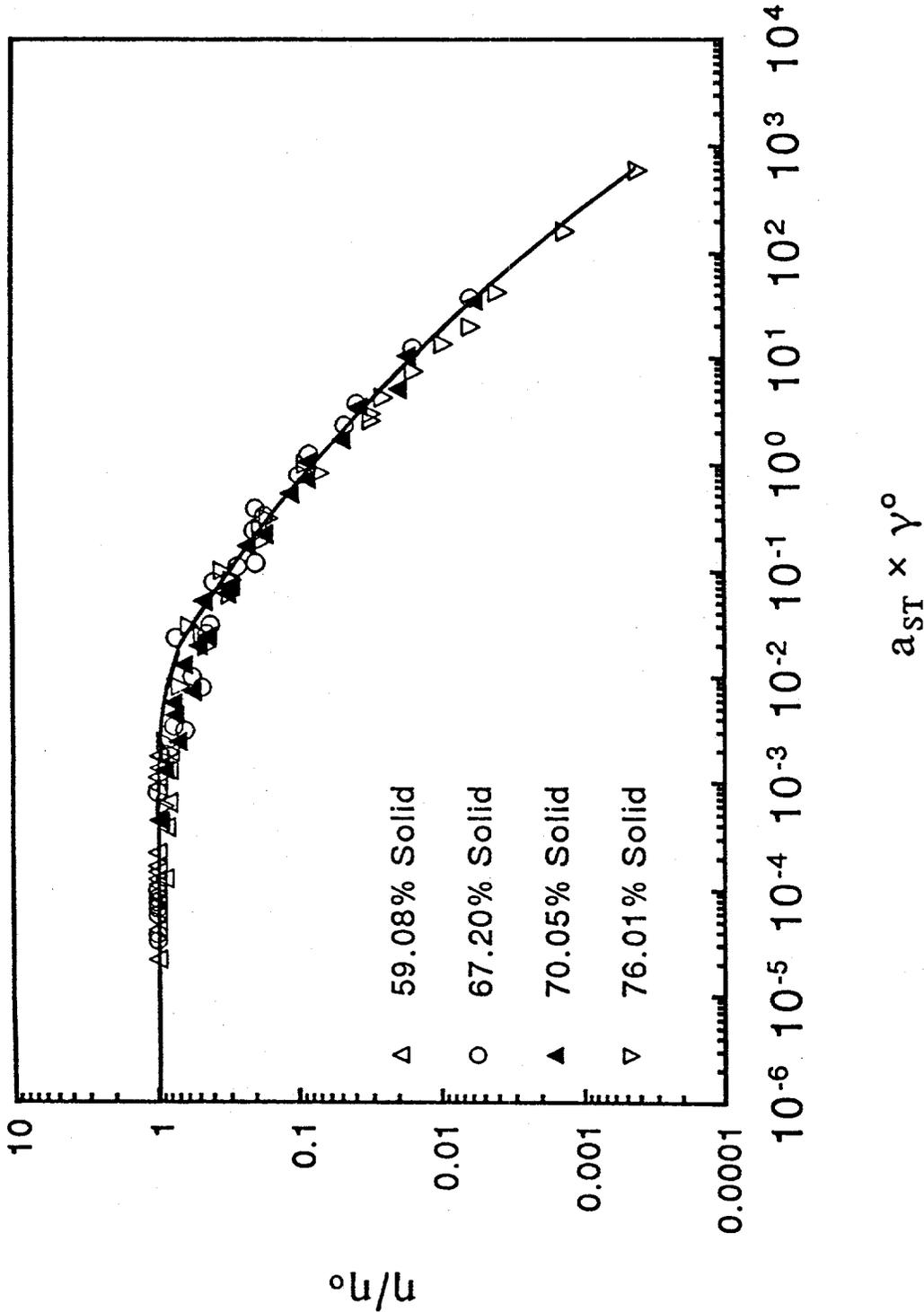


Figure (43): Superposition Curve for Viscosity of an Experimental Slash Pine Kraft Black Liquor Obtained by Combined Shift for Temperature and Solids.

a_{ST}	=	combined shift factor
T	=	absolute temperature
T_s	=	reference temperature
C_1, C_2	=	constants

fits very well. We have found that data can be treated so as to permit C_1 and C_2 to be dependent upon solids composition or to set C_1 and C_2 at average values and let T_s be the adjustable parameter. The latter seems preferable. In this case, the equation for the shift factor becomes:

$$\log_e a_{ST} = \frac{-26.77 (T - T_s)}{(104.16 + T - T_s)} \quad (31)$$

where T_s is adjustable and varies with liquor composition and solids concentration. This still results in a model with three constants to describe behavior for all liquors from the same species, but this is fundamentally based and the number of constants to be evaluated is only half of those required for the more empirical method of superposition developed earlier. Work is in progress to develop superimposed reduced viscosity curves for all of the liquors tested.

The superimposed reduced viscosity curves for different liquors have been modelled using the Cross model equation:

$$\frac{\eta}{\eta_o} = \frac{1}{(1 + (\lambda\dot{\gamma})^a)} \quad (32)$$

and the Carreau-Yasuda model equation:

$$\frac{\eta}{\eta_o} = \frac{1}{(1 + (\lambda\dot{\gamma})^a)} \quad (33)$$

where:

$$\frac{\eta}{\eta_0} = \text{reduced apparent viscosity}$$
$$\dot{\gamma} = \text{shifted shear rate}$$
$$a, \lambda, n = \text{constants}$$

Both of these models fit superimposed curves very well. In these equations, $(n-1)$ is the slope of the Power Law region, a adjusts the breadth of the transition from Newtonian to non-Newtonian behavior, and λ is a characteristic time for the fluid. These three constants for the superimposed relation are dependent only upon the composition of the liquor solids.

Viscoelastic studies of black liquor at high solids have been made on a limited number of black liquors. These studies show that viscoelastic effects are not important at elevated temperatures ($> 110^\circ\text{C}$) up to solids contents of 80-85%. However, at higher solids concentrations, the character of the fluid changes and viscoelastic effects become more evident very rapidly. Due to the complexity of these studies and the fact that we do not believe that current technology based on droplet formation can be practiced above 85% solids with liquors we have studied, we have not explored this type of study extensively.

At this point, we have developed a large data bank for viscosity, developed data reduction schemes that are fundamentally based, applied these extensively to data, and we are proceeding to generalize the constants for the models developed to generate a global set of relations for the viscosity of slash pine liquors. We have also demonstrated that the data reduction schemes, correlation methods, and models apply in principle to all other black liquors tested.

HEAT CAPACITY

Heat capacity is an important property of black liquors that has received a great deal of experimental study in our program. We have used differential scanning calorimetry (DSC) techniques to determine heat capacity as a function of temperature at constant solids. Although extreme care must be exercised in experimental work to obtain accurate measurements of heat capacity by DSC, this method is the only one that could have been used to collect the large amount of data that we have obtained. One key to successful development of a generalized heat capacity model has been our ability to determine the heat capacity of 100% black liquor solids directly.

The fundamental model, based upon lattice parameter theory, was developed in this work earlier. The complete model is:

$$C_p = C_{p_w} (1 - x) + C_{p_s} x + A(1 - x)x^m \quad (34)$$

where:

- C_p = black liquor heat capacity
- C_{p_w} = heat capacity of water
- C_{p_s} = heat capacity of 100% black liquor solids
- x = mass fraction of solids
- A, m = constants

also:

$$A = a + bT \quad (35)$$

where:

- T = temperature

a, b = constants

The three constants in this relation— m , a , and b —are dependent only upon the solids composition. Finally, C_{p_s} can be expressed as:

$$C_{p_s} = d + eT \quad (36)$$

where d and e are constants dependent only upon black liquor solids composition.

In the past, black liquor has been considered to be an ideal fluid so that A has been assumed to be zero. Moreover, the heat capacity for 100% solids was not measured directly and d and e were assumed to be true constants derived implicitly from fitting equation 34 to data for a limited amount of low solids data (< 50%) with A assumed to be zero. This has been shown to be erroneous. The constants d and e vary considerably from liquor to liquor and the excess heat capacity term— $A(1-x)x^m$ —is significant at high solids.

Heat capacity data has been taken on all slash pine liquors and reduction of data using equation 34 is virtually completed. The constants for equations 34 and 35 will be correlated with pulping conditions and solids composition. The result will be a generalized model to predict heat capacity at all temperatures, solids concentrations, and compositions. At this time, it is believed that this will be far easier to do than correlating even low solids viscosity behavior.

Because of the success of this development, future work necessary to define heat capacities for a liquor from another species is very much less than was done in our study. We estimate that only about one-quarter as much effort will be required.

HEAT OF DILUTION

As stated earlier, black liquor has been considered in the past to be an ideal fluid with respect to enthalpy, and heats of mixing or dilution have been ignored. Considering the components present and their ionic or electrolytic nature, we did not believe that this should be true, especially at high concentrations. As a result, determination of heats of dilution was included in our program.

Almost two years was required to develop methods for determining heats of dilution accurately with an absolute microcalorimeter that has been described earlier. Complete details on the method will be published in a paper that is in press and in our final report to DOE. It is sufficient to state here that the method has been developed and has been applied to many black liquors. However, there are a few limitations that are worth mentioning. 100% black liquor solids could not be used because of difficulties in handling and because the high viscosities resulting even after dilution interfered with the experiment. Also, heats of dilution had to be measured at 80°C for good mixing during the experiment. Finally, the solution could not be separated completely from the inert fluid used. Therefore, the final heat of dilution curve is constructed from a series of incremental results. As a consequence, a reference state other than 100% solids at a specified temperature had to be used, and the incremental heats of dilution had to be used to construct a heat of dilution vs. concentration curve.

Generally, samples at 80% solids or slightly higher were diluted to about 50% solids and the heat of dilution at 80°C determined directly. This was repeated for liquors starting at other solids concentrations between 80% and 50%. Below 50% solids, experiments were conducted with a 0.5/1 to about 3/1 dilution. The lowest final concentration that could be used for accurate results was in the range of 1.5-1.7%. Tests were replicated to determine precision. Precision varied

with concentration. Results agreed within about 1% for dilutions to concentrations above 25%, within about 2% for concentration between 25% and about 5%, and to within about 6% for dilutions between 5% and 1.5%. The large heat effect at dilutions from 5% to 1.5%, along with the scatter in the data for duplicate runs, suggested that a chemical reaction or precipitation of some type was occurring. Association and precipitation of lignin is known to occur in black liquors at a pH below 12. The pH at 5% solids for our liquors was calculated to be at or below 12.

Figure 44 is a typical result of the enthalpy change for dilution as a function of solids. This is a graph formed from the adjustment of the incremental measurements on an arbitrary enthalpy scale. Since we cannot experimentally use 100% solids, another reference state must be used. The next most convenient state is infinite dilution of the solids; however, if the solids have changed chemically by reaction or if lignin has precipitated, extrapolation of data taken from 5% to 1.5% would lead to an incorrect reference state. Therefore, the curve was extrapolated from about 5% to zero to determine the reference enthalpy for infinite dilution of solids in the same state as exists for solids at higher concentrations. Fortunately, the data between 5 and about 25% solids are very nearly linear so that extrapolation could be done with very little uncertainty. For the liquor results shown in Figure 44, the extrapolated value was $-3.79 \text{ J/gm-solids}$. This value was then used to adjust the enthalpy scale to give a plot of total heat required to dilute a solution of given solids content to infinite dilution at 80°C , which is denoted as Q^∞ . Different, but similar, results have been obtained for many liquors.

The use of a fictitious infinite dilution state at 80°C as the reference state for solids and the desire to use the normal reference state of liquid water at 0°C leads to the need to construct a "base isotherm" at 80°C as a reference for

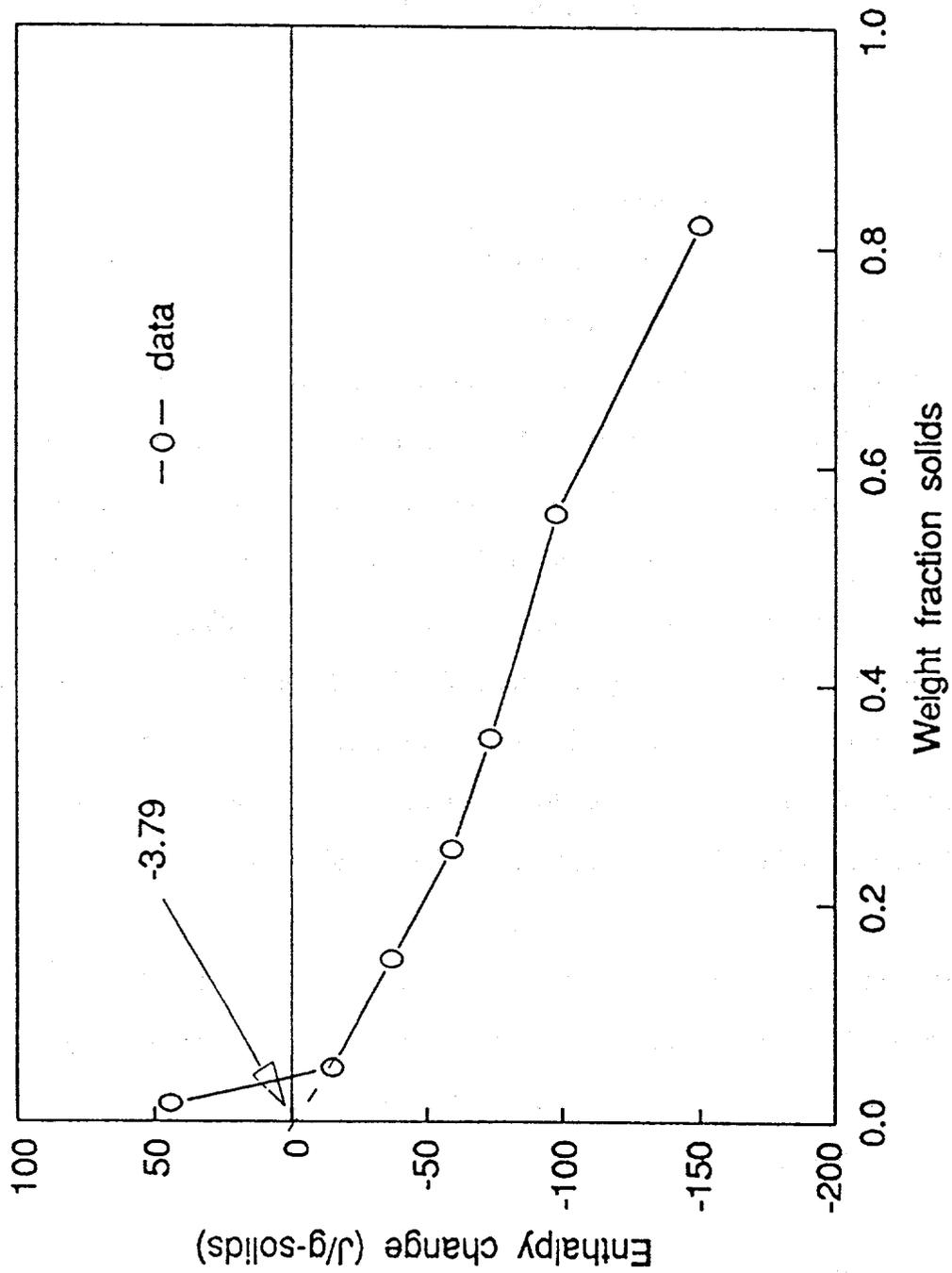


Figure 44. Enthalpy Change for Dilution at 80 °C of an Experimental Slash Pine Kraft Black Liquor

enthalpy calculations. The enthalpy at 80°C at any concentration can be calculated from:

$$H = (1 - x)H_1 + xQ^\infty \quad (37)$$

where:

- H = solution enthalpy at 80°C
- H₁ = enthalpy of water at 80°C
- x = mass fraction solids

Note that the enthalpy of solids at infinite dilution at 80°C is zero. In this manner, the heat of dilution curve can be converted to a "base isotherm" representing the enthalpy of the solution as a function of concentration at 80°C referred to pure water at 0°C and solids in infinite dilution at 80°C. Figure 45 is the base isotherm constructed from the data shown in Figure 44. Note that the enthalpy at zero concentration is the enthalpy of liquid water at 80°C (143.9 Btu/lb) and that the initial slope of the curve must be -143.9 Btu/lb (the negative of the enthalpy of pure water at 80°C) so that the initial slope intersects at zero enthalpy for 100% solids. This defines the solids reference state so that enthalpy calculations can be made.

Heat of dilution data has been taken for all slash pine liquors, but not all base isotherms have yet been developed from the data. We hope to correlate the isotherms so that a base isotherm can be constructed for a given set of pulping conditions or solids composition.

ENTHALPY-CONCENTRATION

Once heat capacity and a heat of dilution base isotherm are available, one can construct an enthalpy-concentration diagram for the liquid state considering

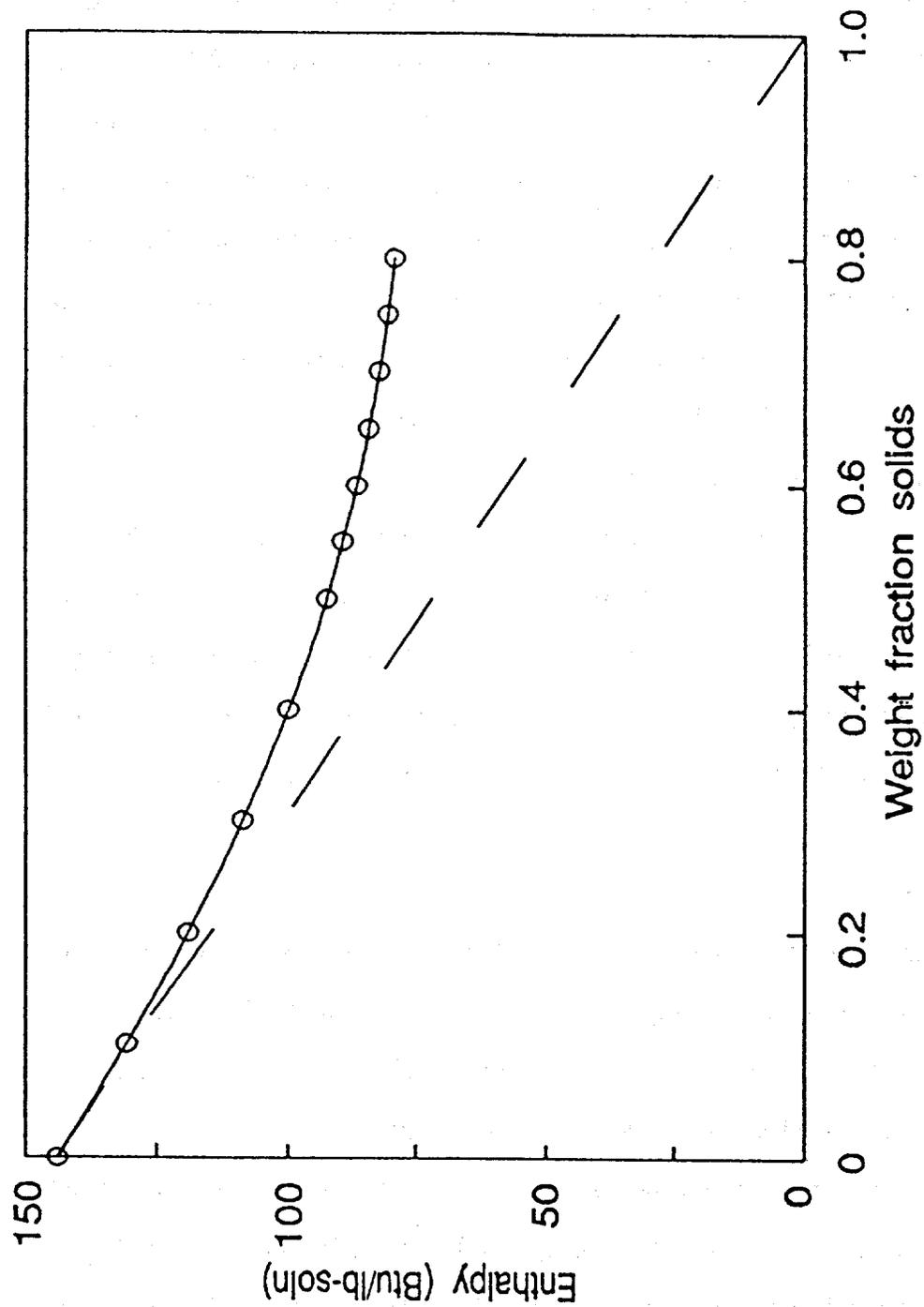


Figure 45. Base Isotherm at 80 °C for an Experimental Slash Pine Black
Liquor

the system to be a pseudobinary. This has been done for six black liquors using straightforward thermodynamic calculation methods. Results can be presented in graphical or tabular form. Figure 45 is an example of an enthalpy-concentration diagram for one black liquor with reference states as pure water at 0°C and solids at infinite dilution at 80°C. Table 2 presents the data in tabular form. Results were checked for thermodynamic consistency by using one experimental vapor pressure curve to calculate fugacities and then correcting these fugacities using the enthalpy relations to predict fugacities at other conditions. Predictions were compared with vapor pressure measurements at these other conditions. Agreement was good, and it appears that a black liquor can be treated as a pseudobinary thermodynamically.

It should be pointed out that the overall error in ignoring excess heat capacity effects and heat of dilution effects in concentrating black liquor to as much as 70% solids is not large (probably less than 3%), because the major change is still energy to evaporate water. However, ignoring these effects would lead to significant errors in estimating the change in liquid enthalpy.

DENSITY

Extensive data on densities of black liquors has been taken. Methods have been developed for determining density accurately at even 100% solids. Density data are important for metering liquors, but results have also been useful in illuminating the character of black liquor at high solids.

Ordinary pycnometry methods are used to determine the density of black liquors at 25-35°C for concentrations up to 60% solids in some cases and up to 50% solids in all cases. At higher concentrations, densities cannot be determined at these low temperatures using ordinary absolute pycnometer methods. In this range, air comparison pycnometry has been used and methods developed to

Table 2. Enthalpy for an Experimental Slash Pine Black Liquor

Enthalpy (Btu/lb)								
Temp	Solids Content							
°C	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80
40	61.8	53.9	47.5	42.5	38.7	36.3	35.3	36.1
45	70.3	61.9	55.1	49.6	45.4	42.5	41.1	41.4
50	78.9	70.0	62.7	56.7	52.1	48.8	46.9	46.7
55	87.5	78.1	70.3	63.9	58.8	55.0	52.7	52.0
60	96.1	86.2	77.9	71.0	65.5	61.3	58.6	57.4
65	104.7	94.4	85.6	78.2	72.2	67.6	64.4	62.8
70	113.4	102.6	93.3	85.4	78.9	73.9	70.3	68.2
75	122.0	110.7	100.9	92.6	85.7	80.2	76.2	73.6
80	130.7	119.0	108.7	99.8	92.5	86.5	82.1	79.1
85	139.4	127.2	116.4	107.1	99.2	92.9	88.0	84.6
90	148.1	135.4	124.1	114.3	106.0	99.3	94.0	90.1
95	156.8	143.7	131.9	121.6	112.9	105.6	99.9	95.6
100	165.6	152.0	139.7	128.9	119.7	112.0	105.9	101.2
105	174.4	160.2	147.5	136.2	126.5	118.5	111.9	106.7
110	183.1	168.6	155.4	143.6	133.4	124.9	117.9	112.3
115	191.9	176.9	163.2	150.9	140.3	131.3	124.0	117.9
120	200.8	185.2	171.1	158.3	147.2	137.8	130.0	123.6

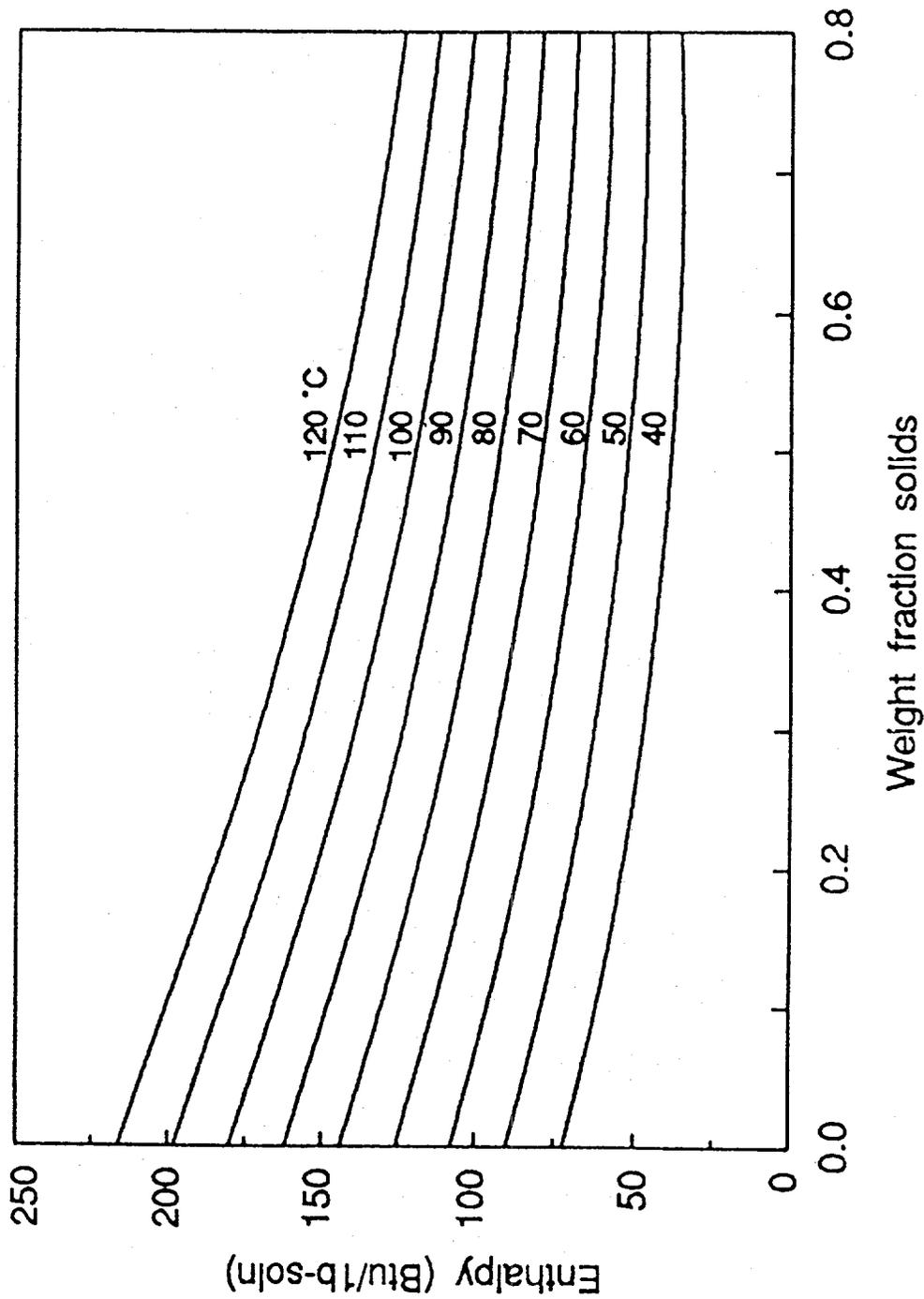


Figure 46. Enthalpy-Concentration Diagram for an Experimental Slash Pine Kraft Black Liquor

determine density at even 100% solids at low temperatures. Densities at other temperatures are determined by dilatometry.

A dilatometer of known volume is loaded with a known mass of mercury and then the remainder of the dilatometer volume is filled with black liquor at a temperature where the liquor is sufficiently fluid for loading the dilatometer. The dilatometer is brought to thermal equilibrium at a fixed temperature and the total fluid volume in the dilatometer at that temperature is measured. This is repeated at different temperatures. Since the mass and density of mercury in the dilatometer are known and the total dilatometer volume is measured, the volume of black liquor in the dilatometer as a function of temperature can be calculated. From the pycnometer results, the density of the black liquor at one temperature is known. Since the volume of liquor in the dilatometer at that temperature is known, the mass of liquor in the dilatometer can be calculated. The dilatometer results can then be converted to yield density as a function of temperature at constant solids. This is repeated at different solids levels. The results can be used to determine density vs. solids at constant temperature or to determine thermal expansion of liquors.

It is difficult to prepare samples reproducibly at solids levels above 85%, except for 100%, which is done by freeze drying.

Typical results are shown in Figures 47 and 48. Figure 47 shows typical results for density at 25°C as a function of solids while Figure 48 shows density as a function of temperature at various solids concentrations. Figure 47 is particularly intriguing. The data presents three straight line segments, representing two abrupt changes in slope. Since density is a thermodynamic state property, an abrupt change in slope represents a second order transition. Thus, there appears to be two such transitions for black liquor, one occurring at about 60% solids at 25°C and the other occurring at about 80-85% solids at 25°C. We

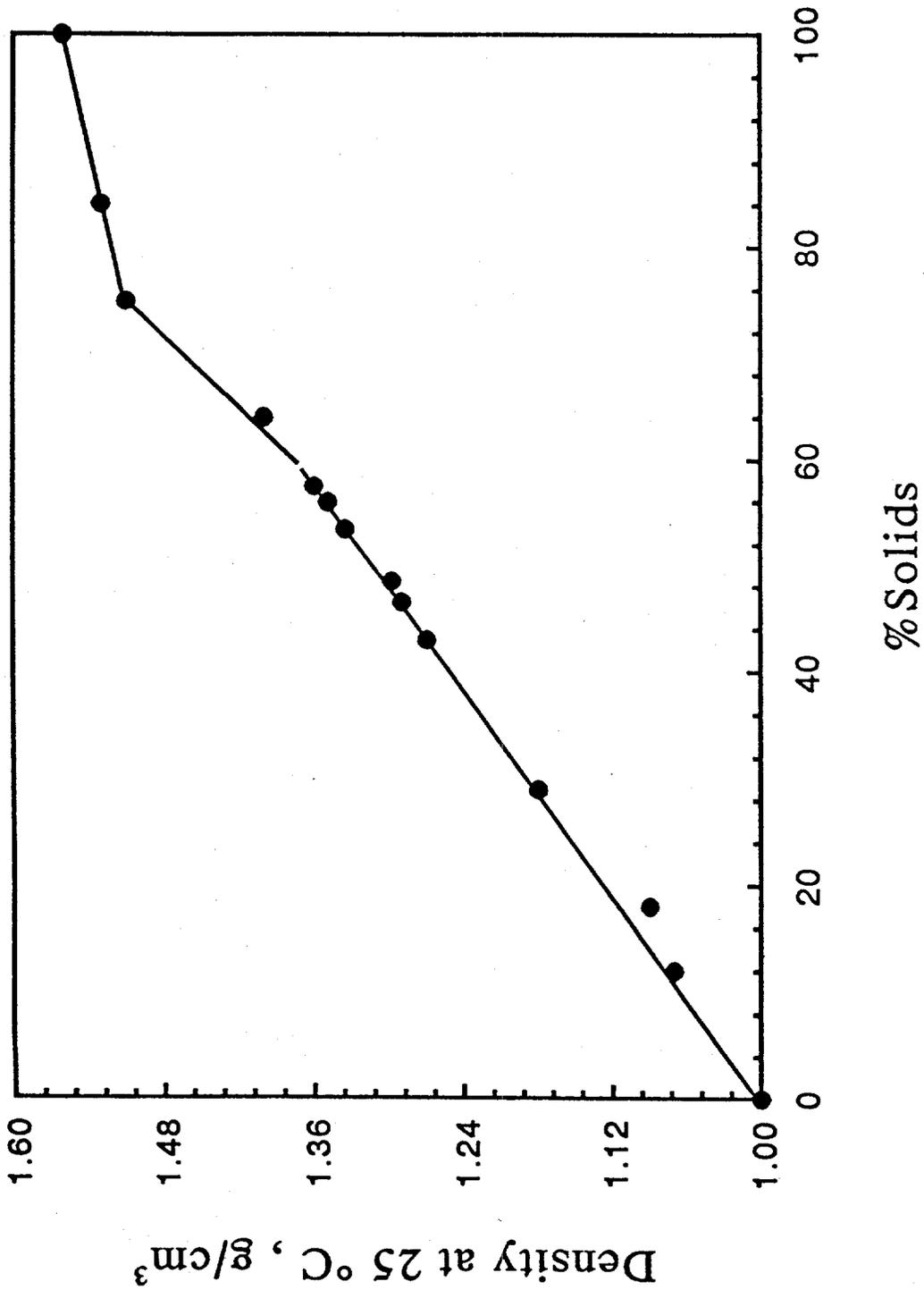


Figure (47): Density of an Experimental Black Liquor at 25 °C.

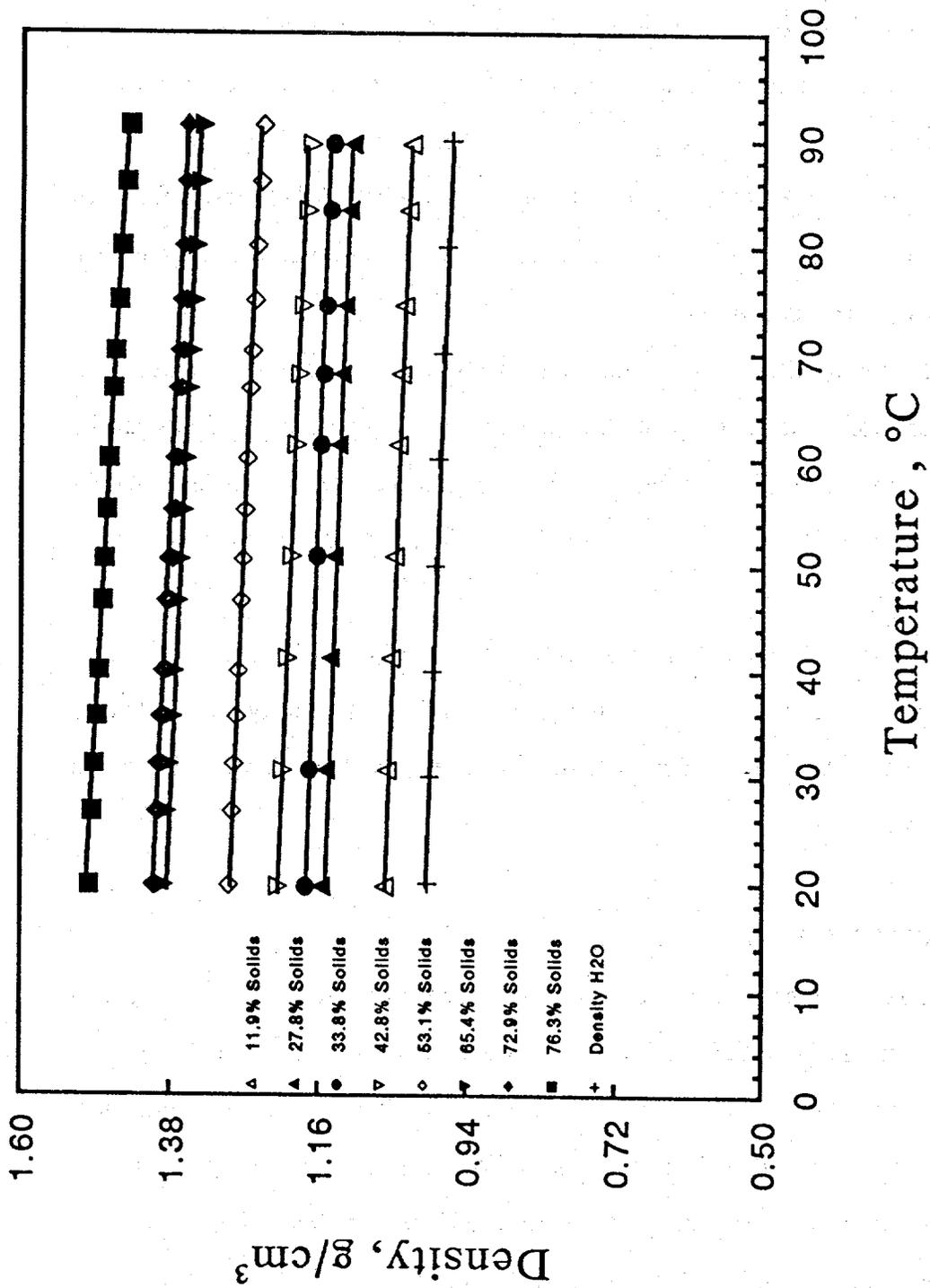


Figure (48):Densities of an Experimental Slash Pine Kraft Black Liquor.

think that the first is the same that occurs at about -85°C and 42-44% solids. If so, precise density measurements should permit defining the boundary for this transition up to at least 100°C . The second transition is puzzling, but does occur in the same solids region where the excess heat capacity is greatest, where the BPE elevation becomes almost flat, and where viscoelastic effects become significant. Also, the change in density that occurs in increasing solids concentration from 80-85% solids to 100% solids is small. All of these effects are consistent with the proposition that black liquor in this region is in a highly associated, almost structured, state.

In the lower solids concentration region, density at any temperature is a linear function of solids concentration and corresponding state principles can be used to correlate density at other temperatures. No suitable method for reducing the data for the intermediate or high solids regions in a similar manner has yet been developed.

Complete data on all liquors has been taken below 60% solids. Some data is yet to be taken at solids levels above 60%, and this should be completed by November, 1993. Correlation will be developed for these data beginning in November.

WORK TO BE DONE

Except for some measurements of density and thermal expansion at solids concentrations above 60% and a few possible checks of results that may have experimental blunders, all experimental work on our liquors has been completed. This consists of complete data on almost 40 liquors made in two designed pulping experiments and data on some properties and analyses for sixteen liquors made in another pulping experiment, all with slash pine, as well as data for some mill liquors. The major effort at present is directed toward systematizing and critically

evaluating this data as data reduction is performed using models described in this report.

A second, concurrent effort evolves developing empirical correlations between pulping conditions for the main experiment and the data reduction correlation constants. This will continue for some time yet. As an extension, this effort will be directed toward developing the correlations ultimately desired—correlations between solids composition and the constants for properties correlations. This effort is expected to continue through the extension to develop computer software.

The final effort is to develop computer software so that results of this work can be used easily for design and optimization. Our goal is to complete this effort by 1995.