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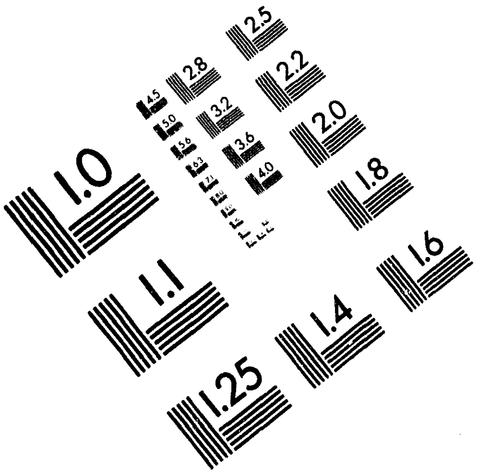

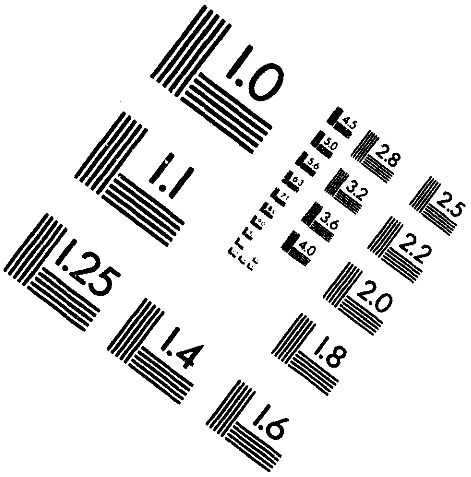

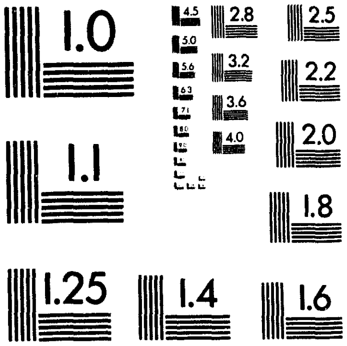

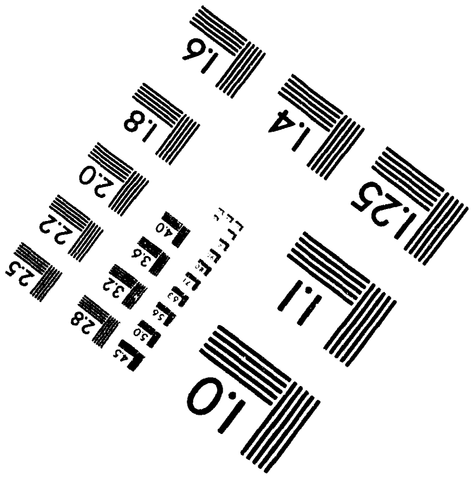

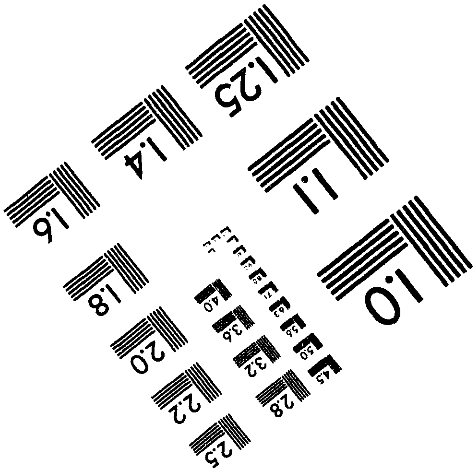

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A COMPREHENSIVE PROGRAM TO DEVELOP CORRELATIONS FOR THE PHYSICAL PROPERTIES OF KRAFT BLACK LIQUOR

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SUMMARY

Experimental effort for the program to evaluate physical properties of kraft black liquors is now proceeding well. Experimental work includes pulping, liquor analysis, lignin purification and characterization, vapor-liquid equilibria, heat capacity, heats of solution and combustion, and viscosity measurements. Measurement of thermal conductivity has not yet begun. Collection of the data necessary for development of generalized correlations is proceeding, but will require about two more years.

The digester is operating very well. It is now possible to operate the digester as a closed, rotating reactor or as a batch reactor with liquor circulation. When operated with liquor circulation, temperatures within the chip bed can be monitored during cooking. Cooking is reproducible, and cooks are being performed to produce liquors for experimental studies. The digester could be further modified to permit us to conduct rapid exchange batch pulping or to permit us to simulate continuous pulping.

Liquors to be used in experimental studies are concentrated in our large scale evaporator or in our small scale evaporator. The large scale evaporator is used to concentrate liquors to about 50% solids for storage and for use in studies requiring high solids liquors. The small scale evaporator is used for preparing final samples to as high as 85% solids and for measuring vapor-liquid equilibria.

Liquors are now routinely analyzed to determine all components, except higher molecular weight organic acids and extractives. Lignin determination by UV-visible means has been improved. Lignin purification from black liquor has been improved and lignin molecular weights are determined routinely. Work on lignin molecular weight distribution is still not satisfactory, but recent developments holds promise.

Comprehensive measurements of thermal properties are proceeding. Vapor-liquid equilibria are determined in our small scale evaporator at concentrations up to as high as 85% solids in some cases. Results indicate that the heat of vaporization is nearly constant. Heat capacities and heats of solution are being determined for black liquor solutions with the use of our DSC and adiabatic calorimeter. Heats of combustion are being determined for black liquor solids. These data are needed for development of complete enthalpy-concentration relations. Densities and thermal expansions are being determined routinely. It is now possible to make these measurements at solids concentrations up to about 80%.

Viscosity measurements for liquors are now being made at concentrations up to 85% solids. It is now possible to make measurements directly at all conditions of concentration, temperature, and shear rate that are likely to be experienced in recovery systems. A data bank of viscosity results for liquors is being developed as rapidly as possible. This work requires the use of eight viscometer configurations to obtain complete data for one liquor.

Our program is now proceeding smoothly. However, the labor necessary for cooking and liquor concentration is much greater than was estimated, and the labor needed for complete study of properties is large. Also, the delays in beginning the program, caused primarily by the decision of the University administration to build a new structure to house our digester and evaporator, have not been overcome to date. Work is in progress on a planned basis to accelerate data collection and data reduction as much as possible.

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DIGESTER

As reported in our progress summaries and in our July, 1989 Summary Report to DOE, our batch digester is operating very well. Full details of the components of the digester system with a process schematic and process control description are given in the July, 1989 Summary Report, and we will not repeat the description. Only modifications, procedures, or explanation of process problems will be described.

The digester has been operated a considerable number of times as a closed, rotating autoclave. There have been no problems experienced in consistently loading chips with the chip basket we are using nor in handling white liquor. After the digester is loaded with the chip basket, the steam to the jacket is started and the digester heated with the vent open to expel air. Alternatively, air can be removed from the digester by vacuum. After is is vented from the digester, white liquor is pumped into the digester through the batch meter. About 1-2 minutes are required to load white liquor, and the white liquor is metered to within ± 0.1% of the volume charged. We have found the Foxboro batch meter to be extremely reliable, reproducible and accurate. After loading of white liquor is completed, rotation of the digester is begun and continued at constant speed during the completion of the heat-up and cooking cycle.

Due to rotation of the digester, the temperature within the digester cannot be measured while the digester is rotating. However, measurements were made in preliminary experiments with the digester full and stationary to determine the heat up time and temperature difference between the digester contents and the condensing steam temperature in the jacket as a function of condensing steam temperature. The digester responded as a first order system. The time constant for the system was calculated and the steam controller tuned to yield a heat up time of about 10 minutes and a temperature control band of ± 1°F or better with no offset.

When the cooking cycle is completed, the rotation is stopped, the digester is connected to the evacuated receiver, and the liquor is drained into the receiver within 10 seconds or less. The time necessary to connect the digester to the receiver introduces some variation. This normally requires about one minute for two people. The time necessary for connection is counted as cooking time, even though the digester is stationary, since the chips and liquor are in contact at the cooking temperature.

After draining the black liquor, the digester drain value is closed, and wash water at 160-180°F is metered into the digester. The wash water is held in contact with the chips for 10 minutes and then drained into the receiver and combined with the black liquor. This washing procedure is repeated to give a combined black liquor product consisting of the drained black liquor plus two volumes of wash. This product contains about 97+% of the soluble solids from the cook and has a concentration of 6-13% solids, depending upon working conditions. The combined liquor and washes are cooled in the receiver to about 85-95°F and then discharged through a 5m polishing filter into a portable plastic tank. The receiver is equipped with a vent to release gases under flow control to a burner to oxidize volatile reduced sulfur compounds before release to the atmosphere. However, use of this system has been found to be unnecessary, since the small quantity of these gases can be diluted with air in the vent line so that there is no detectable odor within about 20 feet of the digester building during venting.

While the combined black liquor and washes are being cooled in the receiver, additional wash water is added to the digester. After the combined black liquor and washes are discharged from the receiver, the additional wash water is drained from the digester to the receiver, and the pulp in the digester is further washed with hot water that is fed to the digester on flow control through the batch meter. About 100 gallons of final wash water is used. After sampling, this final wash water is discharged through the polishing filter to the sewer which feeds into the University sewage treatment system.

The head is removed from the digester, the chip basket is removed from the digester, and the chips unloaded from the basket.

A very reasonable material balance can be performed; there is a problem in determining the oven dry weight of pulp produced due to oven volume limitations. The quantities charged can be determined quite accurately. The chips to be used are thoroughly mixed and moisture determined for three samples of 300-500 grams each of the chips. The wet chip load is about 63-70 lbs ± 0.1 lbs. Fresh white liquor is made for each cook at a concentration of chemicals needed to yield the proper sulfidity and effective alkali at the liquor-to-wood ratio to be used. Normally, 12-16 gallons of white liquor is loaded. This quantity is metered at an accuracy of better than ± 0.02 gallon; therefore, metering is accurate to within ± 0.2% or better. The two initial washes are also 12-16 gallons each and are metered into the digester at the same accuracy. Thus, the uncertainty in oven dry wood charged is about ± 0.1 lbs. The total charge, including the two washes is about 375 lbs ± 0.6 lbs.

Determination of masses and solids contents of product streams is more difficult. It is impossible for us to dry the entire pulp batch. Three samples of the pulp are dried, but the variation is ± 0.4% for the samples vs. about ± 0.15% for the chips. Thus, our uncertainty in determining the mass of oven dry pulp is about ± 0.3 lbs out of about 32 lbs or about ± 1%. Liquid products, the combined black liquor and two washes and the final wash, can only be determined within about ± 1% and ± 0.3%, respectively. The solids contents of these liquid products can be determined with an accuracy of better than ± 2% of the composition. As worst, the material balance on solids can be in error by about 2% and the yield can be in error by about 2.4% with the methods now in use.

After considerable development, a liquor circulation system has been installed and is being used successfully. This system permits us to use the digester as a circulating batch digester. It also permits us to measure temperatures within the chip bed during digestion. The key to this system is a canned centrifugal chempump that is capable of operation at up to 400°F and 300 psi. However, this pump must be protected. The circulating loop contains a screen filter with a minimum mesh size of 80 mesh to prevent chips and fibers from entering the pump. The seal between the pump casing and pump can is fed with water metered with a Lapp pump with pressure controlled to provide a small differential pressure across the seal to prevent leakage of liquor into the pump can. The system has been designed and is operating to provide a leakage of water from the can into the liquor of about 2 ml per minute during operation. The pump is capable of providing a liquor circulation rate of more than 30 gpm, which gives a liquor turnover rate of 24-32 seconds. The liquor contained in the circulation loop (outside the digester) is about 3-4%.

This system has a number of advantages over using the digester as a rotating autoclave. Since temperature can be measured within the digester, the heat up rate and digestion temperature can be measured directly, instead of being indirectly determined from process control calculations. Temperature is measured at four points within the digester during cooking. Experimental work has shown these temperatures to be identical within normal measurement error. The cooking time can be controlled more precisely and washing can be accomplished more conveniently, since no piping connections must be changed after cooking begins. The cook is ended by opening the drain valve to the receiver; thus, cooking time can vary by only about 10 seconds or less. Wash water can be circulated through the chip bed to give more effective washing. As a result, the cooking time, heat up time, and cooking temperature are determined much more precisely with this system and results show that the cook is uniform within the chip bed.

Further future improvements and additions are planned. When funds are available, a strain gage pressure indicator will be added to permit digester pressure to be measured accurately and recorded. This will cost an additional $850 to install. A second chip basket will be fabricated to speed up operation. This will cost approximately $3000. Two additional 50 gallon liquor tanks rated at 300 psi at 400°F will be installed and mounted on load cells. These tanks will be piped through a manifold to the black liquor circulation pulp and through the Foxboro batch meter. With this system, black liquor could be exchanged during pulping to permit us to perform rapid exchange batch pulping or to simulate continuous pulping. The estimated cost for this addition is $23,000. Also, we would like to install a flow meter on the circulation loop to be able to measure the liquor circulation rate. This could cost up to $6000. Finally, the system has been designed to permit us to install a chip blow tank. If this were done, the washing procedure could be changed in the future. Installation of a chip blow tank with filter screens and wash piping would cost an estimated $10,000. Thus, future modifications to provide a totally flexible pilot plant digester for pulping would cost an estimated $43,000. It is worth noting that such a facility would have general pulping capability, not just capability for kraft pulping, and could even be used for biomass conversion with only minor modifications.

Thusfar, a considerable number of kraft pulping cooks have been made in both the rotating and circulating modes of batch operation. Considerable experimental time was consumed in developing procedures, calibrating elements of the system, and performing trial experiments. About six trial cooks were made for calibration and for development of procedures were completed before satisfactory results were obtained. Since that time, nineteen successful cooks have been made.

The conditions for the successful cooks and the results are given in Table 1. These cooks were all made with slash pine chips with the white liquor adjusted to an 85% causticizing efficiency and a 95% reduction efficiency. The liquor-to-wood ratio used was 4/1 in all cases.

Initially, there was some difficulty in determining Kappa number at Kappa numbers above 60. Using the exact procedure as specified by TAPPI, there was insufficient time for reaction with lignin in the pulp at these low levels of lignin removal. Extension of the time for reaction during the Kappa number test yielded more reproducible and apparently more accurate results. This modification of the TAPPI procedure is now being used for determinations when high Kappa numbers are expected.

Pulping requires significantly more manpower than had been anticipated. The steps required for performing a cook with material balance are:

1. Mix chips, sample, and determine chip moisture.
2. Load known weight of chips into basket and load basket into digester.
3. Calculate white liquor chemical requirements, weigh chemicals, and load into white liquor tank with metered volume of water.
4. Mix and heat white liquor.
5. Evacuate digester and receiver.
6. Conduct cook.
7. Wash pulp with two metered volumes of water.
8. Cool black liquor plus two washes in receiver to below 95°F; discharge liquor through filter into portable storage tank.

TABLE 1
Conditions and Results for Kraft Cooking of Slash Pine

Liquor Code	% S	% EA	T, °F	t, min	Kappa No.
ACAFX007	12.5	14.5	340	60	25.8
ACAFX008	27.5	14.5	340	60	43.5
ACAFX009	27.5	14.5	340	20	96
ACAFX010	27.5	17.5	340	60	30.9
ACAFX011	42.5	14.5	340	60	36.5
ACAFX012	27.5	11.5	340	60	92
ACAFX013	27.5	11.5	340	60	90.7
ACAFX014	27.5	14.5	320	60	93
ACAFX015	27.5	14.5	360	60	17.5
ABAXX001	27.5	14.5	340	60	39.6
ABAXX002	27.5	14.5	340	60	44.8
ABAXX003	27.5	14.5	340	60	47.2
ABAXX004	27.5	14.5	340	20	99.3
ABAXX005	27.5	14.5	340	100	25.4
ABAXX006	27.5	14.5	320	60	91.7
ABAXX007	27.5	14.5	360	60	24.6
ABAXX008	27.5	11.5	340	60	91.8
ABAXX009	27.5	17.5	340	60	25.4
ABAXX010	12.5	14.5	340	60	24.6

*ACAFX represents kraft cooks of slash pine in rotating digester.
ABAXX represents kraft cooks of slash pine with liquor circulation.

9. Wash pulp with about 100 gallons of metered water, mix water in receiver, sample water, and discharge water through filter to the sewer.
10. Weigh portable storage tank containing black liquor plus two washes to determine mass and sample liquid.
11. Open digester, remove chip basket, unload pulp, mix pulp, weigh, and take three samples for moisture and Kappa number determination.
12. Determine percent solids of black liquor plus two washes and of final wash.
13. Determine moisture and Kappa number for three pulp samples; report average values.
14. Reported data to include pulping conditions, chip load and moisture, liquor masses and percent solids, pulp mass and moisture, and Kappa number and yield.

A cook requires 3.7 - 4.5 man-days of effort to complete. As designed, a cook normally yields about half of the black liquor needed for a complete study of properties; that is, a cook normally yields 3 - 3.6 gallons of black liquor at 50% solids. This scale of operation was chosen purposely to conserve capital and to require duplication of cooking for those conditions chosen for exhaustive testing of black liquor properties. Thus, each pulping condition requires 7.4 - 9 man-days of effort, or 1.5 - 1.8 man-weeks of effort to complete. Our maximum yearly capacity at present is 27-33 cooking conditions if a technician is used full-time for pulping. At present, only about 70% of a full-time technician is devoted to this work; therefore, our expected rate is 19-23 cooking conditions per year. This rate could be increased to 40-50 per year if another technician and a second chip basket were available. This would cost the project an additional estimated $3000 for capital plus $28,000 per year for labor.

Over the next two years, we anticipate running 38-46 new pulping conditions under present circumstances. These, with conditions already run and with additions of mill liquors, should provide a data base of 60-80 liquors. If funds were available for additional manpower, this could be increased to a data base of 80-100 liquors.

LARGE SCALE EVAPORATOR

Liquors made in our experimental digester and liquors received from mills that are to be incorporated into our properties work are concentrated in our large scale evaporator system to 40-50% solids for use. Two black liquors made at the same cooking conditions are combined if the Kappa numbers, yield, and chemical analyses results are the same. This liquor is then concentrated in our Artisan evaporator system, described in our July, 1989 report, to 26-30% solids and soap is separated from the concentrated liquor. Control of this system is very good. Normally, the evaporator is operated at 0.4 atmospheres absolute (5.88 psia) with a jacket steam pressure of 1.61 atmospheres absolute (23.7 psia) and a liquor feed rate of about 0.27 liters per minute (0.071 gpm) yielding a concentrated liquor and a clear, nearly water white condensate. The time necessary for evaporation of the combined liquors is 16-20 hours, or 2 - 2.5 days. The rate is limited, because a significant portion of the scraped heat exchanger surface is used to heat the feed liquor to boiling. This rate could be increased by 20-30% if a feed preheater were added to heat the liquor feed to the boiling temperature before introduction into the evaporator. Estimated capital cost for addition of the preheater plus controls is $4300 - 4800. Because of this cost, a preheater has not been added.

The concentrated, soap separated black liquor is rerun in the large scale evaporator to concentrate the liquor to 40-50% solids for cold storage and for use in properties studies. The same evaporator pressure and jacket steam pressure used in the previous step are used for this evaporation step, but the liquor feed rate can be increased slightly to an average of 0.34 liters per minute (0.09 gpm). The average time necessary for this concentration step for the combined black liquors is about 3 hours or 0.38 days. Thus, concentration of liquors from two experimental cooks of from a mill requires about 2.5 - 3.0 days. At present, this is not a bottleneck, since cooking to produce the liquor for concentration requires 7.4 - 9 man-days. Even if cooking is accelerated as proposed in an earlier section, the large scale evaporator will have sufficient capacity without addition of a preheater. Therefore, addition of a preheater is a low priority item.

While the evaporator system runs quite well after start-up, it cannot be left to run completely unattended. It is attended by the technician performing cooking, but start-up, clean out, and soap separation does require about an additional man-day of labor per concentration. Thus, cooking and concentration require 8.4 - 10 man-days per cooking condition.

The black liquor that has been concentrated to 40-50% solids is packaged in 18.9 liter (5 gallon) HDPE containers and stored at about 4°C (40°F) until used for properties studies.

LIQUOR ANALYSIS

Chemical analysis of the black liquors and molecular weight characterization of the lignin separated from black liquor are very important parts of our total program, since our ultimate goal is to relate physical properties to black liquor composition. A secondary, but important, goal of this part of our program is to relate black liquor composition to pulping conditions. Since we are conducting rather exhaustive, statistically designed, multi-variable, multi-level pulping experiments, we should be able to also relate black liquor composition to pulping conditions. This will yield the first complete study of pulping that relates both liquor composition and pulp yield and delignification data to pulping conditions.

Analyses can be divided into six categories:

1. Inorganic Anions
2. Inorganic Cations
3. Low Carbon Number Organic Acids
4. Lignin
5. Lignin Molecular Weight
6. TAPPI Tests

The only components that are not being analyzed for on a routine basis or for which a method is not under development are high carbon number organic acids and extractives. For any one wood species, these do not seem to vary much with conditions of kraft pulping that would be used commercially. Since there are practical limits to capital, expertise available, and manpower, these components are not determined on a routine basis.

INORGANIC IONS

The concentrations of inorganic anions in the black liquor are completely determined, principally by the chromatographic methods developed in our earlier program, which methods have now been accepted as standards for analysis by TAPPI. Continued improvements in techniques, columns, and calibrations have been made, and the inorganic anions (with the exception of sulfide) are determined by our ion chromatography methods. Determinations require three separate chromatographic analyses with each made with different columns or carriers. Inorganic anions determined by ion chromatographic methods are: sulfate, sulfite, thiosulfate, carbonate, oxalate, and chloride. These are determined for the black liquor as obtained from the digester and are normally reported as gms/gm solids.

While an ion chromatographic method for determination of sulfide in black liquor was developed in our earlier program and has been adopted by TAPPI as a standard method, we no longer use this method. The method is complex and requires extreme care in diluting and manipulating the sample to be analyzed in order to obtain precise and reproducible results. We have developed an easier and more reliable method to determine sulfide ion concentration in black liquor. This method is based upon use of an ion selective electrode. Our recent work has shown that the response of the electrode used is not affected by other black liquor ions (the electrode is selective for sulfide at better than 1000/1 in the presence of other anions in black liquor) and can be used to obtain quantitative results over a range of concentrations from less than 1 x 10^{-4} moles/liter to about 0.2 moles/liter. Full details for this method are to be included in a publication being prepared.

Anion concentrations of black liquors being used for our properties studies are presented in Table 2.

INORGANIC CATIONS

The concentrations of inorganic cations that are always present in black liquor--sodium, potassium, calcium, and magnesium--are determined for every black liquor studied. Occasionally, the concentrations of aluminum and iron are determined, if there is reason to suspect these ions to be present in significant quantities; concentrations of these ions are usually determined for black liquors from mills that are included in our properties study. The concentrations of all cations, except sodium, are determined by atomic absorption analysis methods.

TABLE 2
Black Liquor Analysis

Lab ID: Type:	ACAFX007 pre-evap.	ACAFX008 pre-evap.	ACAFX009 pre-evap.	ACAFX010 pre-evap.	ACAFX011 pre-evap.
Components, g/g solids					
chloride	.0000588	.000161	.000156	.0000686	.000257
sulfite	.00552	.00550	.00388	.00574	.00806
sulfate	.0646	.0347	.0729	.0564	.0234
oxalate	.0103	.00979	.0103	.00341	.00298
thiosulfate	.0721	.0595	.0578	.101	.0654
carbonate	.0295	.0165	.0381	.0324	.0128
lactate/glycolate	.0428	.0345	.0343	.0236	.0329
formate	.0617	.0491	.0500	.0340	.0376
acetate	.0346	.0286	.0331	.0333	.0232
sulfide	.00605	.00562	.0000618	.0324	.0285
Lignin	.293	.281	.252	.123	.337
aluminum	.0000148	.0000365	.0000199	.0000153	.0000265
calcium	.0000815	.000315	.000152	.000169	.000185
iron	.0000309	.0000868	.0000552	.0000373	.0000530
magnesium	.0000519	.000301	.000201	.0000661	.000141
phosphorus	.0000154	.0000457	.0000574	.0000746	.0000331
potassium	.000370	.000594	.000146	.000864	.000618
sodium	.1369	.1711	.1441	.2503	.1781
pH	13.67	13.30	10.85	13.88	13.64
%solids, %	16.2	4.38	9.06	11.8	9.06
sulfated ash, %					
residual active alkali	9.03	4.00	0	20.2	8.99

TABLE 2 (continued)

Lab ID: Type:	ACAFX012 pre-evap.	ACAFX013 pre-evap.	ACAFX014 pre-evap.	ACAFX015 pre-evap.
Components, g/g solids				
chloride	.000388	.000395	.000417	.000359
sulfite	.00548	.000807	.00270	.00244
sulfate	.0538	.0372	.0451	.0150
oxalate	.00308	.00696	.00593	.00179
thiosulfate	.00193	.0458	.0627	.0302
carbonate	.0560	.0498	.0455	.0381
lactate/glycolate	.0365	.0435	.0300	.0306
formate	.0557	.0463	.0436	.0405
acetate	.0367	.0258	.0290	.0237
sulfide	.0184	.00894	.00393	.0122
Lignin	.383	.405	.285	.370
aluminum	.0000369	.0000410	.0000358	.0000441
calcium	.000169	.000220	.000169	.000144
iron	.0000738	.000118	.0000554	.0000279
magnesium	.000184	.000154	.000179	.000197
phosphorus	.0000621	.0000386	.0000586	.0000395
potassium	.000796	.000578	.000782	.000627
sodium	.15336	.13504	.13402	.10228
pH	11.92	13.06	13.51	13.01
%solids, %	10.3	8.30	6.14	8.61
sulfated ash, %				
residual active alkali	6.12	2.95	3.21	2.49

TABLE 2 (continued)

Lab ID:	ABAXX001	ABAXX004	ABAXX004 duplicate run	ABAXX005	ABAXX005 duplicate run
Type:	pre-evap.	pre-evap.	pre-evap.	pre-evap.	
Components, g/g solids					
chloride	.00458	.00387	.00342	.00474	.00487
sulfite	.00811	.00947	.00386	.0109	.0104
sulfate	.0120	.0123	.00958	.0162	.0135
oxalate	.00276	.00237	.00218	.00498	.00288
thiosulfate	.00881	.0442	.0589	.0382	.00969
carbonate	.0361	.0484	.0572	.0643	.0571
lactate/glycolate	.0344	.0311	.0220	.0452	.0371
formate	.0378	.0407	.0285	.0471	.0390
acetate	.0198	.0299	.0219	.0230	.0199
sulfide	.0170	0	.00387	0	.0217
Lignin	.363	.2850	.305	.280	.390
aluminum					
calcium	.000130	.000141	.000169	.000130	.000169
iron					
magnesium	.000169	.000171	.000213	.000798	.000335
phosphorus					
potassium	.000369	.000396	.000506	.000793	.000444
sodium	.1766	.1642	.1972	.1751	.1756
pH	13.01	12.88	13.08	11.87	13.04
%solids, %	14.42	7.42	7.76	4.42	14.04
sulfated ash, %	36.6	36.7	38.6	35.4	36.0
residual active alkali	10.8	5.42	6.30	2.31	6.36

TABLE 2 (continued)

Lab ID:	ABAXX006	ABAXX006 duplicate run
Type:	pre-evap.	pre-evap.
Components, g/g solids		
chloride	.00537	.00454
sulfite	.0101	.00754
sulfate	.0132	.0150
oxalate	.00245	.00260
thiosulfate	.0332	.0312
carbonate	.0611	.0610
lactate/glycolate	.0316	.0234
formate	.0436	.0398
acetate	.0257	.0256
sulfide	0	0
Lignin	.289	.306
aluminum		
calcium	.000570	.00144
iron		
magnesium	.000480	.000232
phosphorus		
potassium	.000450	.000527
sodium	.1784	.1832
pH	12.53	12.92
%solids, %	2.98	7.51
sulfated ash, %	32.3	35.7
residual active alkali	1.85	4.92

These are standard methods and can be used with no problems for analysis of black liquors.

Because of the high concentrations of sodium in black liquors, it is difficult to obtain precise results by using atomic absorption methods. After extensive trials, an ion selective electrode was found that is highly selective for sodium ion in black liquor, that is stable for long periods of time, and that yields a logarithmic linear response over a very wide range of sodium ion concentration. With our technique, sodium ion concentration can be accurately determined from about 5 moles/liter to less than 5×10^{-2} moles/liter.

Cation concentrations are normally reported as gm/gm solids in black liquor. Cation concentrations of black liquors being used for our properties studies are presented in Table 2.

LOW CARBON NUMBER ORGANIC ACIDS

The concentrations of formate, acetate, lactate, and glycolate in black liquor are determined by direct ion chromatographic analysis of black liquor using modifications of column and techniques for the method developed in our earlier program. The method we developed has been adopted as a test method by TAPPI.

Low carbon number organic acid concentrations, reported as gm/gm of black liquor solids, for black liquors being used in our properties studies are presented in Table 2.

LIGNIN ANALYSIS

Lignin analysis is quite involved and very important to our work, since lignin concentration and the molecular weight of the acid precipitatable lignin has been shown to affect properties, particularly rheological properties. Also, lignin analysis is important in interpreting pulping results. Extensive effort continues to be devoted to improvement or development of methods. These are directed toward determination of lignin concentration in black liquor, separation of lignin from black liquor and purification, and molecular weight characterization of separated, purified lignin. Work on lignin separation, purification, and molecular weight determination will be discussed in a subsequent section.

Determination of lignin concentration in black liquor suffers from a number of limitations, not the least of which is a lack of clear understanding and agreement on exactly what lignin is. Therefore, a detailed study was performed. Purified lignins obtained by acid precipitation from black liquor followed by purification by washing, extraction, and freeze drying were used as standards. The purity, weight average and number average molecular weight, and GPC response of these lignins were determined by methods to be described later. These lignins were dissolved in caustic and instrumental analyses performed. UV-visible analysis proved to be the most useful.

A study of the effects of lignin concentration, lignin molecular weight, lignin source, temperature, solvent solution pH, presence of selected ions other than sodium, and time on UV-visible response was performed. A summary of results of this study has been reported in a recent paper (72). A Perkin-Elmer Lambda 4C double beam UV-visible spectrophotometer with System 7 digital control is used. The instrument is equipped with a circulating temperature bath to maintain the sample and reference cells at constant temperature to within ± 0.1°C or better. The spectra were determined from 190 to 500 nm with a slit of 0.25 at a scan rate of 60 nm/minute with a response of 3.

Spectra were determined for lignin dissolved in caustic, DMF, THF, and DMSO. In each case, the reference liquid was the solvent used. At room temperature, lignin exhibits a sharp absorption peak at the same wavelength, 283 nm, in DMF, THF, and DMSO. For THF solution there is a second, maximum

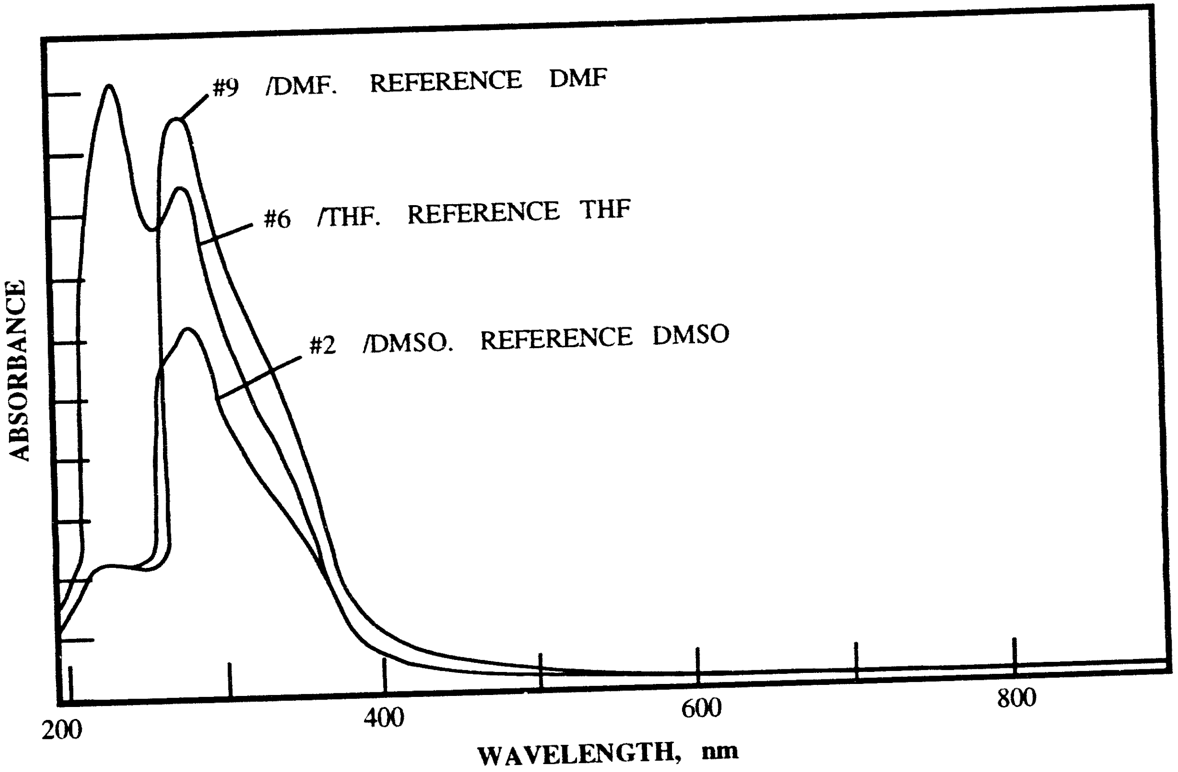


FIGURE 1. UV - Visible Spectra of Software Kraft Lignins in Organic Solvents

peak at 240 nm that does not appear for DMSO or DMF solutions. The UV-visible spectra of softwood lignin in DMF, THF, and DMSO are shown in Figure 1. It does appear that the guaiacol absorption band at about 280 nm is the most reliable absorption for softwood lignin in organic solvents.

The UV-visible spectrum of purified softwood lignin dissolved in 0.1 N NaOH (pH = 13) at 25°C is shown in Figure 2. The spectrum exhibits a broad band of low level absorption between 190 and 210 nm, a sharp absorption peak near 215 nm (in the 210-220 region), decreasing absorbance to about 270 nm, an absorbance "platform" between 270 and 300 nm, and slowly decreasing absorbance thereafter. Also shown in Figure 2 are spectra for a mill softwood and an experiment cook softwood liquor adjusted to pH = 13. These spectra show the same absorption peak at 210-220 nm and the same absorption "platform" at 270-300 nm as does the purified lignin. The spectra for a mill hardwood liquor, also shown in Figure 2, is different in that there is no absorption "platform" at 270-300 nm; however, there is a peak absorption at 210-220 nm.

Even though peak absorbance for both hardwood and softwood black liquors occurred at 210-220 nm, the absorbance at 280 nm was chosen for analysis for reasons that will be explained in detail.

Since we are interested in developing a reliable method for determination of lignin in black liquor, which as normally aqueous solutions, the most useful media is caustic solution at high pH. We examined the spectra of 0.01 N (pH = 12) and 0.1 N (pH = 13) NaOH solutions. NaOH solution absorbs UV strongly in the low wavelength range, and the absorption range extends to higher wavelengths as the NaOH concentration is increased. However, no absorbance exists at above 240 nm for NaOH concentrations up to 0.1 N. Therefore, absorbance of NaOH can interfere at 210-220 nm. The absorbance for lignin at 205 nm and at 210-220 nm is saturated at lignin concentrations of 0.02 gm/liter and 0.08 gm/liter, respectively.

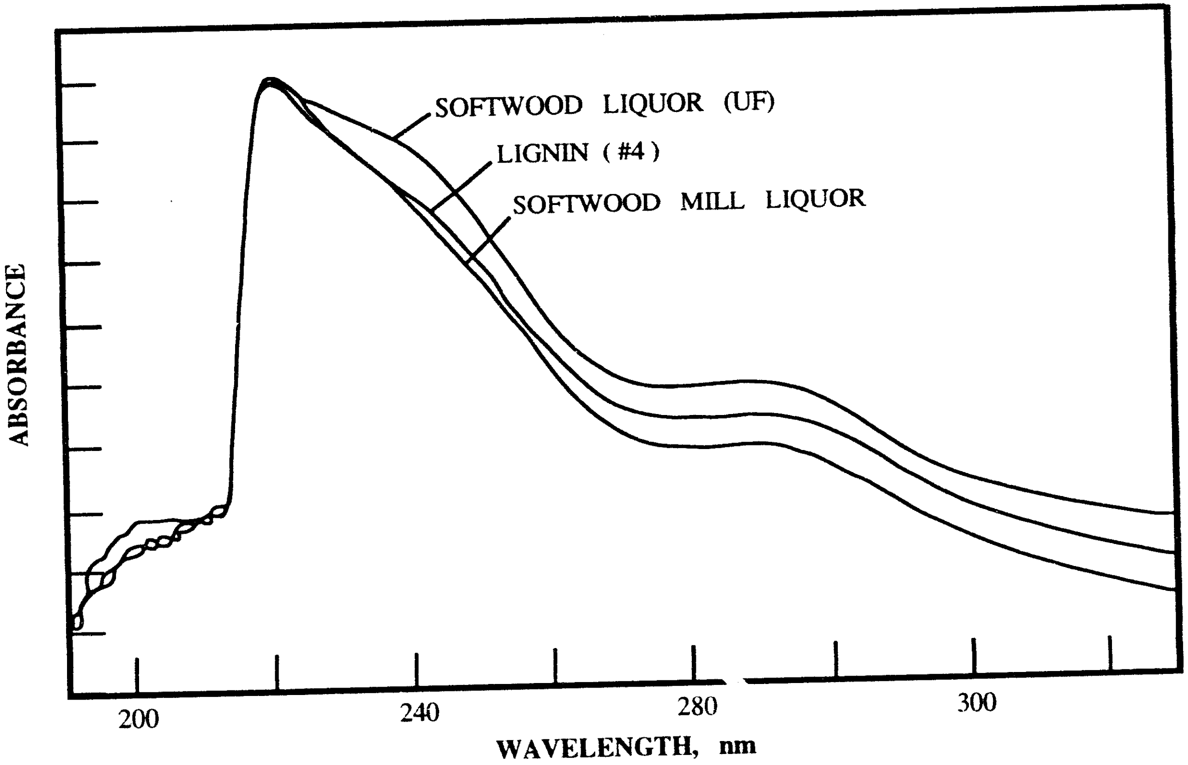


FIGURE 2. UV - Visible Spectra of Kraft Lignins in 0.1 N NaOH Solution

Furthermore, the relation between absorbance at 205 nm and concentration of lignin is not linear. For these reasons, the use of absorbance at 205 nm and 210-220 nm are not recommended as best for lignin determination.

Study was concentrated on the 270-300 nm band. The absorption "platform" in this region is saturated at about 0.15 gm/liter for lignin. At concentrations below 0.08 gm/liter, the absorbance of lignin is linear with lignin concentration in this region, as shown in Figure 3. Absorbance vs. lignin concentration is shown in Figure 3 for results at pH = 13 and pH = 12. As can be seen, there is a small effect of pH upon absorbance by lignin at pH ≥ 12. This effect was expected; therefore, a study of the effects of pH and method of sample preparation was made. Our results indicate the solution to be analyzed should not be diluted in such a way as to decrease the pH below 12 and preferably not below 13. When treated in this manner, lignin apparently cannot associate and absorbance is only slightly affected by pH; above pH = 13, there is no effect of pH on absorbance.

The effect of molecular weight on absorbance by lignin and the extinction coefficient were studied in detail using lignins recovered and purified from kraft softwood lignins. Five purified lignins were studied in detail. Purities of these lignins were determined by analyzing for impurities by ion chromatography, atomic absorption, and elemental analysis. The concentration of total impurities ranged from 4.38 to 5.42%. Metal ion content ranged from 0.037 to 0.049% with over half of the metal ion present as sodium. Organic acid content ranged from 2.29 to 3.20%. Inorganic anions ranged from 0.54 to 1.00%. Total sulfur ranged from 0.95 to 1.52%. More than 0.5% of the sulfur appears to be chemically bonded to the lignins, since it cannot be removed by physical means. Number average ($\overline{M}_n$) and weight average ($\overline{M}_w$) molecular weights were determined for these lignins by VPO and LALLS techniques developed earlier in this program. The ranges of

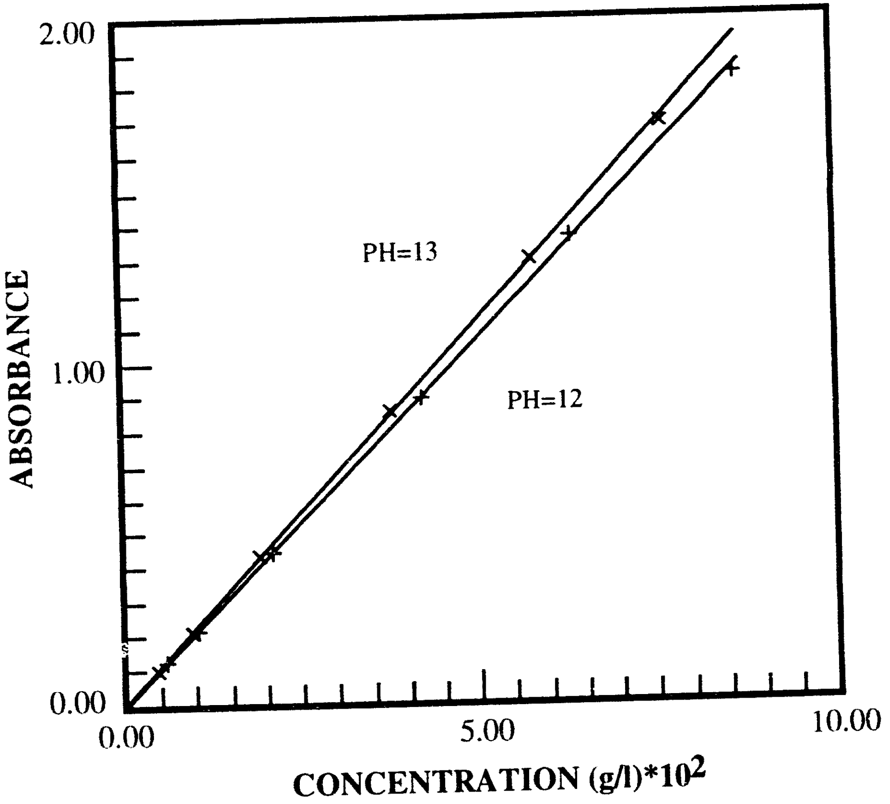


FIGURE 3. UV-Visible Absorption of Softwood Kraft Ligning at 280 nm in 0.1 NaOH Solution at Different pH

$\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_w / \overline{M}_n$ for the five lignins used were 2,250 to 6,090, 14,000 to 48,300, and 3.53 to 17.3, respectively. Extinction coefficients for these five lignins were detennined in NaOH solutions at pH = 12 and pH = 13 for absorbance at 280, 290, and 300 nm. The results are given in Table 3. No dependence of absorptivities on molecular weight or molecular weight distribution is discernable. Absorptivities given have been corrected for lignin purity, assuming that the impurities present do not absorb in the 270-300 nm range. On the basis of these results, an averaged corrected extinction coefficient of 23.7 $(\text{gm}\cdot\text{cm})^{-1}$ at 280 nm has been chosen for use in determining lignin concentration in solution.

The procedure adopted to determine lignin content in black liquors is as follows:

1. Determine black liquor solids concentration by a modification of the TAPPI method T650 pm-84 described earlier in our program reports.
2. Adjust the black liquor to a solids concentration of about 15% and a pH = 13.
3. Weigh 1.0 gm of the adjusted liquor and dilute to 50 ml with 0.1 N NaOH and use as analytical solution.
4. Prepare two dilutions of the analytical solution; dilute 1.0 ml of the analytical solution to 50 ml with 0.1 Na NaOH to form solution 1, and 2.0 ml of the analytical solution to 50 ml with 0.1 NaOH to form solution 2; this will yield two solutions with lignin contents between 0.012 gm/liter and 0.054 gm/liter with solution 1 having exactly twice the lignin concentration of solution 2.
5. Determine absorbances of solutions 1 and 2 at 280 nm and 25.0°C with 0.1 N NaOH as a reference.

TABLE 3

UV-Visible Extinction Coefficients for Softwood Kraft Lignins

Lignin No.	2	4	16	9	1	AVG.
$M_w \times 10^{-3}$	2.38	4.17	6.09	4.06	2.25	
$M_n \times 10^{-3}$	14.0	17.2	21.5	48.3	39.0	
M_w/M_n	5.88	4.12	3.53	11.9	17.3	
Extinction Coefficients, Experimental, 1/gm-cm.						
pH = 13						
280 nm	22.6	22.4	22.9	22.5	22.7	22.6
290 nm	22.8	22.4	23.2	22.8	22.8	22.8
300 nm	21.6	21.5	22.3	21.7	21.6	21.7
pH = 12						
280 nm		21.7	22.4			
290 nm		21.1	22.4			
300 nm		19.0	20.9			
Extinction Coefficients, Corrected for Lignin Impurities, 1/gm-cm.						
pH = 13						
280 nm	23.7	23.5	24.2	23.6	23.7	23.7
290 nm	23.9	23.5	24.5	23.9	23.8	23.9
300 nm	22.6	22.5	23.6	22.8	22.6	22.8
pH = 12						
280 nm		22.8	23.7			
290 nm		22.2	23.7			
300 nm		20.2	22.0			

6. Calculate the lignin concentration in the analytical solution as percent of black liquor solids by:

$$X_1 = 10.54\ A_1/S$$

$$X_2 = 5.27\ A_2/S$$

$$X = 1/2\ (X_1 + X_2)$$

where:

S = % black liquor solids in analytical solution

A_1, A_2 = absorbances for solutions 1 and 2, respectively

X_1, X_2 = % lignin in black liquor solids in solutions 1 and 2, respectively.

= % lignin in black liquor solids

Values of X_1 and X_2 agree within ± 0.2% or less, usually within ± 0.1% or less.

While the absorbance spectra for lignin from hardwood pulping is obviously different and the detailed study that we have performed on lignin from softwood pulping should be repeated for hardwood lignin, we believe that our work can serve as a basis for estimation of lignin concentration in hardwood black liquors. The extinction coefficients at 280, 290, and 300 nm for the hardwood black liquors that we have studied are nearly the same for a black liquor and the absorbance is linear with concentration at lignin concentrations estimated to be in excess of 0.1 gm/liter of lignin. At present, we are using the extinction coefficient determined for softwood lignin at 280 nm to determine the lignin concentration in hardwood black liquors.

The lignin concentrations of black liquors used in our properties studies, as determined by the method described, are given in Table 2.

TAPPI TESTS

In addition to the analyses performed on black liquors that have been described, a few other tests are performed as prescribed by TAPPI test methods. The pH of the liquor plus washes or the liquor as received from the mill is measured. The pH of liquors concentrated to 26-30% solids is also measured after soap separation.

Solids concentration is determined by a modification of TAPPI T650-pm-84. A sample of the liquor is diluted to about 15% solids or used as received. A weighed amount of liquor is placed on glass filter pads contained in a small (about 6 cm dia) aluminum foil dish that have been preweighed. The liquor and dish are dried to constant weight at 105°C (usually 4-10 hrs), allowed to cool in a dissicator, and weighed quickly. The percent solids is calculated from the net loss in weight. This analysis is performed in triplicate and the average percent solids reported. Detailed statistical study shows that this result should be accurate to within at least two parts per thousand, or within at least 0.03% solids at 15% solids. At 80% solids, values are accurate within 0.16% solids or better.

Solids contents for the liquors used in our program as received or made are given in Table 2. Solids contents reported in all properties work were determined in this manner.

Although simple, solids concentration determinations consume considerable effort, since this determination must be made for <u>every sample used</u>.

Sulfated ash is routinely determined for black liquors used in our program. This is determined by the TAPPI method. Values determined for the black liquors used in our program are given in Table 2.

Residual active alkali is determined by the TAPPI method for black liquors used.

LIGNIN MOLECULAR WEIGHT

Determination of lignin molecular weight is very important. It is necessary to recover as much of the lignin as possible from black liquor in as pure a state as possible. Recovery and purification are performed by acid precipitation and washing as previously described in earlier reports. The techniques used have been refined and standardized to yield lignins with purities above 98% currently without much change in the fraction recovered from black liquor. The purified lignins now being recovered are a tan to light brown color as compared to a dark brown to greenish black color for lignins recovered in the past.

For the extreme pulping conditions of the experimental design for pulping slash pine, the fraction of lignin recovered varies substantially from 56 to 75%. This is not unexpected. The fraction of purified lignin recovered for these pulping conditions, expressed as percent of lignin contained in black liquor solids as determined by UV-visible analysis, is given in Table 4.

Number Average Molecular Weight. Using VPO, number average molecular weights ($\overline{M}_n$) of the purified lignins, obtained by precipitation and washing from the pulping liquors as described above, have been determined. As before, $\overline{M}_n$ was measured by VPO using DMF as a solvent at 80°C and the values determined were corrected for the effects of impurities. Corrected values determined are given in Table 4. It is worth noting that these values for the extreme

TABLE 4
Molecular Weights of Softwood Kraft Lignins

Liquor	Lignin in Black Liquor, %	Lignin Recovered, %	M_n	$M_w \times 10^{-3}$	M_w/M_n
ACAFX007	29.3	55.9	903	24.93	27.61
ACAFX008	28.1	75.1	601	18.93	31.50
ACAFX009	25.2	57.4	853	35.45	41.56
ACAFX010	12.2	53.2	597	45.48	76.18
ACAFX011	33.7	62.3	968	28.25	29.18
ACAFX012	38.3	64.4	1220	21.54	17.66
ACAFX013	40.4	67.0	884	13.23	14.97
ACAFX014	28.5	58.2	999	31.67	31.70
ACAFX015	37.0	70.3	1116	21.11	18.92
AXAGB001	37.4	62.0	1313	20.33	15.48

pulping conditions are all lower than values determined for pulping conditions for the two level factorial experiment performed earlier.

Weight Average Molecular Weight. Earlier work has shown that, while optical corrections must be applied to raw light scattering results, these corrections can be theoretically justified and quantitatively determined by auxiliary measurements to permit one to determine weight average molecular weight of lignin if a solution of lignin at a temperature above the theta temperature for the lignin-solvent pair is used. Furthermore, work with lignins of varying molecular weights obtained from pulping the same wood shows that the first virial coefficient of the light scattering curves varies inversely with the square root of the weight average molecular weight, as it should. Furthermore, these molecular weights have been shown to correlate with rheological properties in a theoretically based manner. In spite of this, others have raised questions or doubts concerning the values determined.

To settle the doubts, additional work has been done. Replicate determinations made with DMF at 80°C exhibit an experimental precision of 10% or less. To determine if association is a factor, determinations were made at 80°C in DMF containing 0.1 M LiBr, which is claimed by many workers in the field to prevent lignin association. In one case, the difference in values determined in DMF, with and without LiBr, was 17%. In most cases, the difference was less than 10%; i.e., equal to or less than the maximum difference in replicate measurements in DMF only.

Determinations were also made with THF at 50°C. Theoretically, the molecular weight determined for the polymer should be independent of the solvent used. Determinations made in THF at 50°C were always lower than determinations made in DMF at 80°C, but the largest difference was 17%. While the difference is larger generally than is desirable, when one considers that the difference can be caused by the cumulative effects of solution preparation, lignin analysis, and errors in six experimental measurements made on each solution, differences of 17% or less show with reasonable certainty that the procedure is sound and yields a true measurement of the weight average molecular weight with a maximum uncertainty of 17% for a single measurement.

Values of weight average molecular weight ($\overline{M}_w$) for the lignins recovered from the liquors being used are given in Table 4.

Molecular Weight Distribution. While $\overline{M}_n$ and $\overline{M}_w$ values determined for lignins from black liquors by the methods described have been shown to be consistent with thermodynamics and theory and have been shown to be useful in correlating results such as viscosity, the methods are extremely laborious and provide no information on molecular weight distribution (MWD). Determination of $\overline{M}_n$ and $\overline{M}_w$ for a single lignin requires over 100 man-hours, even for an experienced operator. Equilibrium centrifugation conducted under very strict conditions can be used to determine MWD, but this is even a more laborious method than those being used to determine $\overline{M}_w$ and $\overline{M}_n$.

Size exclusion chromatography (SEC) can be used, but this is a secondary or derived method of analysis and requires calibration with standards. Unfortunately, standards for lignin calibration are not available. Nevertheless, SEC has been used extensively for molecular weight analysis of lignins because it is rapid and convenient. Unfortunately, the analyses are also incorrect. There are substantial questions concerning the application of SEC that involve polymer association, polymer-column interaction, solvent-column interaction, and calibration. As a result, past work with SEC can be used at best to yield relative information on the MWD of lignin. As a consequence, molecular weight averages determined by SEC are very questionable, if not quite incorrect, values of $\overline{M}_w / \overline{M}_n$

are certainly in error, and even the relative shape of the MWD, as shown by the raw chromatograph, may be in error.

A major effort to eliminate these problems and to develop a method for accurately and conveniently determining the MWD of lignin has been conducted for nearly two years. The basic concept is to conduct SEC with solvents above the theta temperature for which is has been shown that lignin association is negligible and to use $\overline{M}_n$ and $\overline{M}_w$ values determined by VPO and LALLS for internal calibration by resolution of moments of the distribution. This work, to date, has been largely unsuccessful; however, work does show the problems involved and does show that molecular weights for lignin determined by SEC in past work elsewhere are highly questionable.

A Waters Model 150C high temperature high pressure liquid chromatograph (HTHPLC) and a Dynamic Solutions Maxima 820 chromatography workstation have been used in this work. Columns supplied by Waters Division of Millipore and Jordi Associates, Inc. have been used. The Jordi columns are mixed bed or 10^3 Å limit columns. The Waters columns are limit columns with limits of 10^2, 10^3, and 10^4 Å. This particular instrument was chosen so that measurements could be made in solvents above the theta temperature for lignin to minimize or eliminate polymer association effects. A wide ranging study of columns, temperature, solvent, injection volume, concentration, and solvent flow rate has been made.

Association of lignin can have a profound effect on the apparent MWD of a lignin. Figure 4 shows a chromatogram for lignin in DMF at 50°C. Figure 5 shows a chromatogram produced by the same column for the same lignin in DMF at 85°C. The chromatogram at 50°C is shifted toward higher molecular weights and the shape of the chromatogram at high molecular weight is quite different from that obtained at 85°C. Addition of LiBr to DMF produces no significant change in the chromatogram for lignin in DMF at 85°C, indicating, as expected, that lignin does

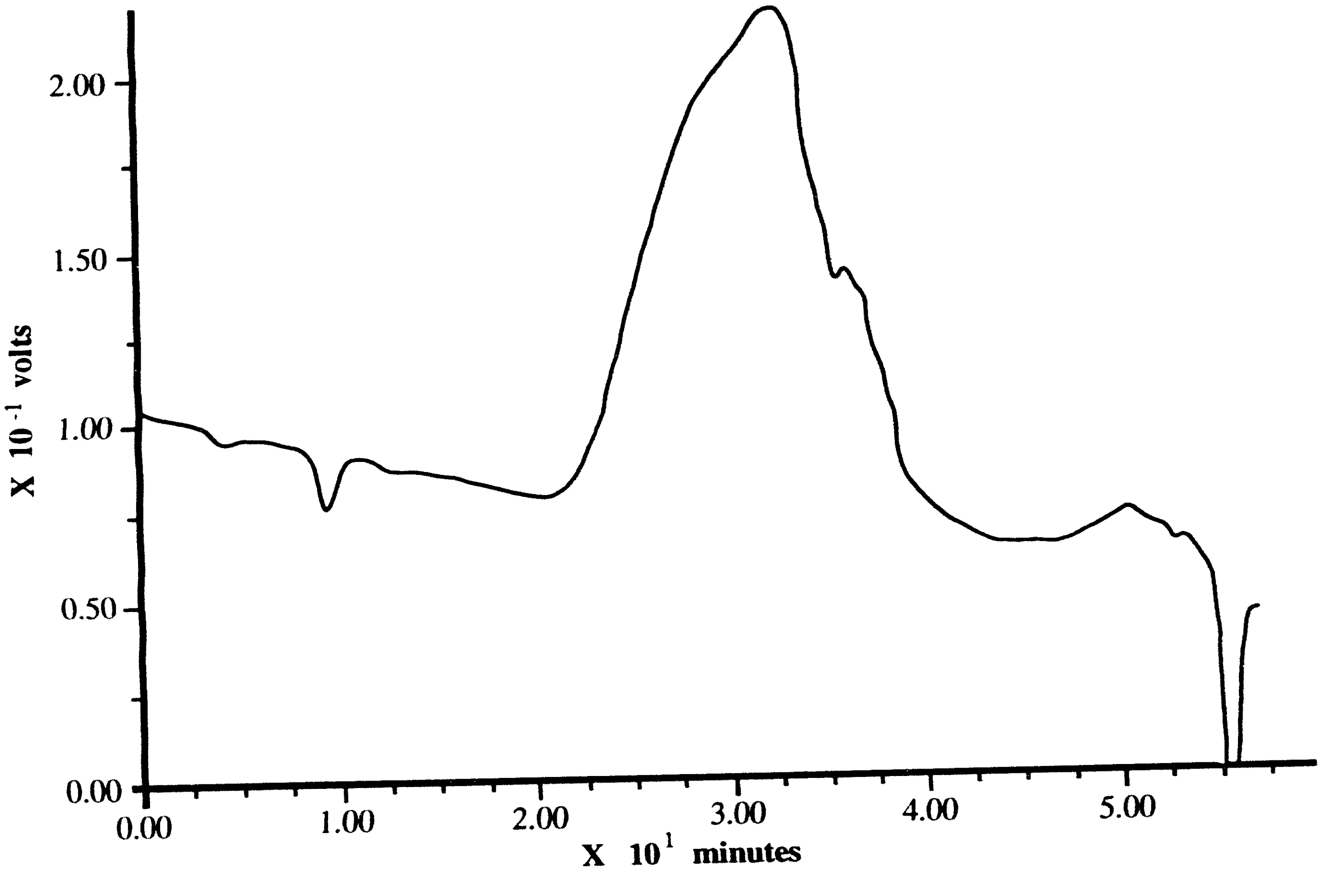


FIGURE 4. Chromatograph of Softwood Kraft Lignin T-2823 in DMF at 50 C

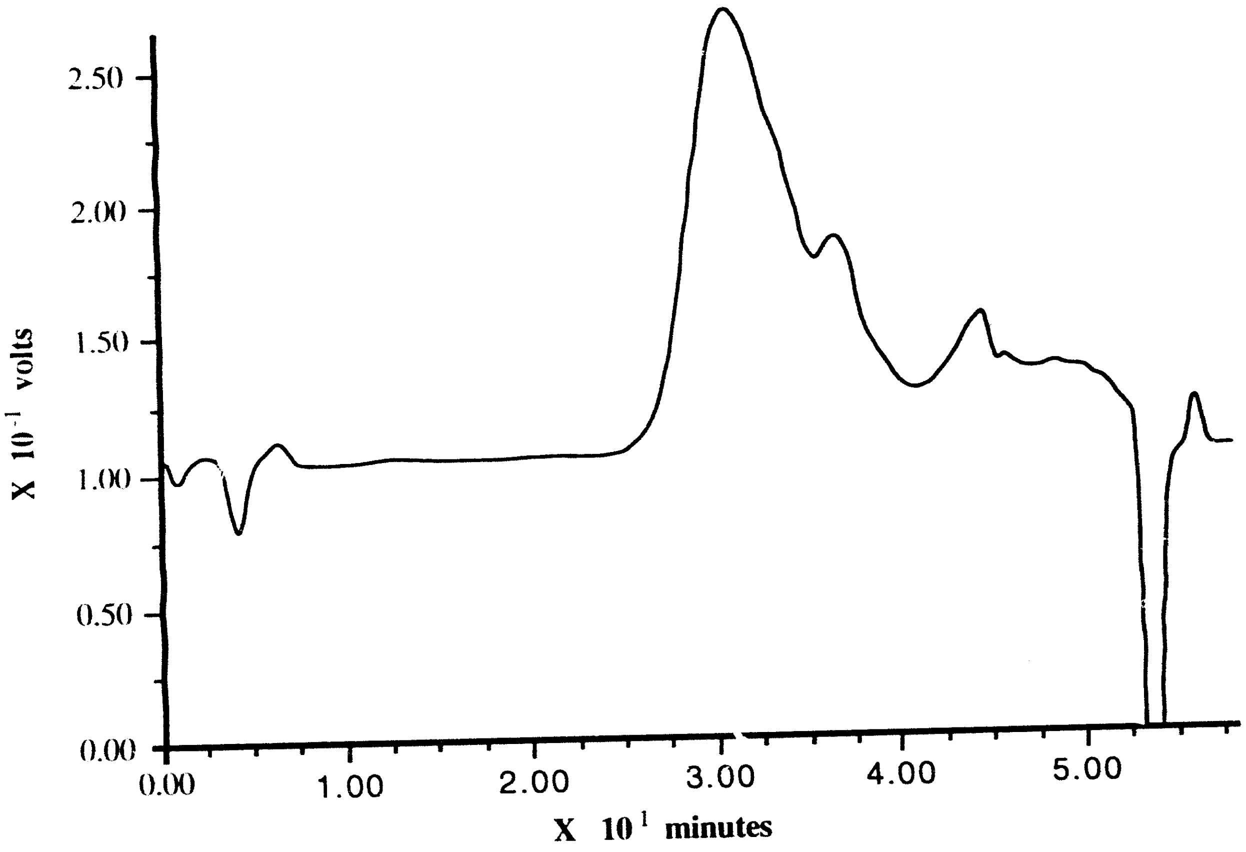


FIGURE 5. Chromatograph of Softwood Kraft Lignin T-2882 in DMF at 85 °C

not associate in DMF at 85°C. Addition of LiBr does make it much more difficult to maintain a stable baseline.

Work with DMF has been largely unsuccessful. The problem with the lignin-DMF system appears to be polymer-column association. Repetitive chromatograms similar to Figure 5 can be obtained only with flushing of the column with the solvent for many hours, even days, between runs. Even then, the end of the chromatogram occurs at or nearly at the solvent front and the baseline is hard to define. More than eight months of effort was expended testing various injection volumes and concentrations, solvent rates, temperatures, and column combinations with no success. The problem does appear to be polymer-column interaction, because the plate count and calibration with poly(ethylene glycol) and poly(ethylene oxide) showed no change in column characteristics after extended flushing.

The use of mixed solvents, with DMF as the primary solvent, was tried. Second solvents used were triethyl amine (TEA), a strong H-bond donor, and ethylene glycol or glycol ethers. The glycol ether used in most cases was ethylene glycol mono propyl ether (EGMPE).

TEA promoted polymer association without moving the chromatogram from the solvent front nor solving baseline problems. As a result, addition of TEA, even as low as 2%, distorted the chromatogram severely without solving the basic problem. Figure 6 is an example of a chromatogram for lignin in 98% DMF/2% TEA at 85°C.

Ethylene glycol (EG) was used with DMF. Figures 6a and 7 are chromatograms of an experimental and of a mill lignin, respectively, in 95% DMF/5% EG at 85°C. The chromatogram is compressed and there is an extended low molecular weight tail in both cases. However, there are qualitative similarities and the chromatograms are clearly multi-modal. There are still base-line problems

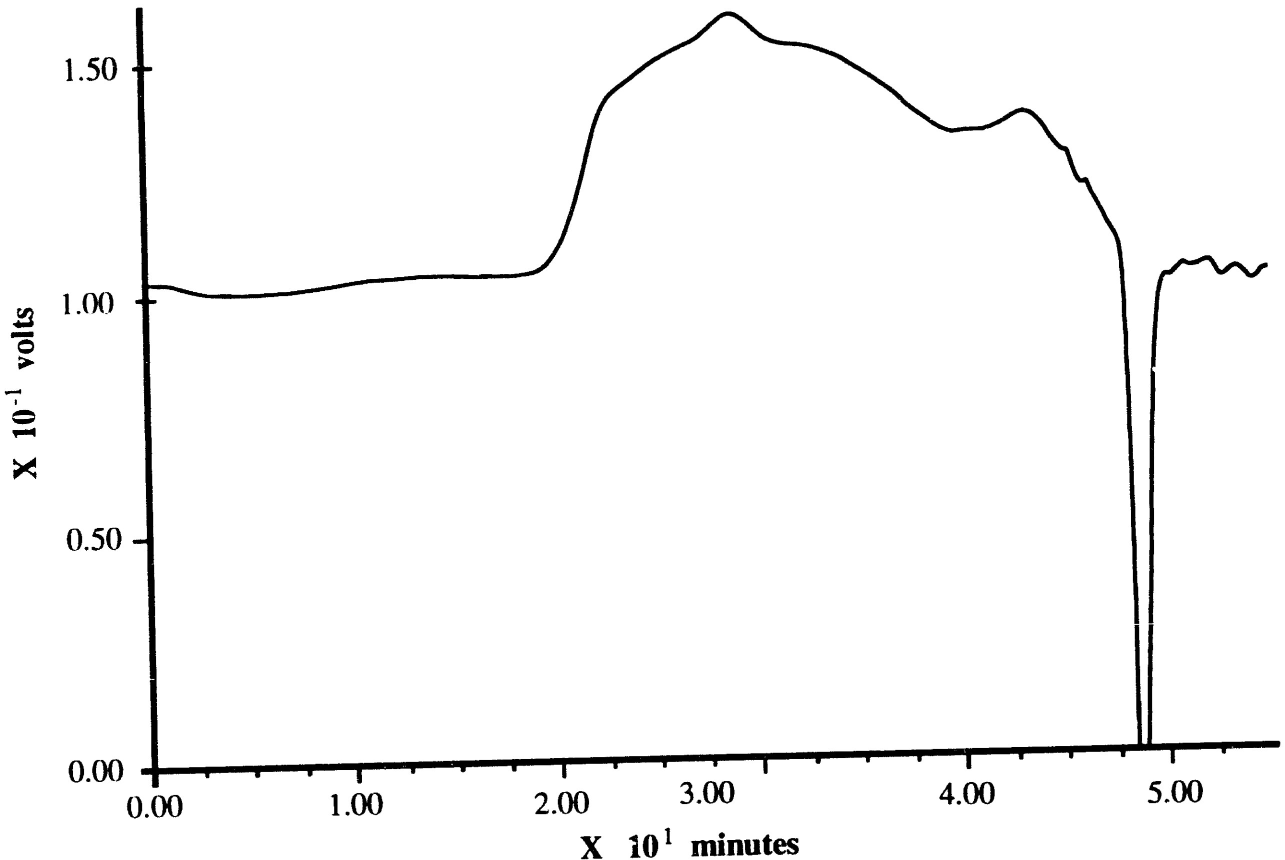


FIGURE 6. Chromatograph of Softwood Kraft Lignin T-2878 in 98% DMF/2% TEA at 85 °C

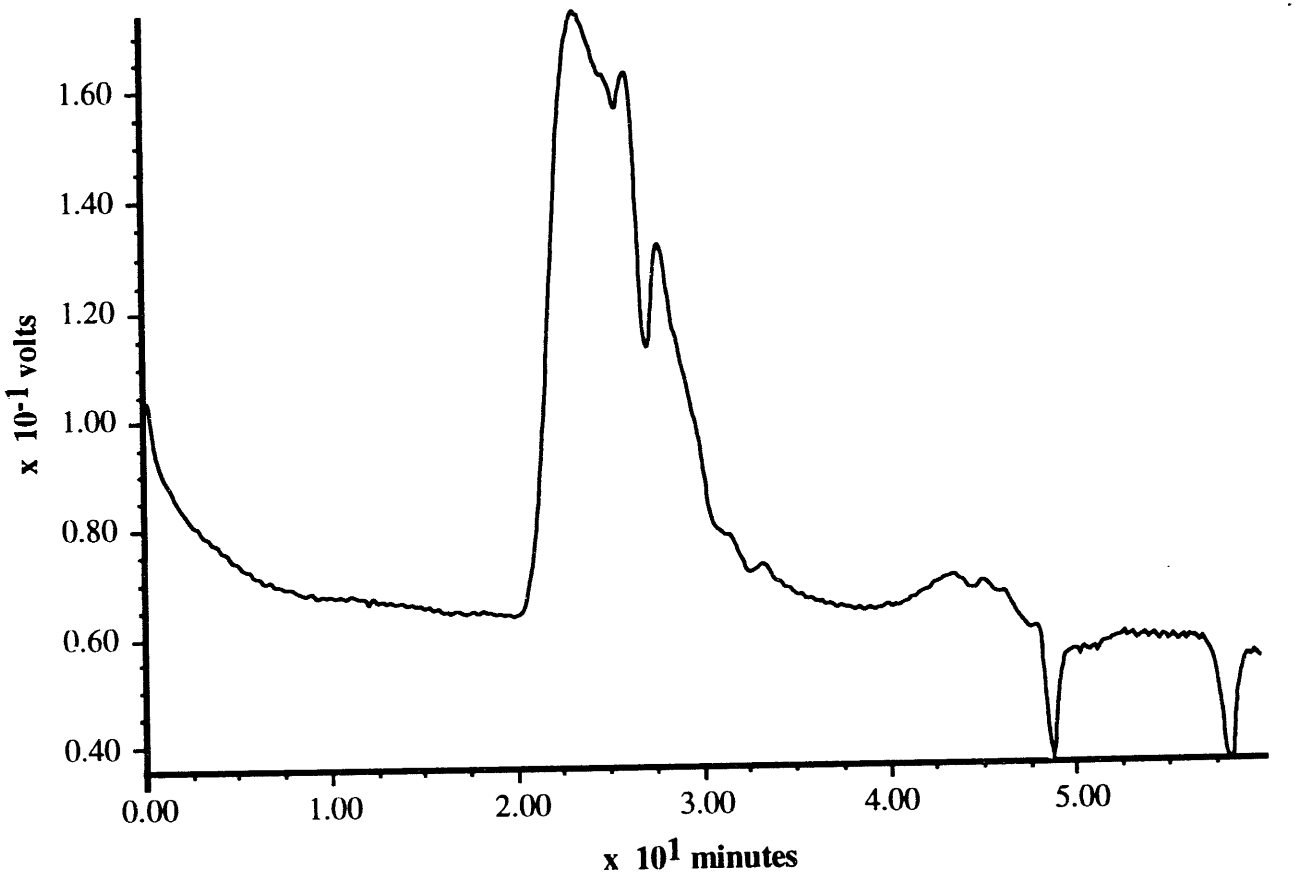


FIGURE 6a. Crhomatograph of Softwood Kraft Lignin T-2823 in 95% DMF/5% EG at 85°C

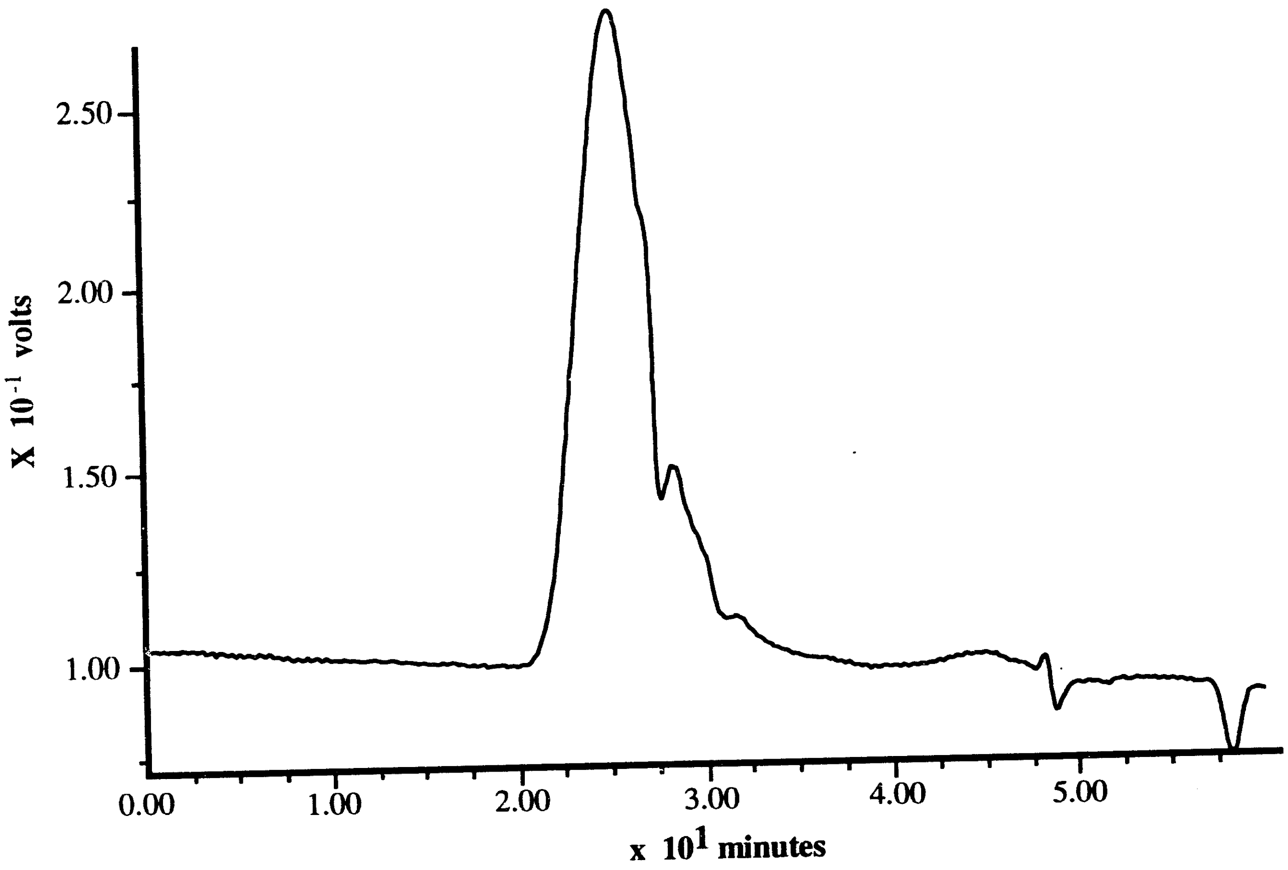


FIGURE 7. Chromatograph of Mill Softwood Kraft Lignin in 95% DMF/5% EG at 85°C

and problems with reproducibility without extended column flushing. Chromatograms run in this system at 100°C are given in Figures 8 and 9. There are no significant changes in the chromatograms, but running at higher temperatures did not lead to either improved baseline stability or reproducibility.

A third solvent, EGMPE, was tried. Chromatograms were run for lignins in 95% DMF/5% EGMPE at 85°C and 100°C, and in 98% DMF/2% EGMPE at 85°C. Figure 10 is a typical chromatogram for a lignin in 98% DMF/2% EGMPE at 85C. Baseline and solvent front problems are obvious. Figures 11 and 12 are chromatograms for an experimental and a mill lignin, respectively, in 95% DMF/5% EGMPE at 85°C. This system is much better behaved, but the chromatograms are compressed and there are still problems with reproducibility. This system was also run at 100°C. Chromatograms are compressed and there are problems with reproducibility.

Work has also been done using tetrahydrofuran (THF) with a small amount of water to enhance lignin solubility. Figure 14 shows chromatograms for four experimental lignins run in THF at 45°C. This system can be run successfully without the severe adsorption and reproducibility problems experienced with DMF. However, molecular weights calculated from the chromatograph calibration with common standards are very much lower than those determined for the lignins by VPO and LALLS. Even more serious, the values of $\overline{M}_w$ calculated from the chromatograms vary over a range of only about 23%, while the $\overline{M}_w$ values for these lignins from LALLS vary by more than 100%.

Overall, this work has been extremely disappointing and largely unsuccessful. All that we have determined is that, in general, the MWD of kraft lignin is broad with a low molecular weight tail and that the MWD is multi-modal in nearly every case. During the course of this work, we have made use of the advice of experts in chromatography at the University of Florida and elsewhere. There

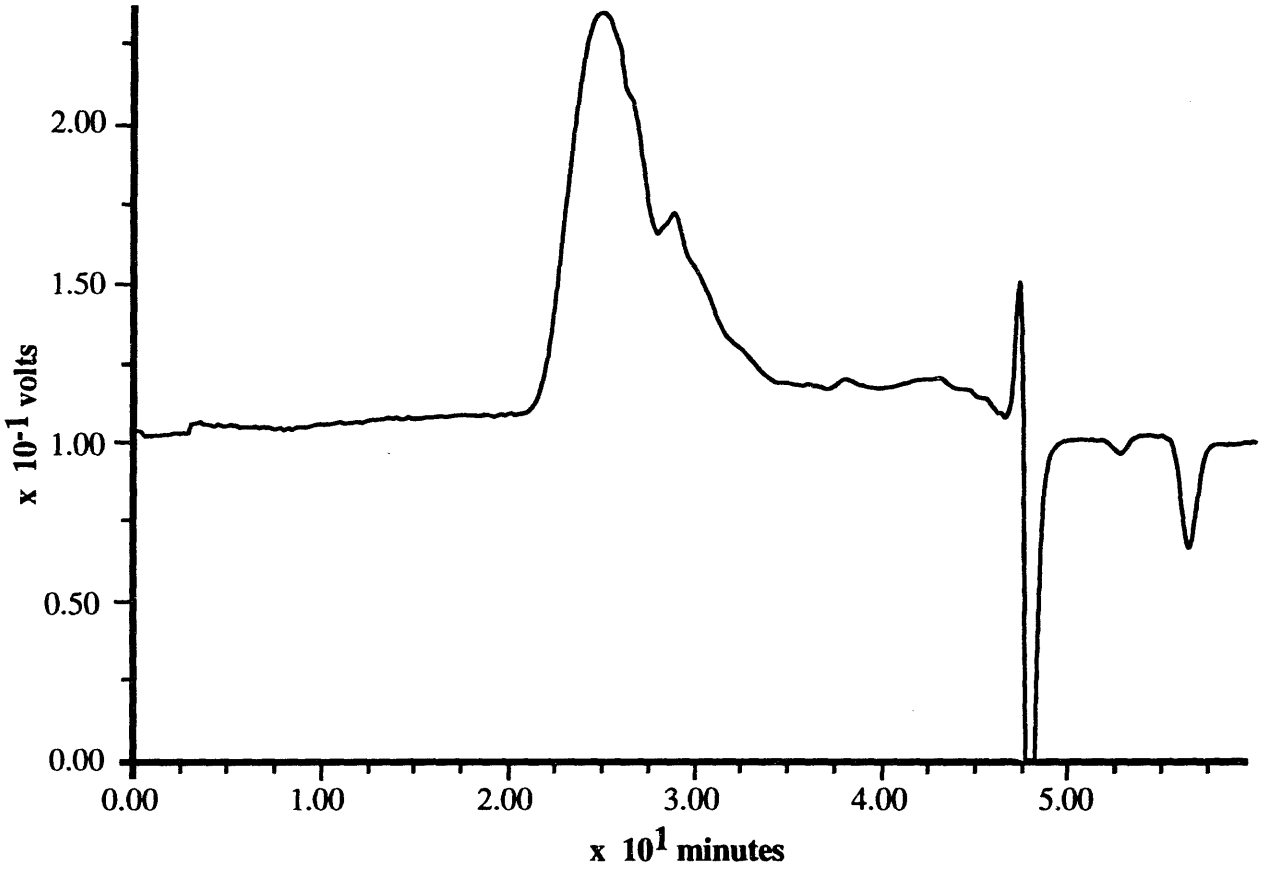


FIGURE 8. Chromatograph of Softwood Kraft Lignin T-2823 in 95% DMF/5% EG at 100°C

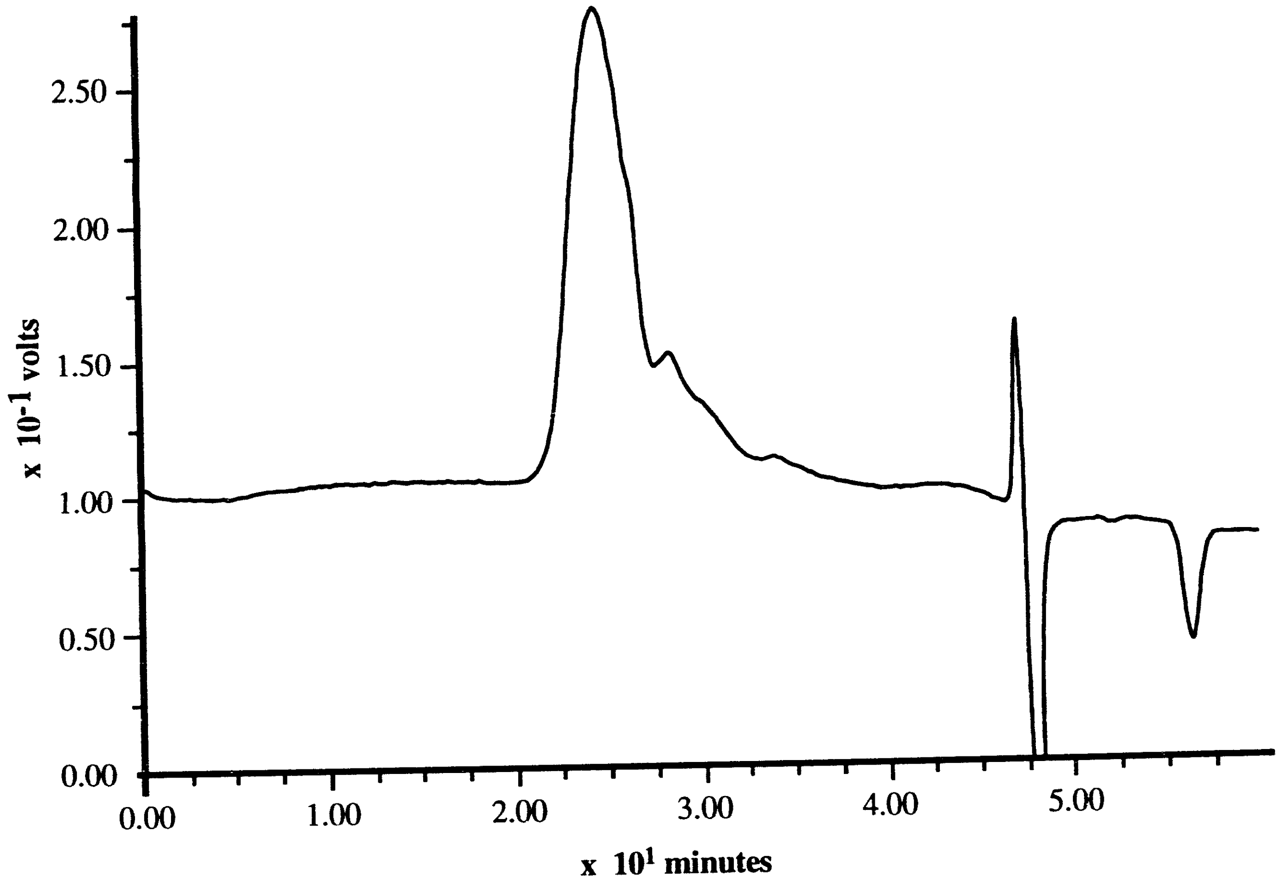


FIGURE 9. Chromatograph of Mill Softwood Kraft Lignin in 95% DMF/5% EG at 100°C

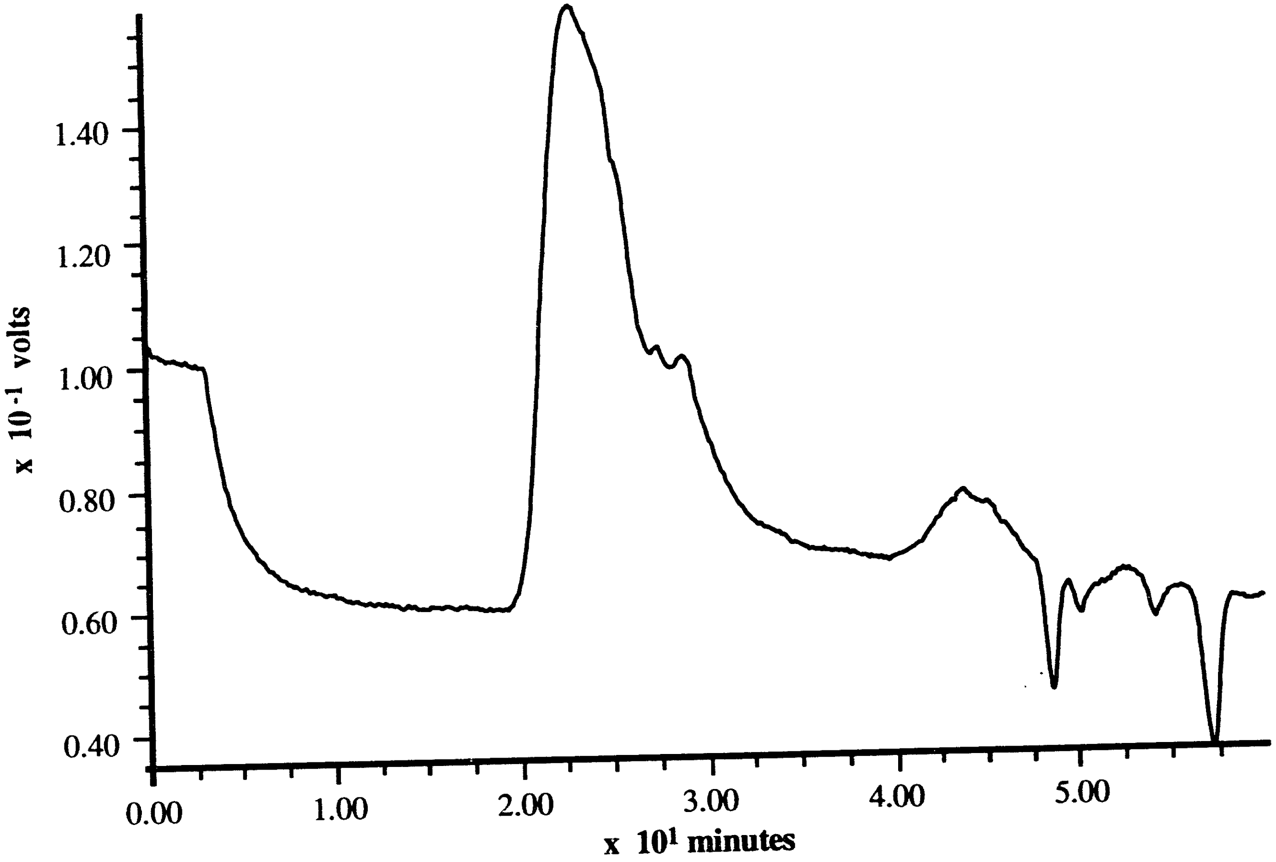


FIGURE 10. Chromatograph of Softwood Kraft Lignin T-2823 in 98% DMF/2% EEMP at 85°C

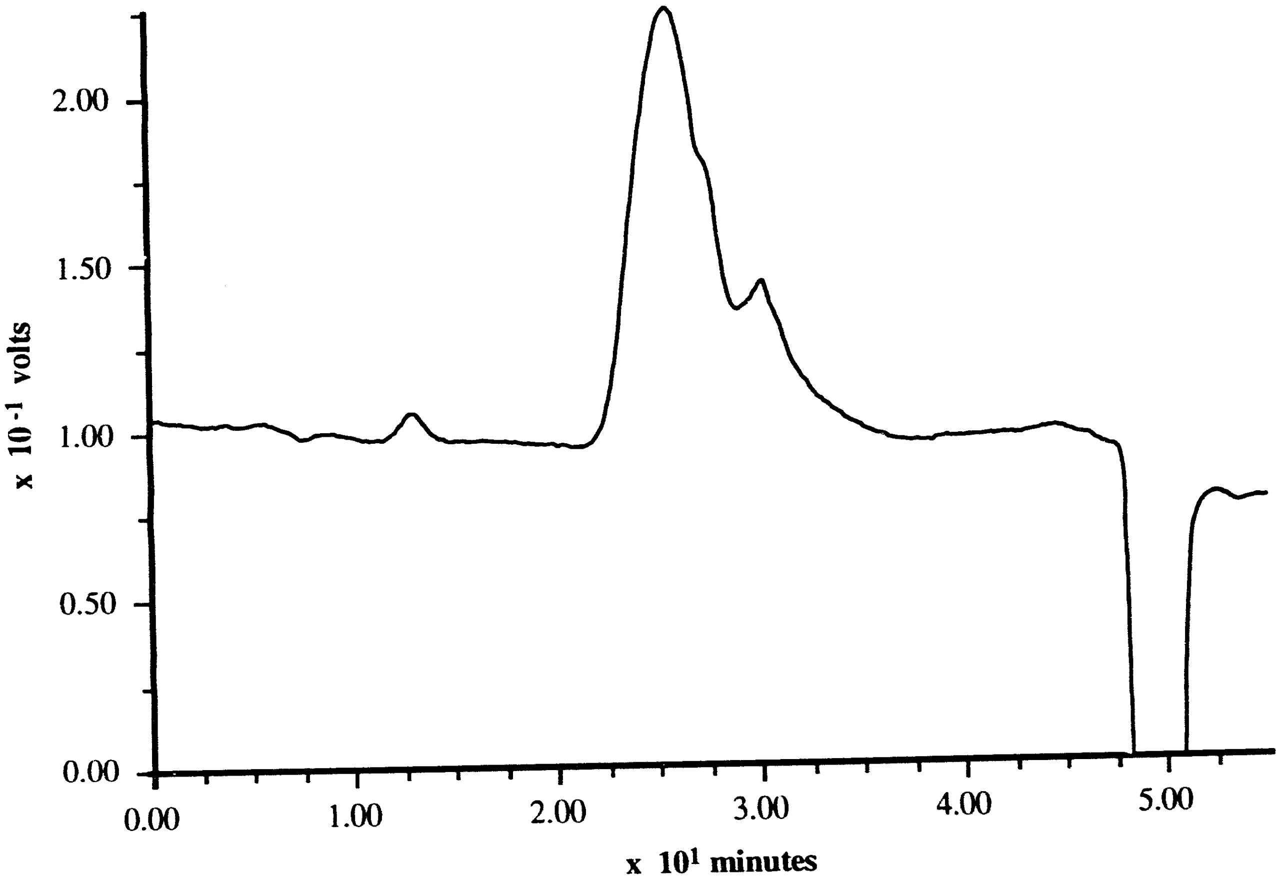


FIGURE 11. Chromatograph of Softwood Kraft Lignin T-2823 in 95% DMF/5% EGMPE at 85°C

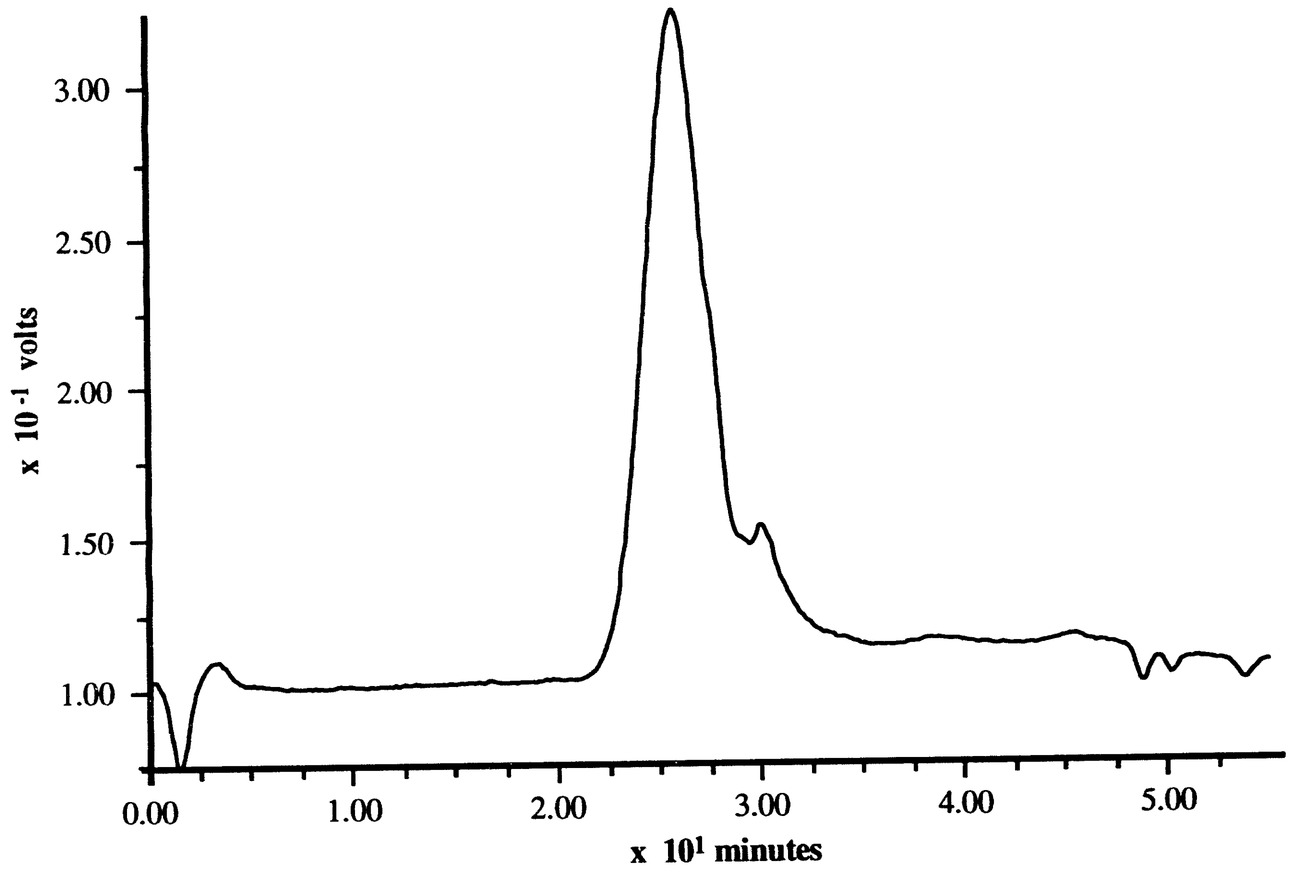


FIGURE 12. Chromatograph of Mill Softwood Kraft Lignin in 95% DMF/5% EGMPE at 85^{O}C

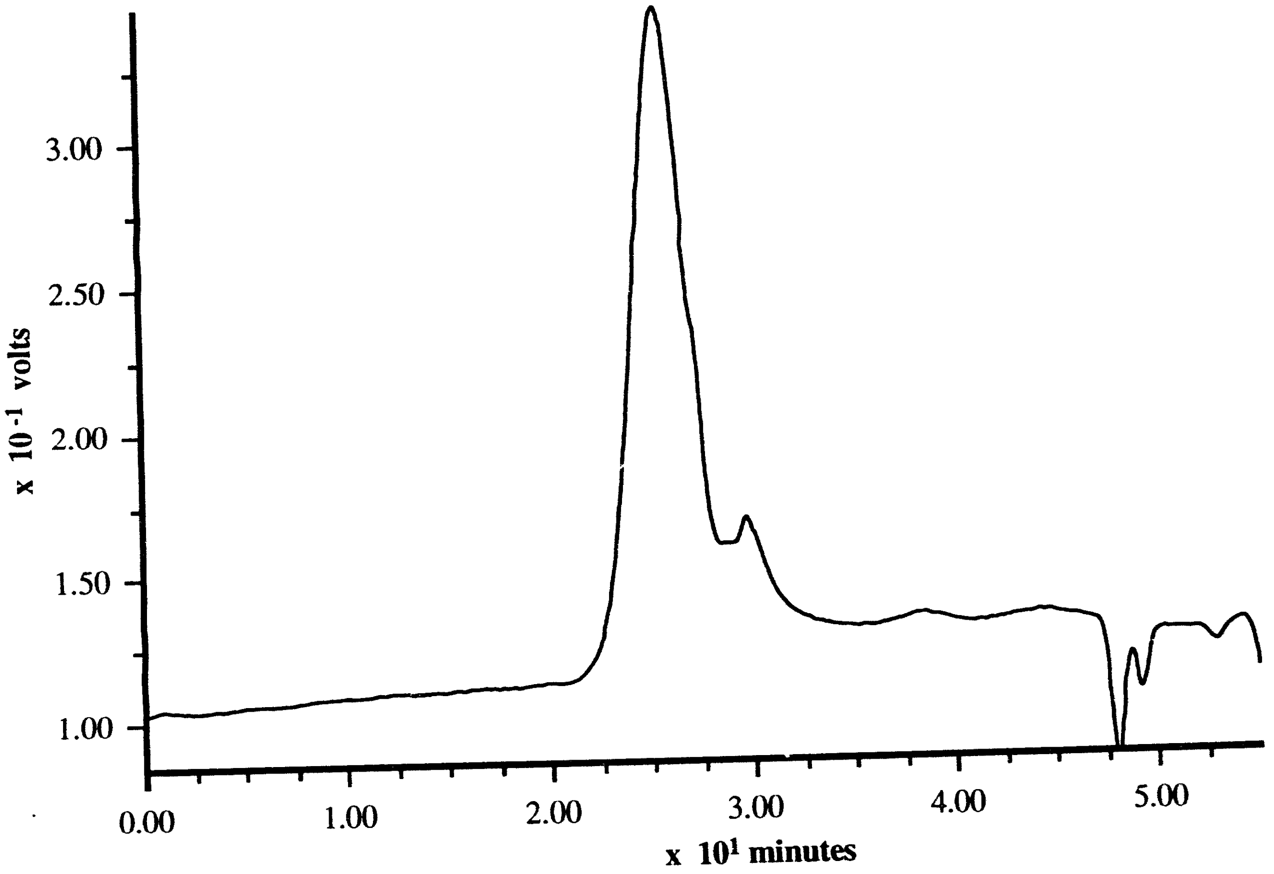


FIGURE 12a. Chromatograph of Softwood Kraft Lignin T-2823 in 95% DMF/5% EGMPE at 100°C

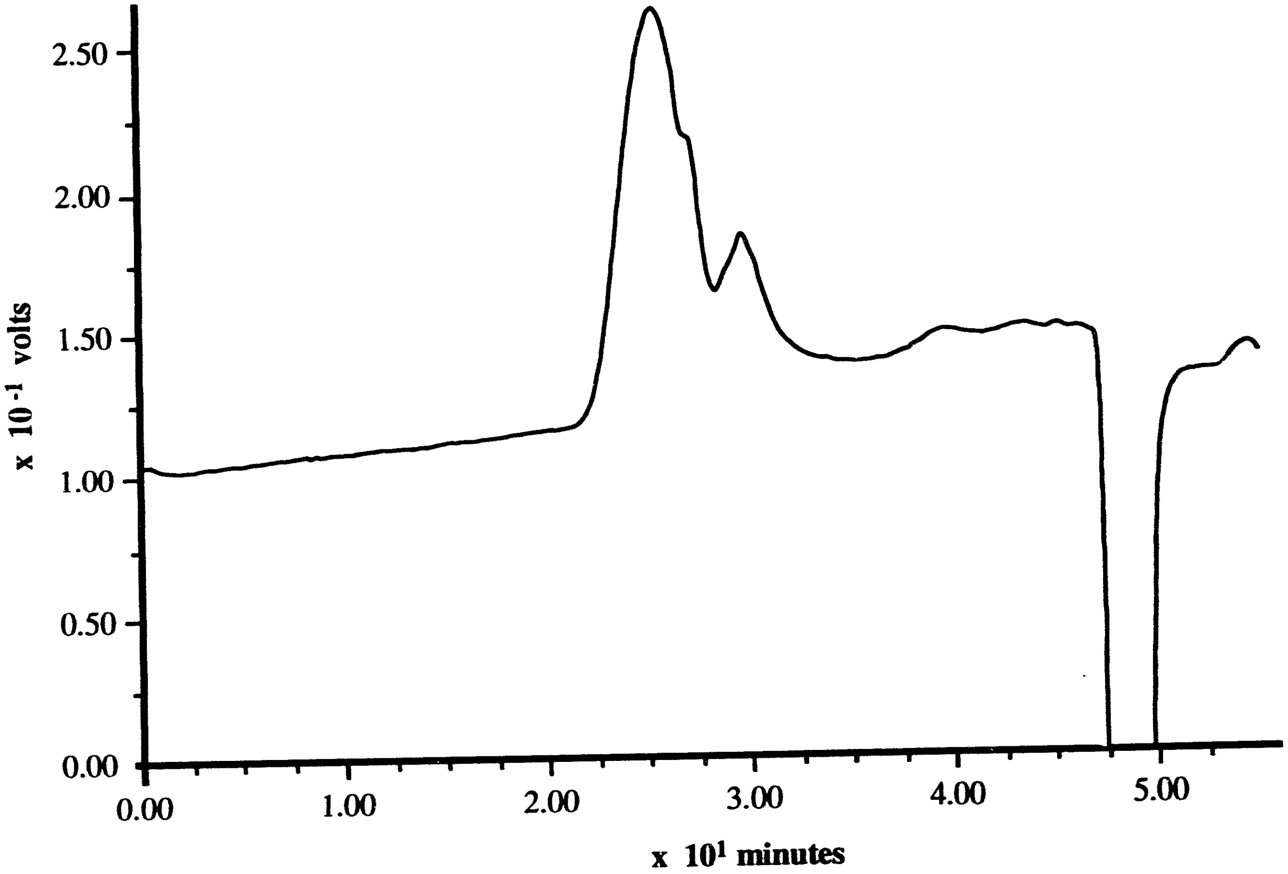


FIGURE 13. Chromatograph of Mill Softwood Kraft Lignin in 95% DMF/5% EGMPE at 100°C

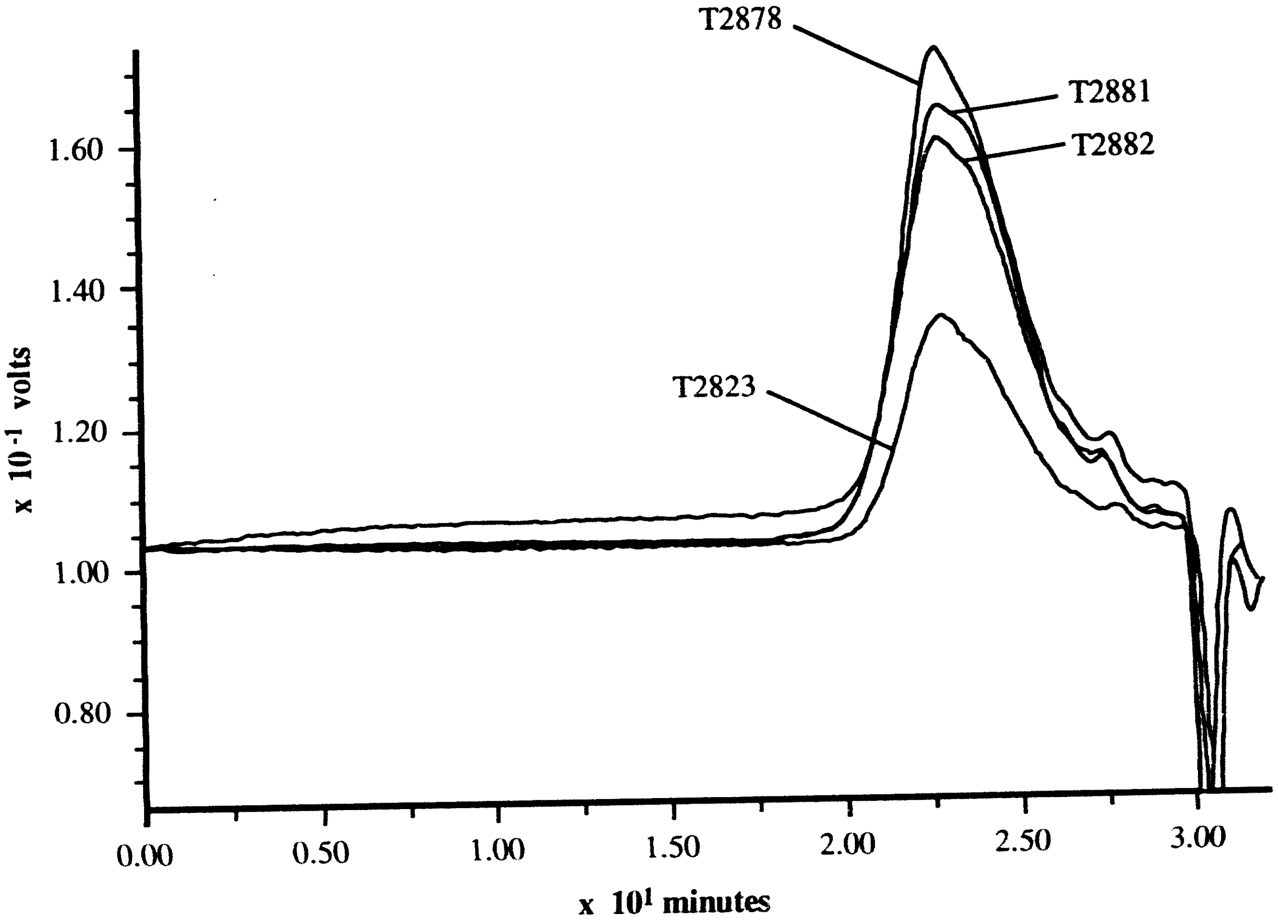


FIGURE 14. Chromatograph of Four Softwood Kraft Lignins in THF at 45°C

seems to be no better approach than we have taken and no promising approaches for use of organic solvents have been suggested that we have not tried.

We are currently beginning to work with an expert from industry who claims to have developed a procedure for SEC for aqueous systems. Since we have shown in our UV-visible work that lignin probably does not associate at pH > 13 and that UV-visible absorption of lignin at 280 nm is not dependent on molecular weight, we will begin work with aqueous systems to solve this problem. A UV-visible detector and columns developed by the industrial expert for use with high pH solutions will be obtained and chromatographic experiments performed.

THERMAL STUDIES

Definition of the properties important for performing energy calculations for systems to process black liquors are an important part of our program. Properties that are being investigated actively at present in this area as a function of liquor, solids concentration, temperature, and pressure (where appropriate) are:

1. density and thermal expansion
2. vapor pressure-solids concentration equilibrium
3. heat capacity
4. heat of solution
5. heat of combustion

These are all needed for accurate metering of flows and for exact calculation of enthalpy balances. Vapor pressure-solid concentration, heat capacity, and heat of solution will be used to develop total enthalpy-concentration relations. Heats of combustion are necessary to predict furnace performance.

In the near future, work to determine the thermal conductivity of black liquors will begin.

VAPOR PRESSURE EQUILIBRIUM

Our small scale laboratory evaporator has been extensively revised so that the evaporator can be used to determine equilibrium vapor pressure at the boiling point as a function of solids concentration as well as to concentrate samples to above 80% solids concentration for other work.

The vessel volume has been increased to slightly more than 4 liters, the bottom half of the vessel has been changed for better heat control, and baffles and turbine blade agitator(s) have been installed in the bottom half of the vessel for good mixing. A new head and bearing system have been designed and installed with a new bearing scaling system to permit agitation at up to 350 rpm with virtually no air leakage. Measured air leakage rates have been less than 10 cm^3 at STP per minute. The agitator is driven by a DC motor so that the agitator speed can be varied. The bottom half is electrically heated by a heating mantle connected to a variable transformer so that the rate of addition of heat can be varied.

The measuring and control systems have been thoroughly revised. Liquid temperature is measured by using a resistance thermometer with a small time constant (a few seconds) that is connected to an unbalanced linear bridge to give an output of 1.0 mv per °C. The entire system has been checked against air saturated ice water and boiling water as well as against the temperature of water between these points, as determined by a thermometer traceable to the NBS. The temperature measuring system is accurate to within 0.01°C over the range from 0 to 100°C and the output can be read to 0.01°C. The pressure within the evaporator vessel is determined with an electronic force balance pressure gage that is connected to an electronic indicating controller. Calibration tests against a manometer show that the pressure system is accurate to within one mm Hg (1.32 x 10^{-3} atm) or less (usually less) from 100 mm Hg (0.132 atm) to 760 mm Hg (1.00 atm) absolute pressure. The output of the indicating controller is in mm Hg absolute pressure. The condensate receiver is mounted on a load cell with a maximum capacity of 4.54 kg. The load cell output is conditioned to give a response of 0.25 mv per gm with stepping every 96 mv so that the mass of the receiver can be recorded on a 100 mv scale recorder continuously. The exhaust from the receiver flows through a cold trap to a vacuum pump. The vacuum pump is run at full load. Air is bled into the vacuum pump between the cold trap and the pump suction at a controlled rate to maintain constant pressure in the boiling vessel. The indicating pressure controller controls the bleed air flow in response to the signal from the absolute pressure transducer mounted in the head of the boiling vessel. Work shows that pressure can be controlled to ± 1 mm Hg or better.

There are two condensers mounted between the boiling vessel and the receiver. One is a 400 mm long glass Graham type condenser directly above the boiling vessel that is used when the system is run at total reflux. The other is a 19 tube, 18" long, single pass shell and tube exchanger with three baffle plates on the shell side. This exchanger is mounted directly above the receiver and is connected to the receiver by a flexible tube. The two exchangers are connected by a 1/2-inch copper tube. Except for small areas left open for visual observation, the system is insulated with fiberglas insulation to the shell-and-tube exchanger.

The system can be operated in either of two modes. It can be operated at total reflux (constant composition) and the boiling point determined as a function of pressure by increasing the pressure stepwise. Alternatively, it can be operated at constant pressure and the boiling point determined as a function of composition, since the initial concentration and mass in the vessel are known and the temperature and condensate mass are measured as a function of time.

This system has been checked for accuracy with water, sodium chloride solution, and sucrose solutions. The boiling point for water at a number of constant pressures from 76 mm Hg (0.1 atm) to 766 mm Hg (1.00 atm) all agreed with literature values within ± 0.3°C or better. The pressure-temperature curve determined for water with these data agreed with the literature to within 0.1°C. Heats of vaporization for water calculated from the slope of the experimental curve agreed with literature values to within 20 Btu/lb or less. Values determined for sucrose solution were in agreement within ± 0.4°C at worst with values reported in the literature that had been determined in a quite sophisticated vapor-liquid equilibrium apparatus. We believe that we can assume that individual values of the pressure-temperature relation at the boiling point determined for black liquors in this apparatus are accurate to within 0.4°C at worst and that a smooth curve of pressure vs. temperature at constant solids is even more precise. In general, we have found that the system operates essentially at equilibrium at boiling rates of up to 6 gms per minute of condensate at constant pressure with as little as 1000 gms in the vessel. The pressure control cycles at a frequency of about one minute. The system has been tuned to maintain the amplitude of the cycle to within ± 1.5 mm Hg or less. At constant reflux, the temperature also cycles and lags the pressure cycle by about 20 seconds. In practice, the average values of pressure and temperature are recorded.

Normally, data is taken at constant composition. The vessel is loaded with 1.3 to 3.3 liters of liquor, closed, and vacuum drawn to 100 mm Hg (0.132 atm). The liquor is concentrated to the desired concentration, if necessary, at this pressure. When the desired concentration is attained, the system is switched to constant reflux and boiling temperatures determined at six to eight pressures between about 100 and 760 mm Hg (0.132 and 1.00 atm). Boiling is stopped, the contents cooled as much as possible, and the contents are drained into preweighed plastic bottles for storage for other uses. The solids concentration of the liquor is determined directly on the final liquor. To determine the full relation as a function of pressure and composition for one liquor requires 10-14 separate experiments as described. This requires 8-11 working days; this work is time consuming.

At present, the small scale evaporator is a bottleneck. A second system is being built and will be in operation in January, 1991. This will permit us to determine vapor-liquid equilibria and prepare small samples of concentrated liquor as required for other studies at the same rate that we will be receiving liquors.

The vapor pressure-temperature relationships for ten liquors have now been determined from 10-20% solids concentration to 70-85% solids concentration. The limit of solids concentration that can be used for accurate results in this system depends upon liquor viscosity. Analysis of the data for these ten liquors is not yet complete. However, several things can be noted. There seems to be little variation in boiling point, liquor-to-liquor, at up to 20% solids concentration for softwood liquors. The maximum rate of change of boiling point elevation with solids concentration occurs in the range of 40 to 60% solids for softwood liquors, and the boiling point elevation at a fixed composition is dependent upon pressure. There does not appear to be a significant change in heat of vaporization with concentration, since the slopes of the pressure equilibrium curves do not change very much, if at all, with increasing composition.

The data of pressure vs. boiling temperature for a constant solid concentration are regressed in the form:

$$\ln P = A + B/T + C/T^2$$

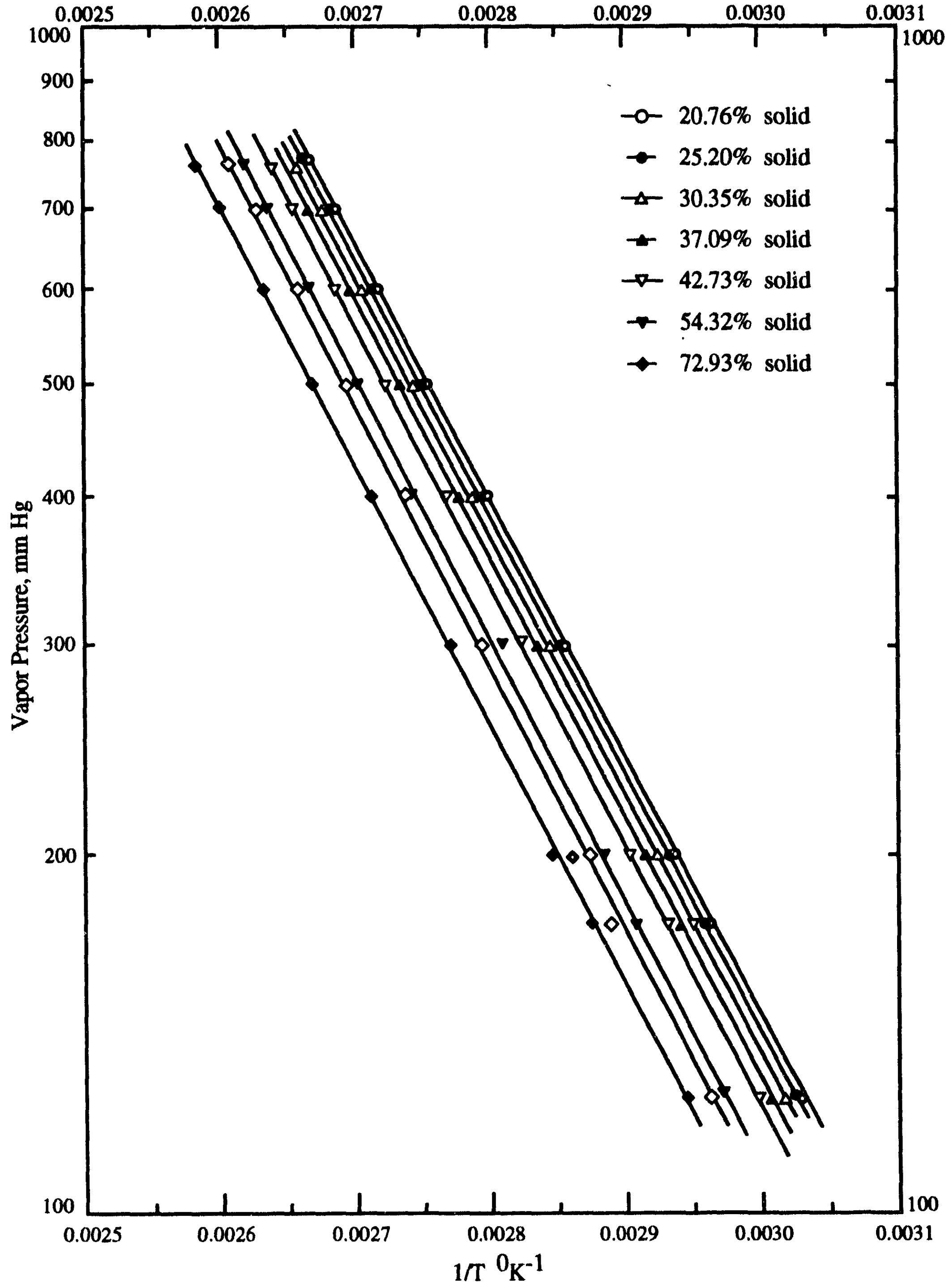
where:

P = pressure
T = absolute temperature
A,B, and C = constants

Normally, the data yield a relation with a correlation coefficient of 0.9999 or better with a standard error of estimate for pressure of 0.16% or less (about 1.2 mm Hg at 1.00 atm). The equations determined by regression for each solids concentration are used to calculate smoothed values for each solids concentration at 300, 450, 600, and 760 mm Hg (0.395, 0.592, 0.789, and 1.00 atm). Boiling point elevations are calculated for each of these smoothed points by subtracting the appropriate boiling point of water from each point. Graphs are plotted of log P vs. 1/T with solids as a parameter, T vs. solids with P as a parameter for the smoothed data, and boiling point elevation (BPE) vs. solids with P as a parameter. Examples of these are shown in Figures 15, 16, and 17. At present, methods to reduce and correlate the boiling point elevation data are being sought.

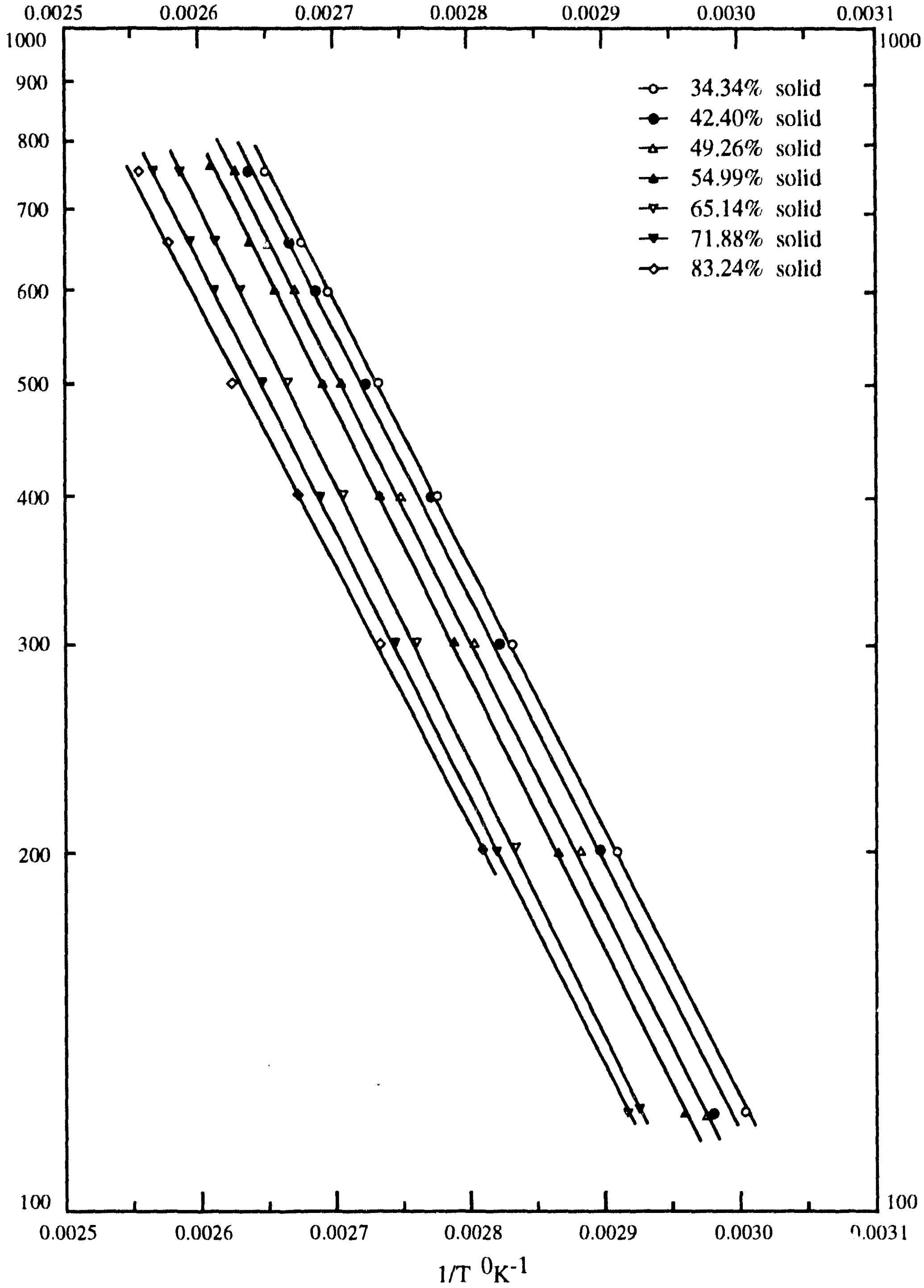
DENSITY AND THERMAL EXPANSION

Work continues on collection of data for these properties. Techniques useful for determinations at solids concentrations below about 55% solids have been improved to increase accuracy. The major effort has been on revising techniques or developing new ones to measure density and thermal expansion for liquors up to 80-85% solids concentration. The problems with loading devices for these determinations at high solids concentrations are severe. Thermal expansion has now been determined by dilatometry at up to 85% solids in some cases. It appears that such data can be obtained at up to 80% solids concentrations, in general. We have just recently developed a promising technique to determine true density at up to 85% solids concentration. It appears that, at constant temperature,



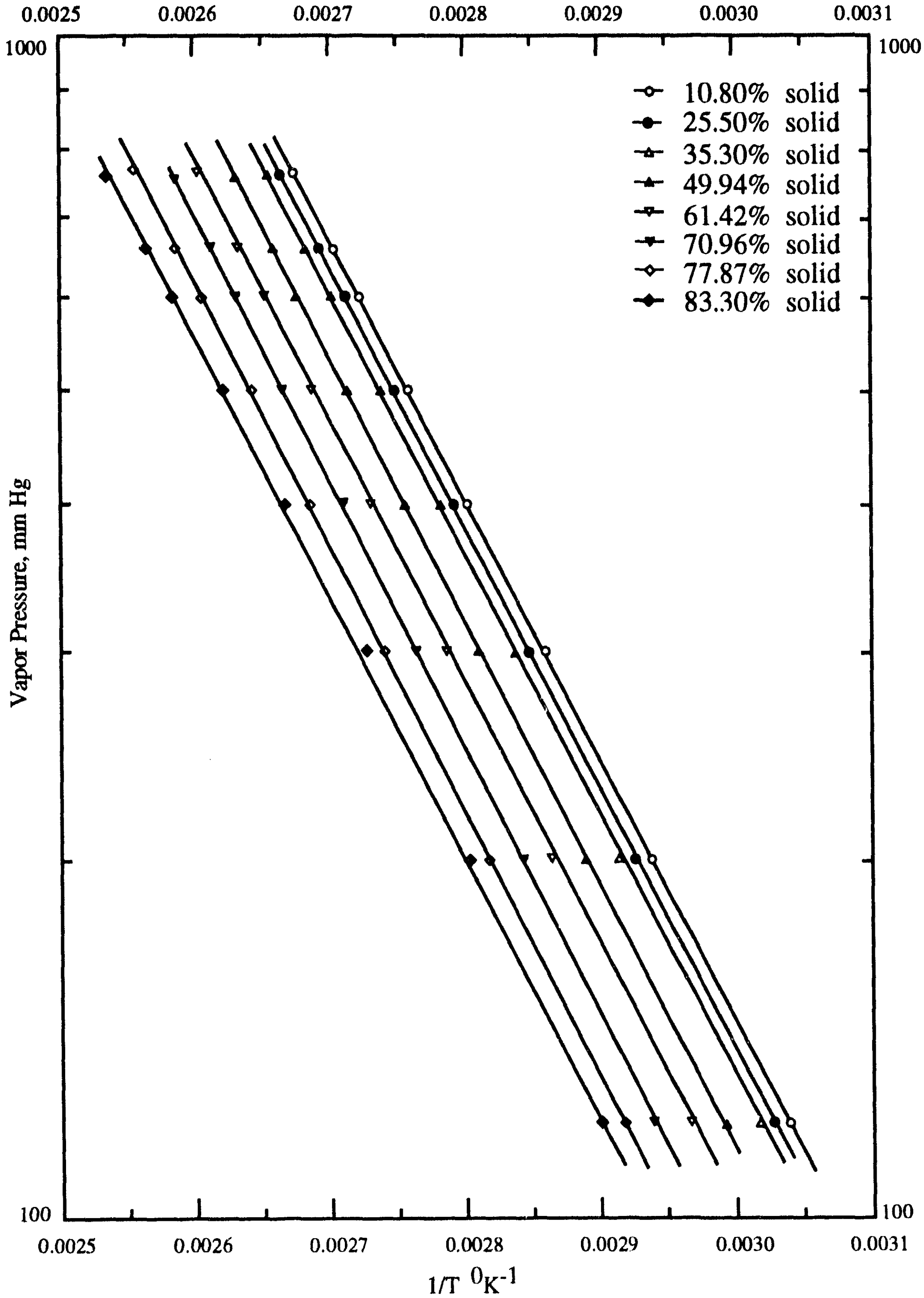
Vapor Pressure vs. temperature for black liquor ACAFX011.

FIGURE 15. Vapor Pressure at Boiling of Softwood Kraft Liquor ACAFX008 at Various Concetrations



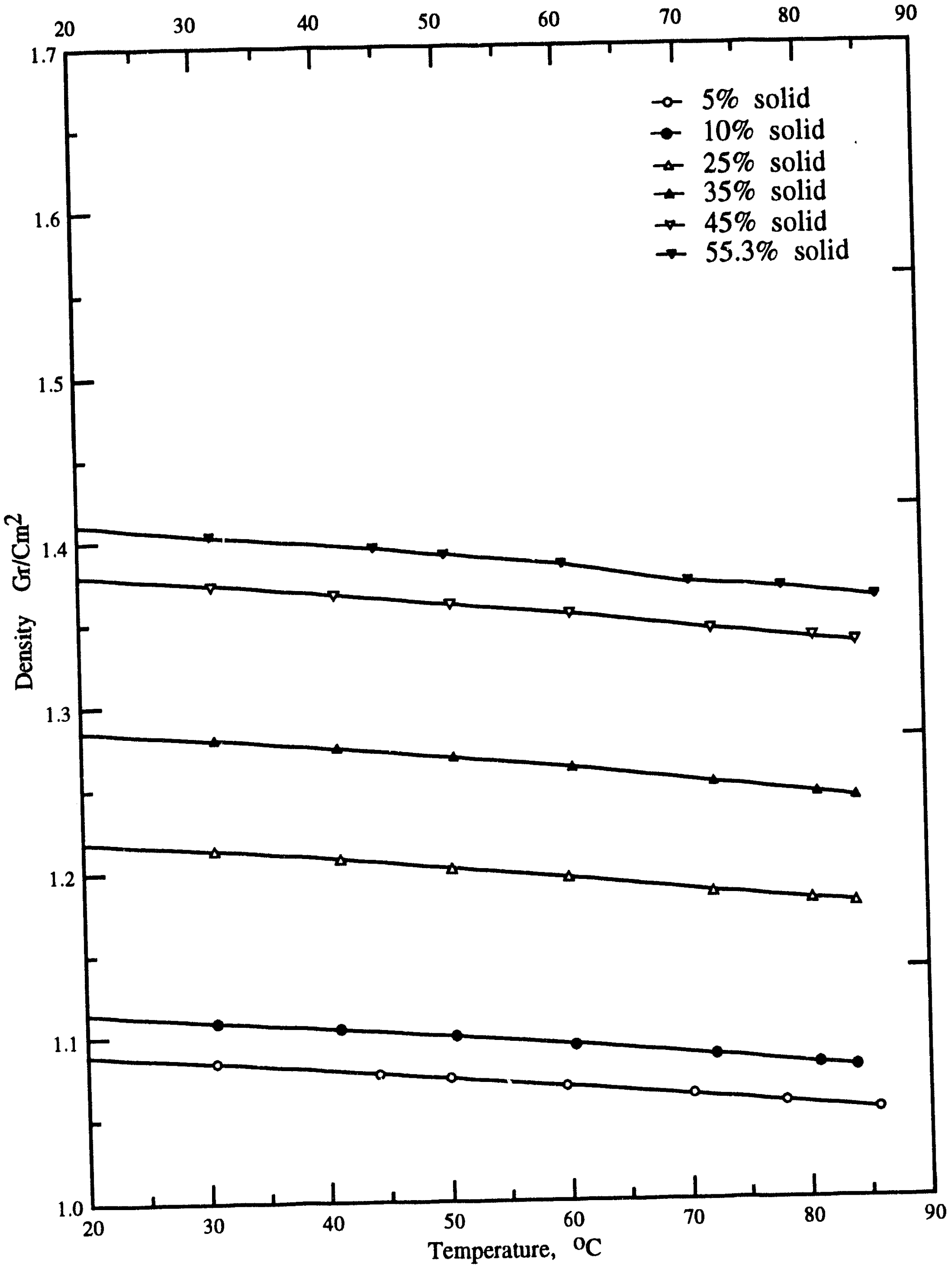
Vapor Pressure vs. temperature for black liquor ACAFX011.

FIGURE 16 Vapor Pressure at Boiling of Softwood Kraft Liquor ACAFX011at Various Concetrations



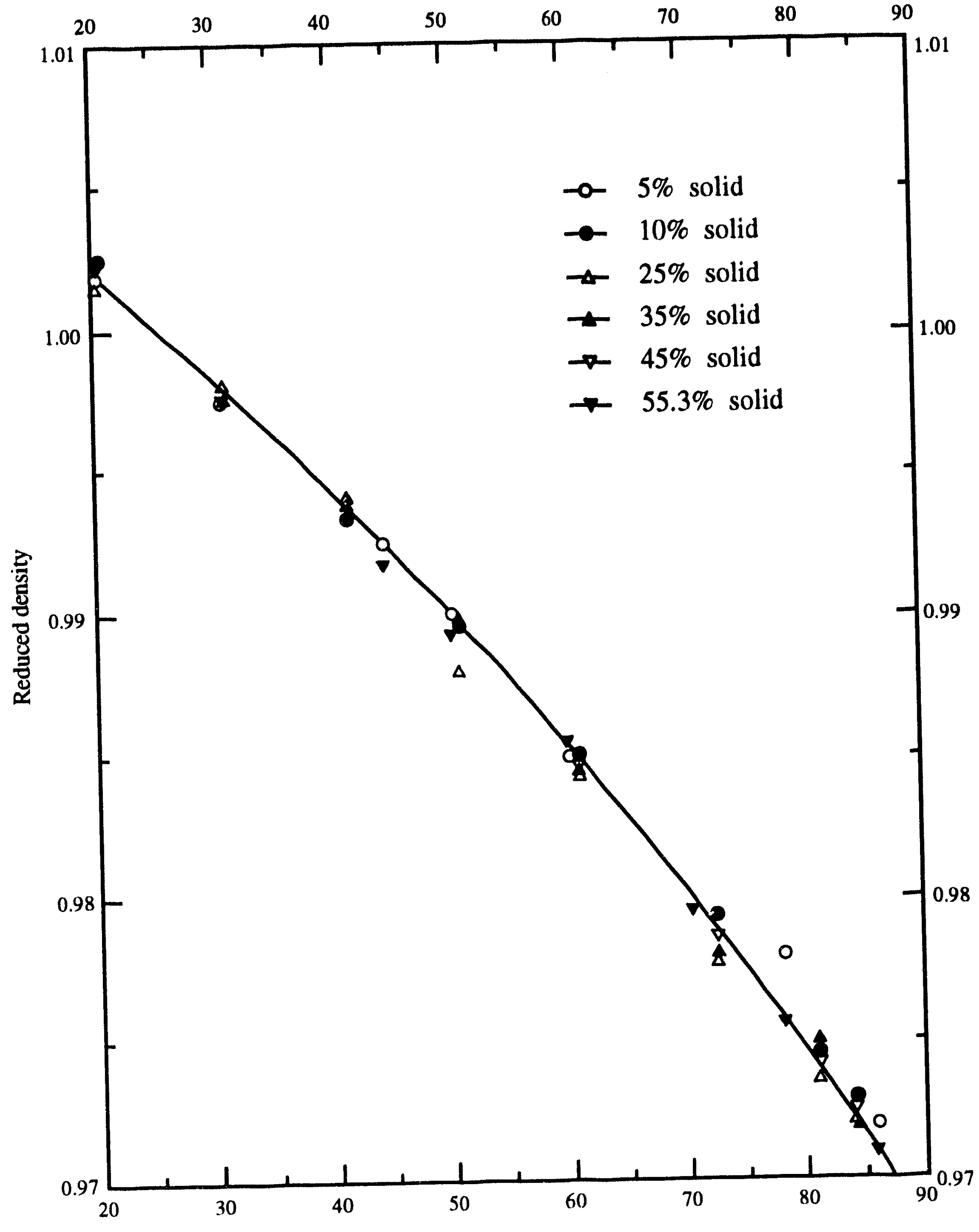
Vapor Pressure vs. temperature for black liquor ACAFX011.

FIGURE 17 Vapor Pressure at Boiling of Softwood Kraft Liquor AXAGB001 at Various Concetrations



Density vs. temperature for black liquor ACAFX007.

FIGURE 18. Density of Softwood Kraft Black Liquor ACAFX007



Reduced density vs. temperature for black liquor ACAFX007

FIGURE 18a. Reduced Density of Softwood Kraft Black Liquor ACAFX007 as a Function of Temperature density is very nearly, if not exactly, a linear function of concentration up to about 65-70% solids concentration, and that density increases at a slower rate with concentration beyond that point. There will be a concentrated experimental effort in this area over the next few months now that techniques have been developed and many liquor samples are available.

Data already taken on 16 liquor systems at solids concentrations up to 50% and at temperatures up to 100°C will be thoroughly analyzed and data reduced by methods reported earlier. Programs for this that are also capable of handling experimental data taken at high solids concentration have been written and are being used for reduction and analysis.

HEAT CAPACITY, HEAT OF SOLUTION, TRANSITIONS

Determination of these properties is an important part of our program. The Perkin-Elmer System 7 Differential Scanning Calorimeter (DSC) and Thermogravimetric Analyzer (TGA) are used to determine heat capacity, transitions, and weight loss as a function of temperature. Even though the DSC is a comparative device, it can be used for absolute determination of heat capacity as a function of temperature. This is being done for liquors currently under study as was done in the past. A data bank continues to grow with regard to heat capacity.

The DSC is also used to determine transition temperatures as described in earlier work. The glass transition temperatures (Tg) of purified lignins are determined, since these are affected considerably by impurities. Also, this is an important property with respect to other studies of lignin. Tg is being determined for black liquor solids at 100% solids for the same reason. The Tg establishes the upper temperature limit for processing 100% black liquor solids as solid fuels without tackiness. Also, the Tg of black liquor as a function of solids concentration will be determined for several new black liquors to be used in attempts at reduction and correlation of viscosity at high solids concentration.

The TGA is used to "fingerprint" the black liquors by determining weight loss as a function of temperature during pyrolysis.

The Setaram C-50 absolute microcalorimeter is fully operational. It is being used to determine the heats of solution of black liquor solids. Considerable effort was devoted to developing experimental techniques to permit work with 100% solids. This has not yielded satisfactory results to date. Therefore, experimental work is now concentrated upon obtaining data with infinite dilution at 25°C as the standard state for the solution. This permits us to work in the other direction as we have done successfully with other properties; i.e., from the dilute state to as high a concentration as can be attained.

Heats of solution are not negligible. Work to date indicates that the errors in energy balances calculated for concentrating black liquors to above about 40% solids occur because the solution is considered ideal (no heat of solution and additive heat capacity), not due to change in the heat of vaporization of the vapor evolved. We earlier developed methods based on a sound theory to describe the heat capacity. Additional results are directed toward development of a general, empirical relation. Data on heats of solution will be analyzed in the same way; a theoretically based model for heat of solution will be developed that is successful for several liquors and then a general, empirical relation will be sought.

The Setaram calorimeter can be used conveniently to measure heat capacity as well as heat of solution. In fact, it is more accurate than the DSC, since it is an absolute instrument. The Setaram is also being used, where practical to measure heat capacities.

HEATS OF COMBUSTION

A Parr Automatic Combustion Calorimeter equipped with several bombs is fully operational. Heats of combustion of 100% black liquor solids can be determined to accuracies of ± 0.18% or better by performing triplicate tests, and heats of combustion can be determined for black liquors at 65% solids concentration to accuracies of ± 0.4% or better by performing triplicate tests. The poorer accuracy at 65% solids is due to the fact that it is difficult, apparently, to obtain complete combustion at 65% solids concentration. Heats of combustion are routinely determined for liquors at 100% solids concentration, and are occasionally determined for liquors as a function of solids concentrations between 65 and 100% solids. Heats of combustion for 100% black liquor solids determined for five experimental softwood liquors and heat of combustion vs. solids concentration for one experimental softwood liquor are given in Table 5 as examples. These five liquors were made at extremes of the ranges for pulping conditions. As one can see, the heats of combustion can be expected to vary considerably with pulping conditions.

SAMPLE PREPARATION

Sample preparation presents some problems and, for good quantitative study of thermal properties, requires special care. Samples at up to about 80% solids can usually be conveniently prepared almost to the exact concentration required in the small evaporator. Samples at these concentrations are loaded while still hot into 500 ml or smaller containers and the solids concentration determined on a sample taken at that time. These small containers are stored until needed for experimental work. The contents are then heated to approximately 50°C, mixed, and transferred to the appropriate apparatus for measurement.

TABLE 5
Heats of Combustion of Kraft Black Liquors

Liquor	Solids %	Heat of Combustion BTU/lb
ACAFX007	65.7	4007
	69.5	4305
	73.2	4582
	100.0	5732
ACAFX008	100.0	5299
ACAFX010	100.0	3722
ACAFX011	100.0	5715
ACAFX012	100.0	6251

Samples at 100% solids are made in small batches by concentrating a liquor from about 65-80% solids to 100% solids by freeze drying. This has proven to be rather simple and quite reliable. These samples are uniform in concentration, but highly hygroscopic. These samples must be stored under dry conditions in sealed containers. Transfers and weighings are made in a dry box.

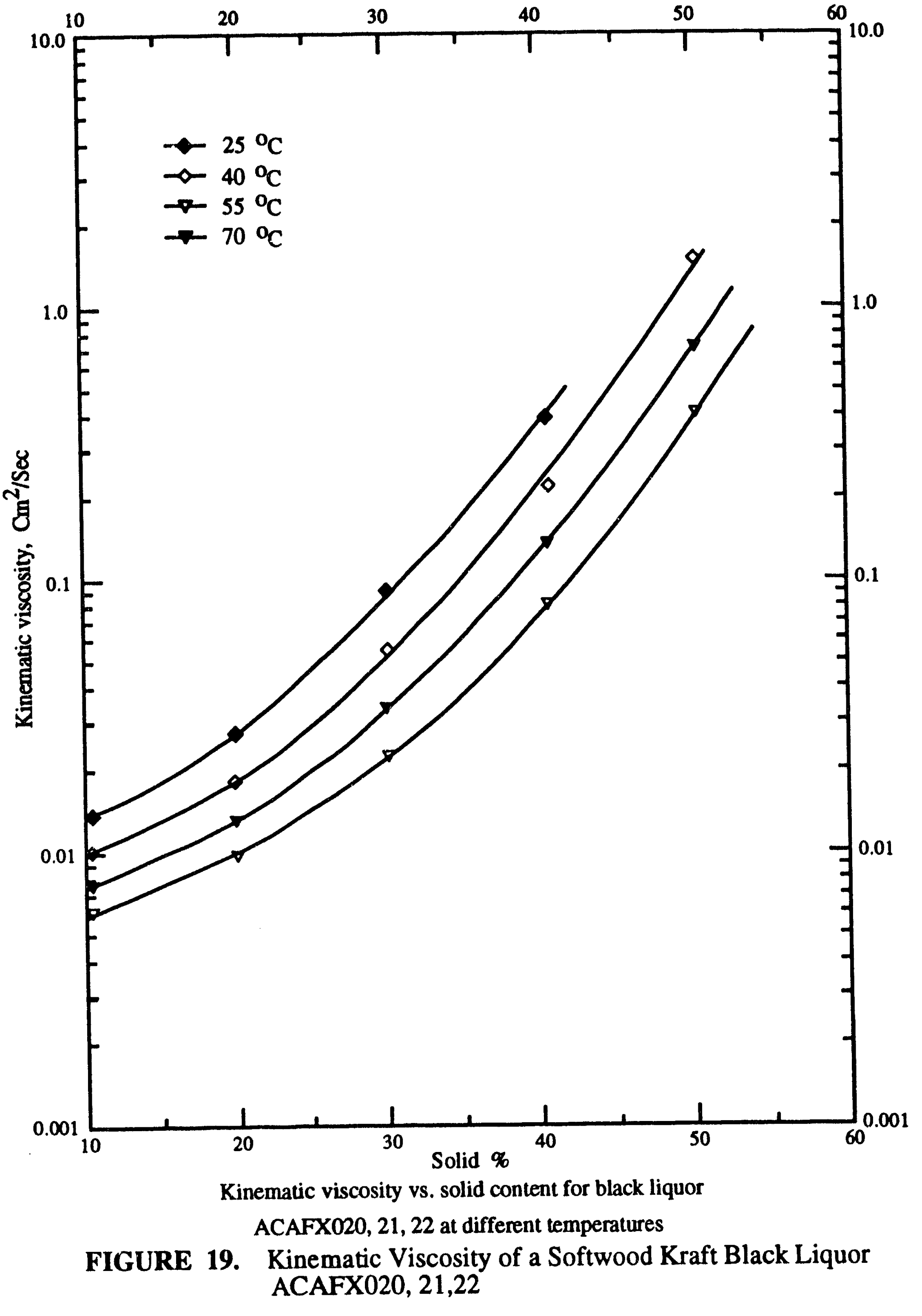
It is most difficult to prepare uniform samples at concentrations between the highest concentration attainable in the small scale evaporator and 100% solids. For small samples for DSG and calorimetry, an aliquot of sample at the highest concentration attainable in the small scale evaporator is weighed directly into the sample container to be used for the specific experiment, dried under heat and vacuum to a specified weight, encapsulated, and equilibrated by holding the encapsulated sample at elevated temperature (50-90°C) for an extended period. For larger samples, an aliquot is dried under heat and vacuum to a specified weight, chilled with dry ice and ground with dry ice, mixed cold, and then allowed to equilibrate at elevated temperature in a small, closed container. Obviously, most of the work will be done at concentrations up to the maximum attainable in the small scale evaporator and at 100% solids. At present, we appear to be able to concentrate in the small scale evaporator up to 85% solids, even though we cannot always obtain reliable vapor pressure-temperature data up to that concentration.

VISCOSITY

The primary emphasis of the program continues to be determination of viscosity over as wide a range of solids concentration, temperature, and shear rate as possible. A total of five instruments in ten configurations are used for these measurements. All viscometers have been recalibrated and accuracies checked to improve precision to a level equal to or beyond, normally beyond, the level accepted for research with viscous solutions or melts. Where necessary, changes have been made to improve temperature control; all instruments, except the dual chamber, can now be controlled to ± 0.1°C or better. The dual chamber can be controlled within about ± 0.5°C or better. Considerable effort has been devoted to developing better loading and cleaning procedures to increase the rate of data collection and to permit data to be taken at high solids concentration and temperature without fear of lignin degradation. We are currently able to measure viscosity at up to 180°C, up to 80% solids concentration, and up to 10^4 $\sec^{-1}$ with the combination of instruments now in use. Data is being routinely taken up to about 80% solids concentration for temperatures ranging from 40 to 130°C and for shear rates ranging from less than one to about 800 $\sec^{-1}$. Data is routinely taken for solids concentrations from about 60 to about 80% solids for temperatures ranging from 40 to 90°C at shear rates up to 10^4 $\sec^{-1}$. Some data is taken for this solids range and shear rate range for temperatures up to 130°C. Thus, we are finally in a position to determine directly the viscosity of a liquor at any condition likely to be used for furnace firing. Work is now proceeding full time on liquor viscosity measurements.

LOW SOLIDS CONCENTRATION VISCOSITY

No black liquor has yet been found that exhibits non-Newtonian behavior at concentrations below 50% and temperatures above 25°C. Therefore, hydraulic capillary measurements are adequate for this range. Furthermore, all liquors studied to date follow corresponding states principles; i.e., reduced viscosity is a function of S/T where S is the solids concentration and T is temperature. Therefore, the complete relation can be defined by 16-20 experimental determinations made at four temperatures between 25 and 80°C for four to five concentrations between 10 and 50% solids. An example of such data is presented in Figure 19. Examples of the reduced viscosity relation for liquors are shown in



Kinematic viscosity vs. solid content for black liquor ACAFX020, 21, 22 at different temperatures

FIGURE 19. Kinematic Viscosity of a Softwood Kraft Black Liquor ACAFX020, 21,22

Figures 20 and 21. A considerable data bank is being built to permit us to develop a general correlation for low solids viscosity.

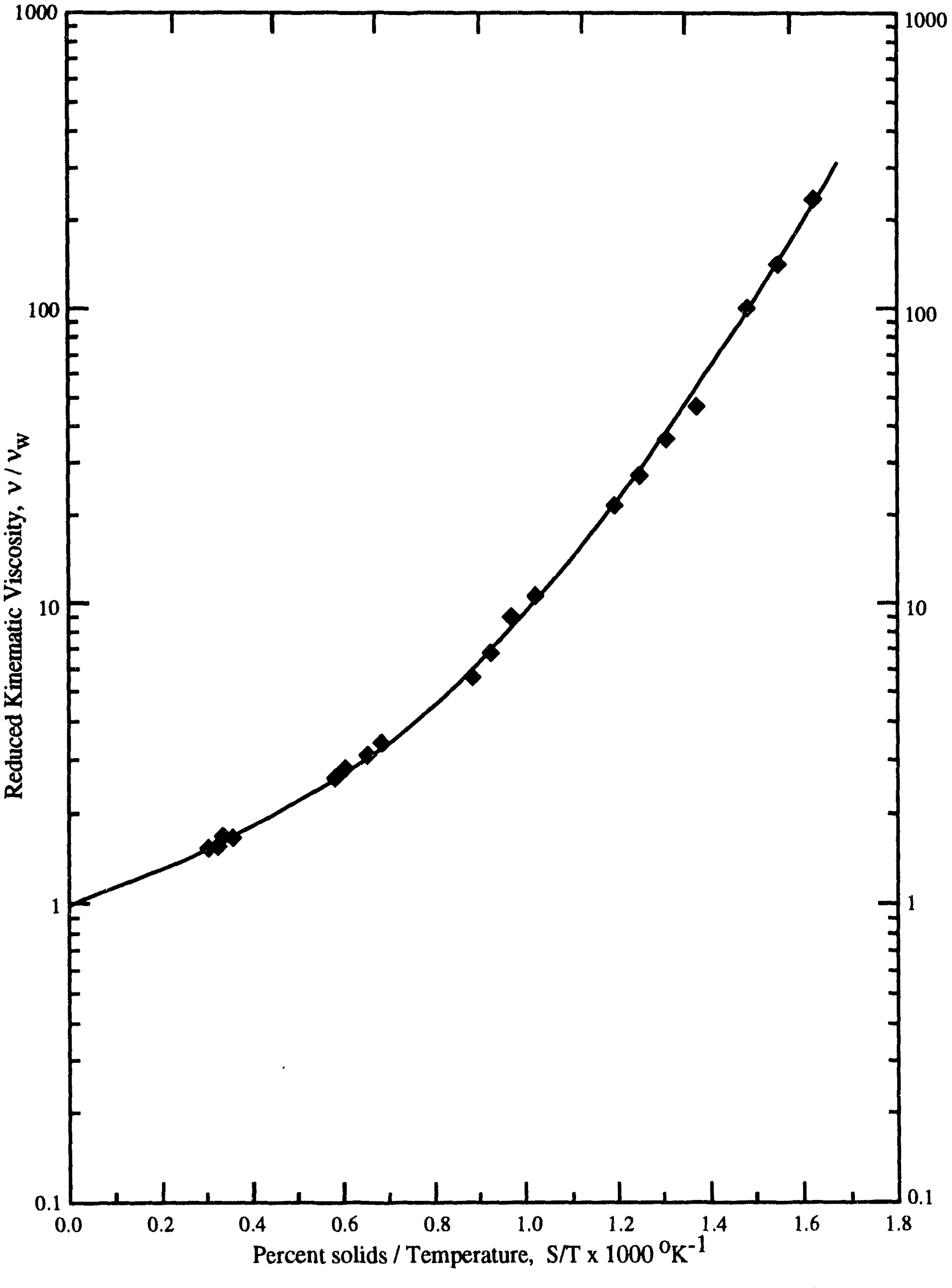
HIGH SOLIDS CONCENTRATION VISCOSITY

A combination of instruments are being used for these measurements. We are particularly interested in the zero shear rate viscosity as a function of solids concentration and temperature and the onset of non-Newtonian behavior at high solids concentration. Figures 22 through 29 exhibit data for a black liquor at 53.5 to 83.3% solids concentration temperatures ranging from a low of about 0.01 sec^{-1} to 1000 sec^{-1}. These data were taken using the Instron 3211 capillary rheometer, the Haake RV-12 rheometer with open parallel plates, open coaxial cylinder, and pressurized coaxial cylinder, and the Rheometrics RMS-800 with parallel plate geometry. Even though the data have not been properly fitted to a viscosity model (note the peculiarity in the curve for 60°C in Figure 24), this is a fairly complete set. The data shows the definite onset of non-Newtonian behavior at:

1. 60°C and about 1 sec^{-1} for 71.0% solids
2. ~95°C and less than 100 sec^{-1} for 77.9% solids
3. ~120°C and less than 300 sec^{-1} for 83.3% solids

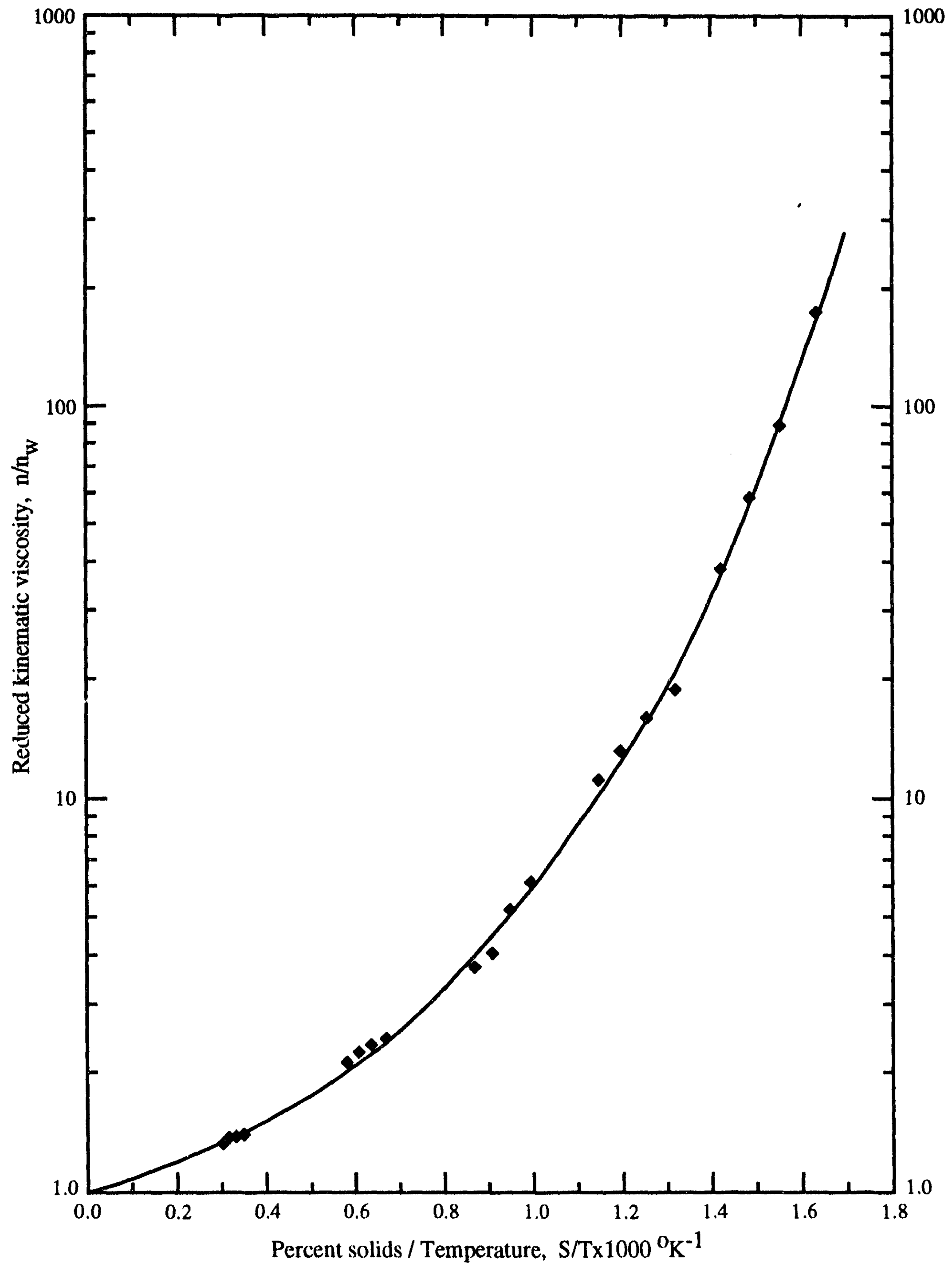
The effects of concentration on zero shear rate viscosity at various temperatures and the effects of temperature on zero shear rate viscosity at various concentrations for this liquor are shown in Figures 30 and 31.

These are examples of the data that is currently being collected for experimental and selected mill liquors. Because of the limited quantities of liquor usually available, experimental work must be carefully planned and there is seldom sufficient material to repeat specific experiments. Even so, complete mapping of



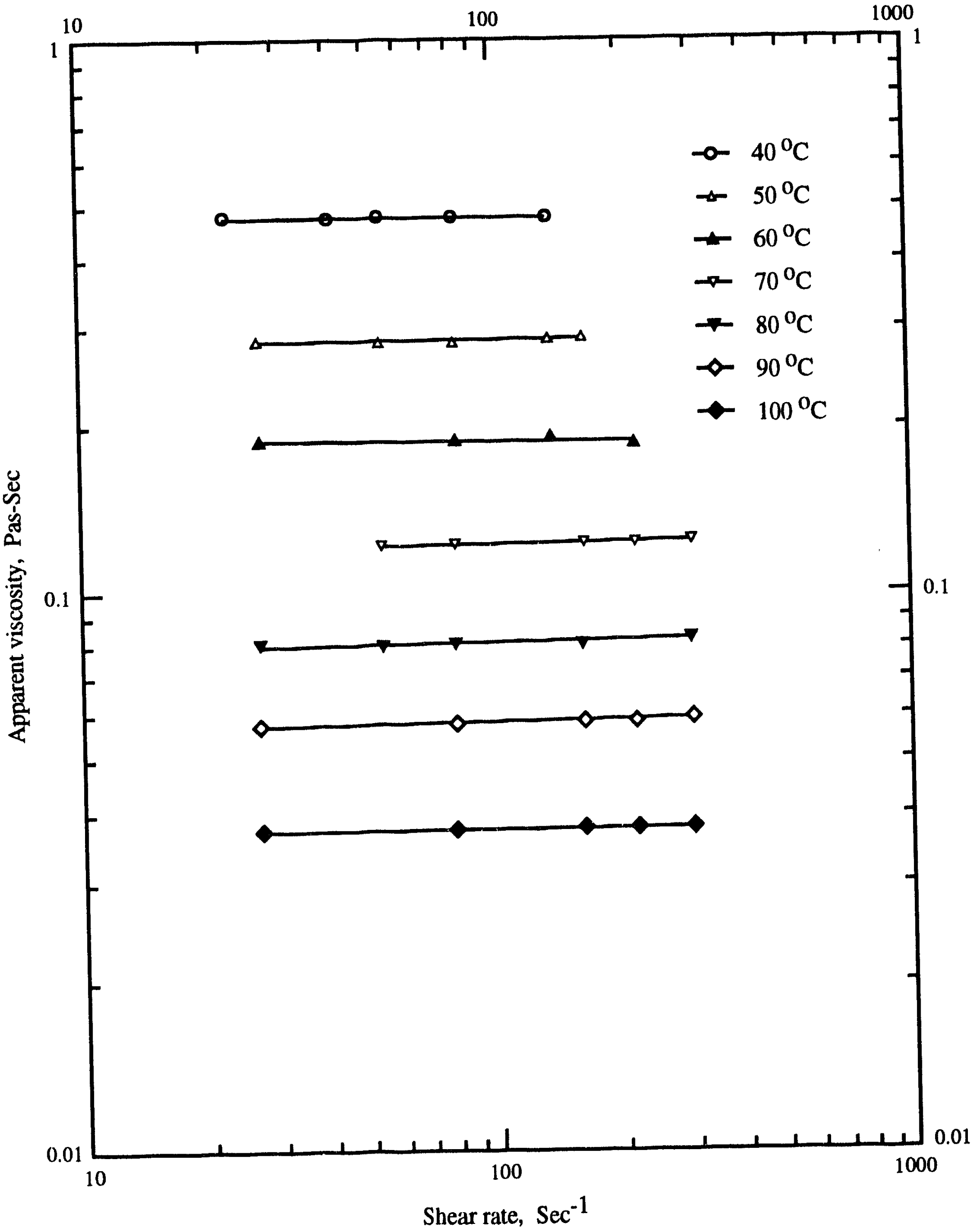
Reduced kinematic viscosity curve for black liquor ACAFX20, 21, 22

FIGURE 20. Reduced Kinematic Viscosity of Softwood Black Liquor ACAFX20, 21, 22 as a Function of S/T.



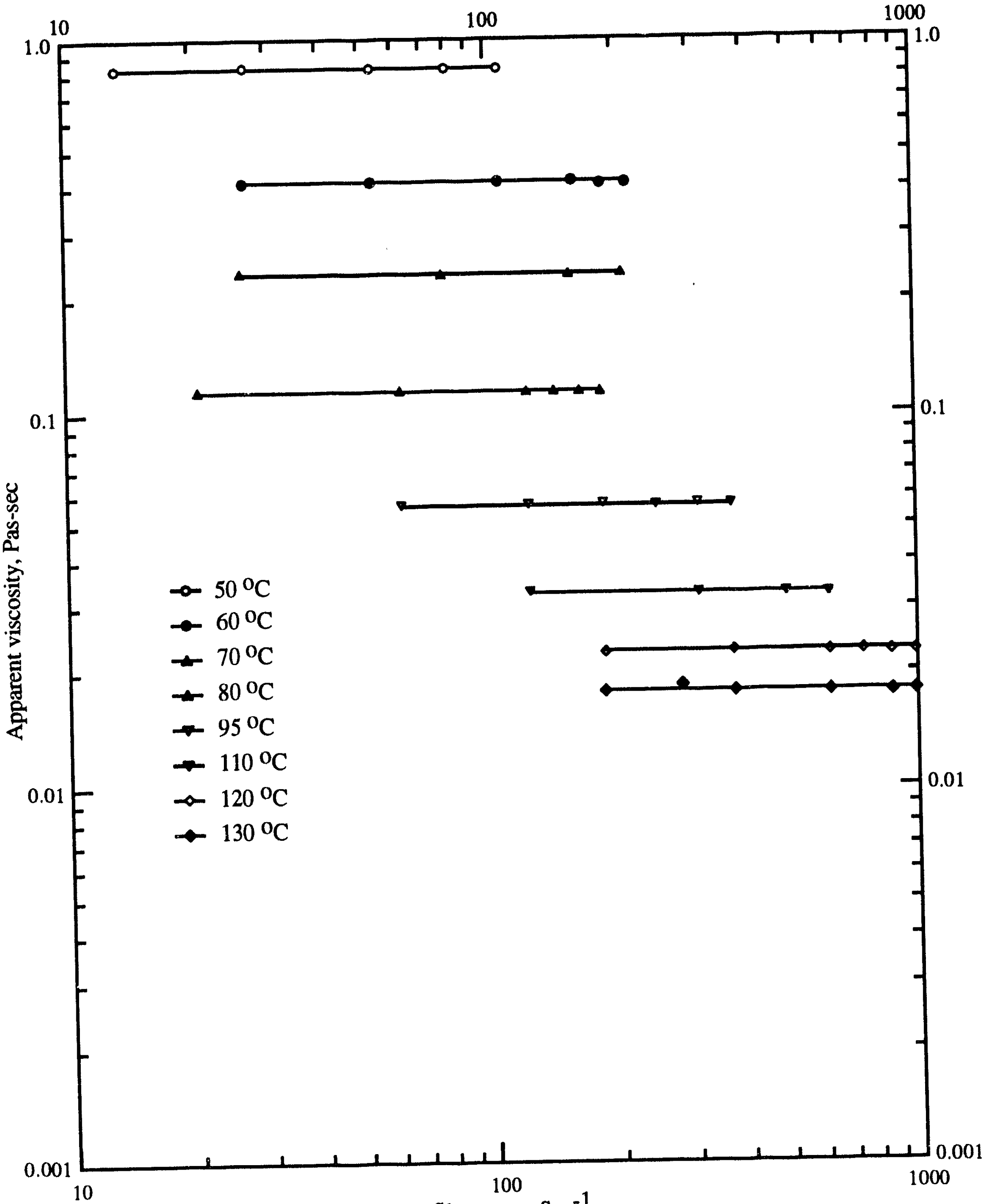
Reduced Kinematic Viscosity for black Liquor AXAGB001

FIGURE 21. Reduced Kinematic Viscosity of Softwood Kraft Black Liquor AXAGB001 as a Function of S/T



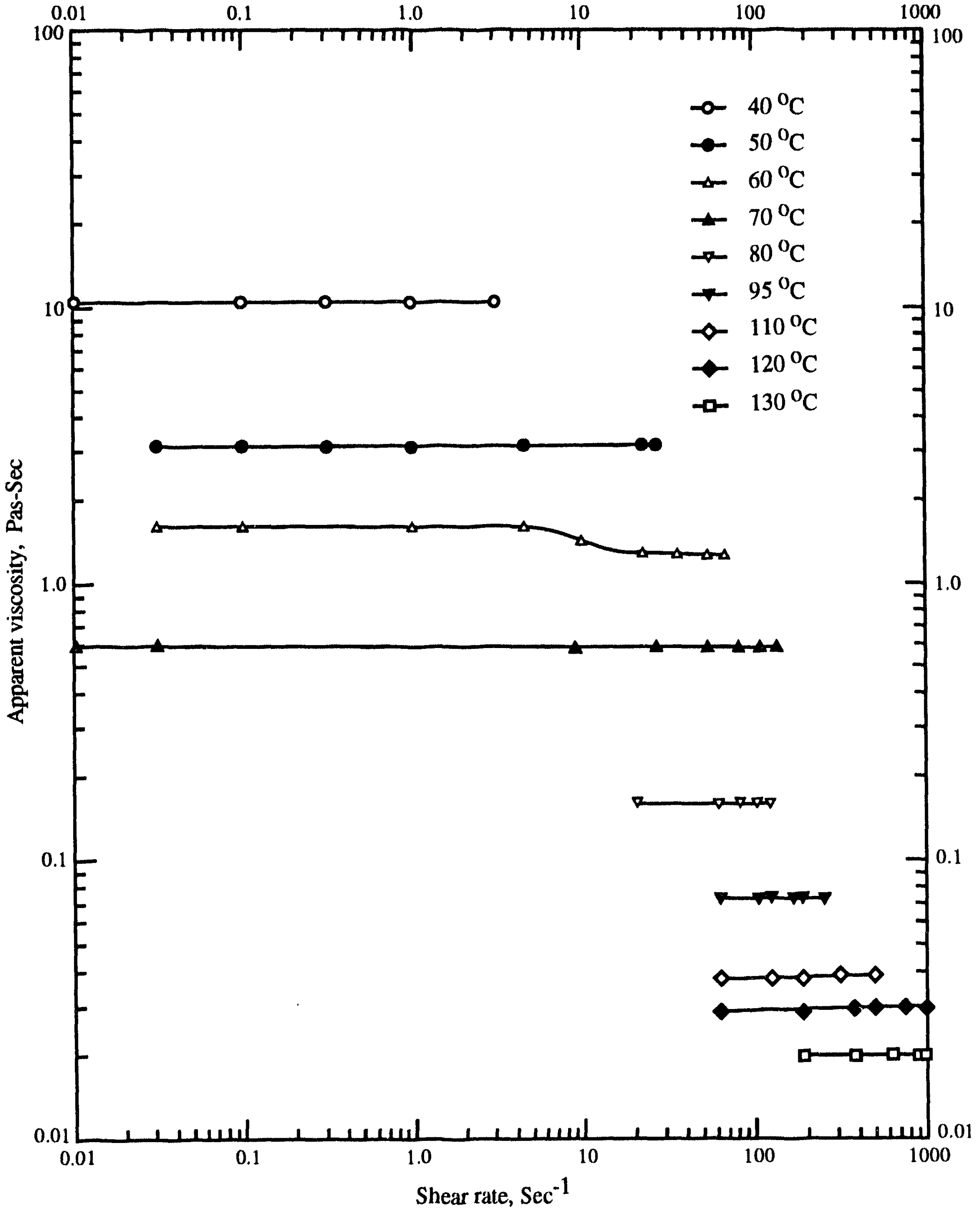
Dependence of viscosity on shear rate for 53.54% of solid black liquor AXAGB001

FIGURE 22. Viscosity of Softwood Kraft Black Liquor AXAGB001 at 53.54% Solids



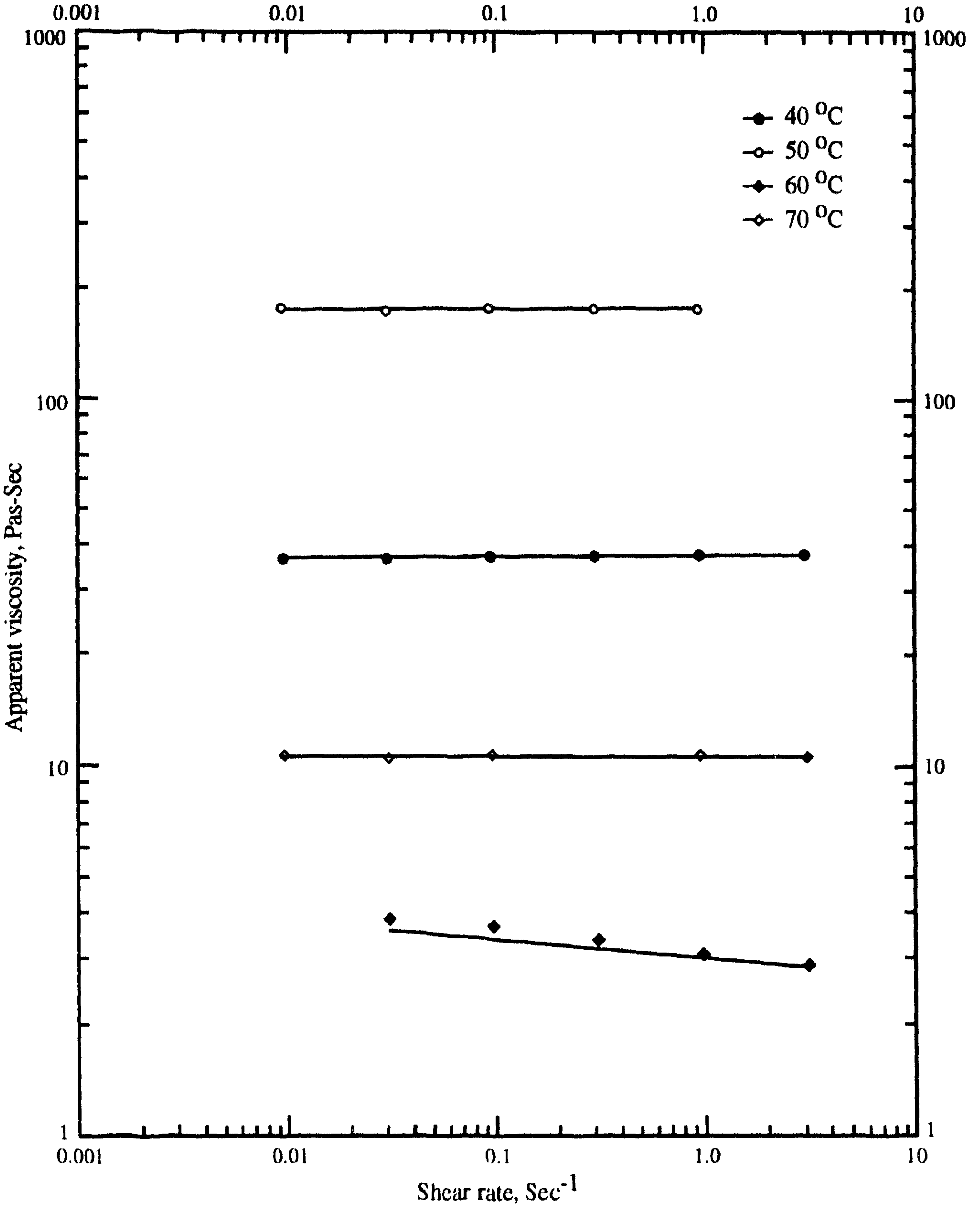
Viscosity vs. shear rate for 61.42% solid black liquor AXAGB001

FIGURE 23. Viscosity of Softwood Kraft Black Liquor AXAGB001 at 61.42% Solids



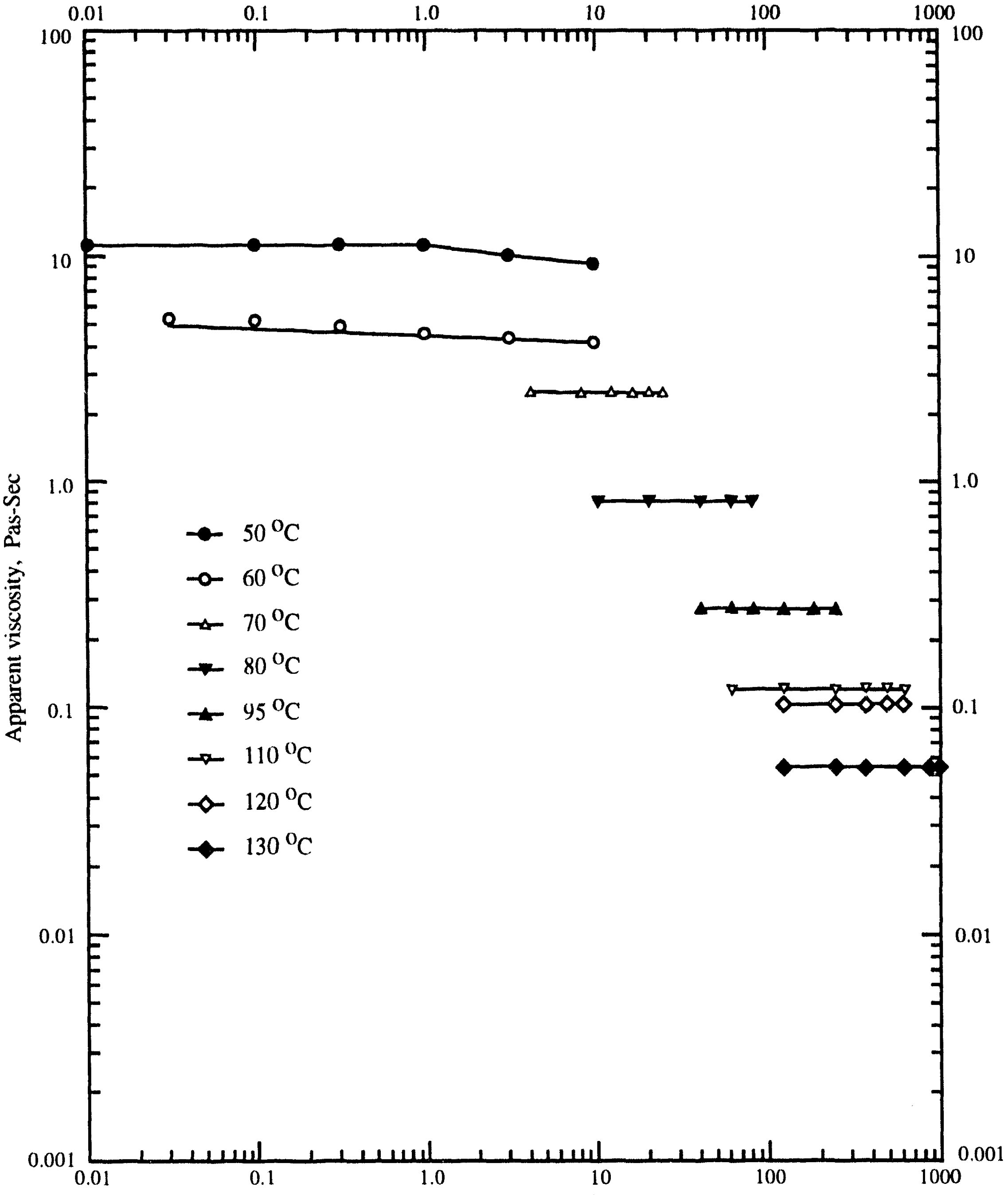
Dependence of viscosity on shear rate for 64.26% solid black liquor AXAGB001

FIGURE 24. Viscosity of Softwood Kraft Black Liquor AXAGB001 at 64.26% Solids



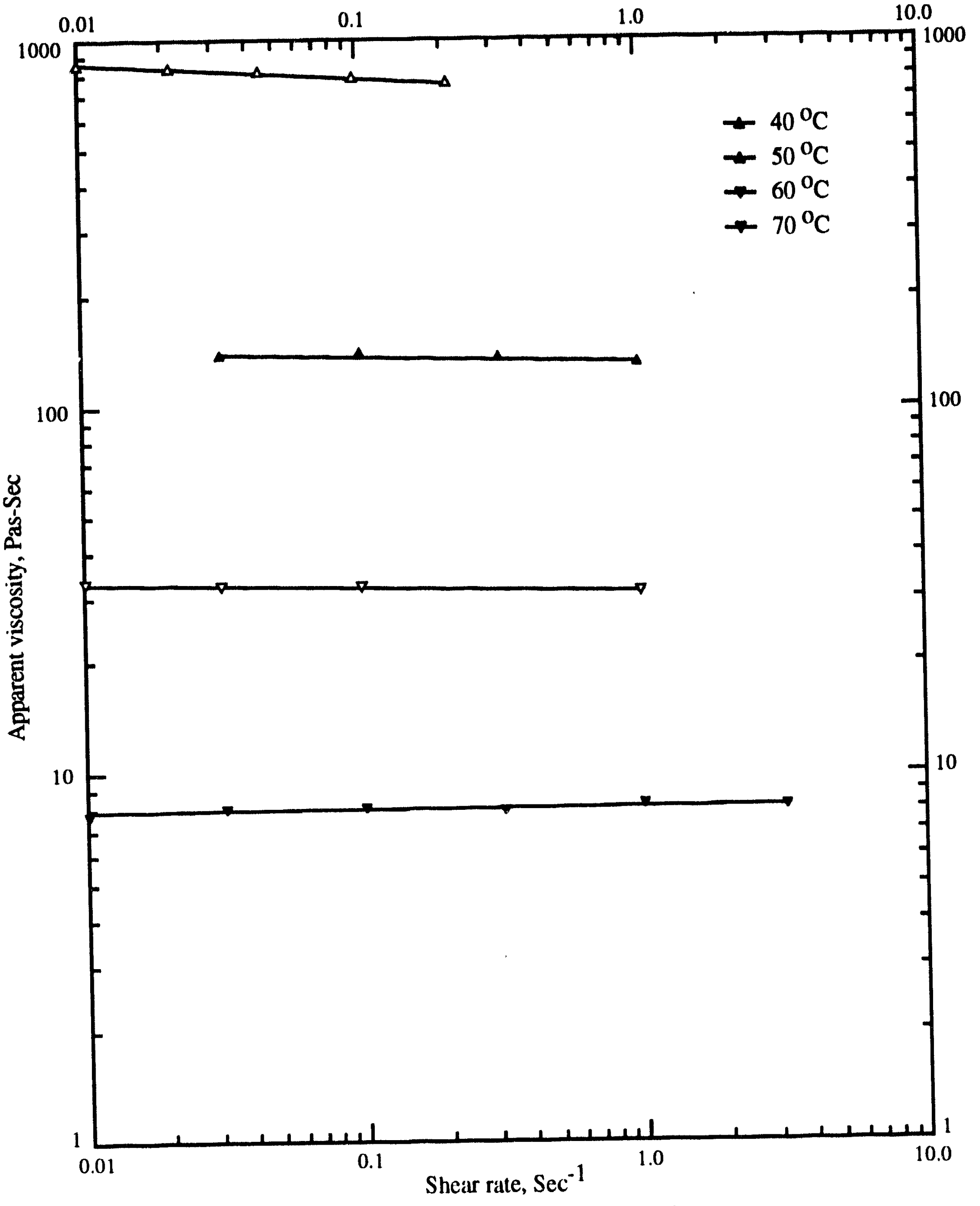
Dependence of zero shear rate viscosity on shear rate for 70.96% solid liquor AXAGB001

FIGURE 25. Viscosity of Softwood Kraft Black Liquor AXAGB001 at 70.96% Solidos and Low Shear Rates



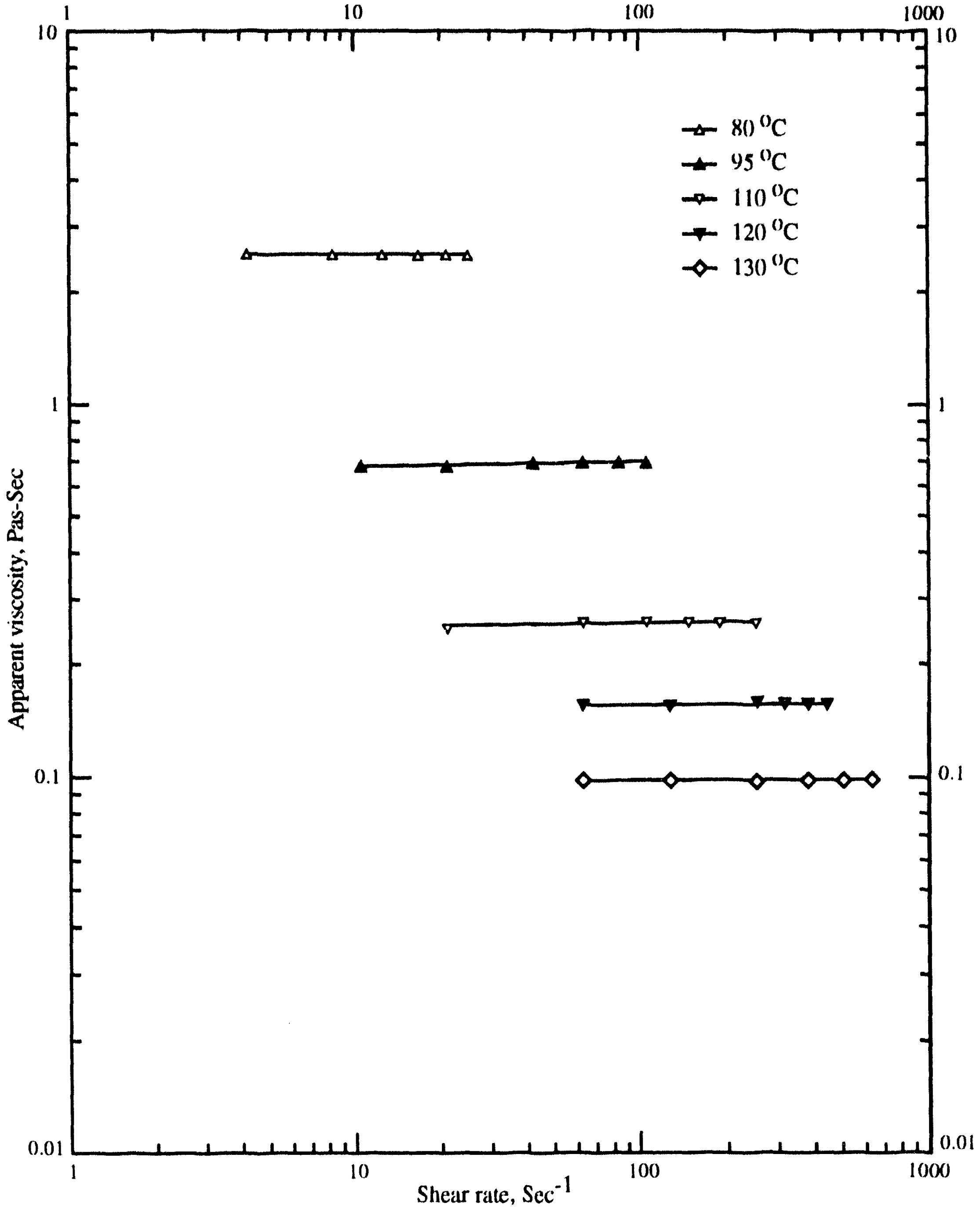
Viscosity vs. shear rate for 70.96% solid black liquor AXAGB001

FIGURE 26. Viscosity of Softwood Kraft Black Liquor AXAGB001 at 70.96% Solids and High Shear Rates



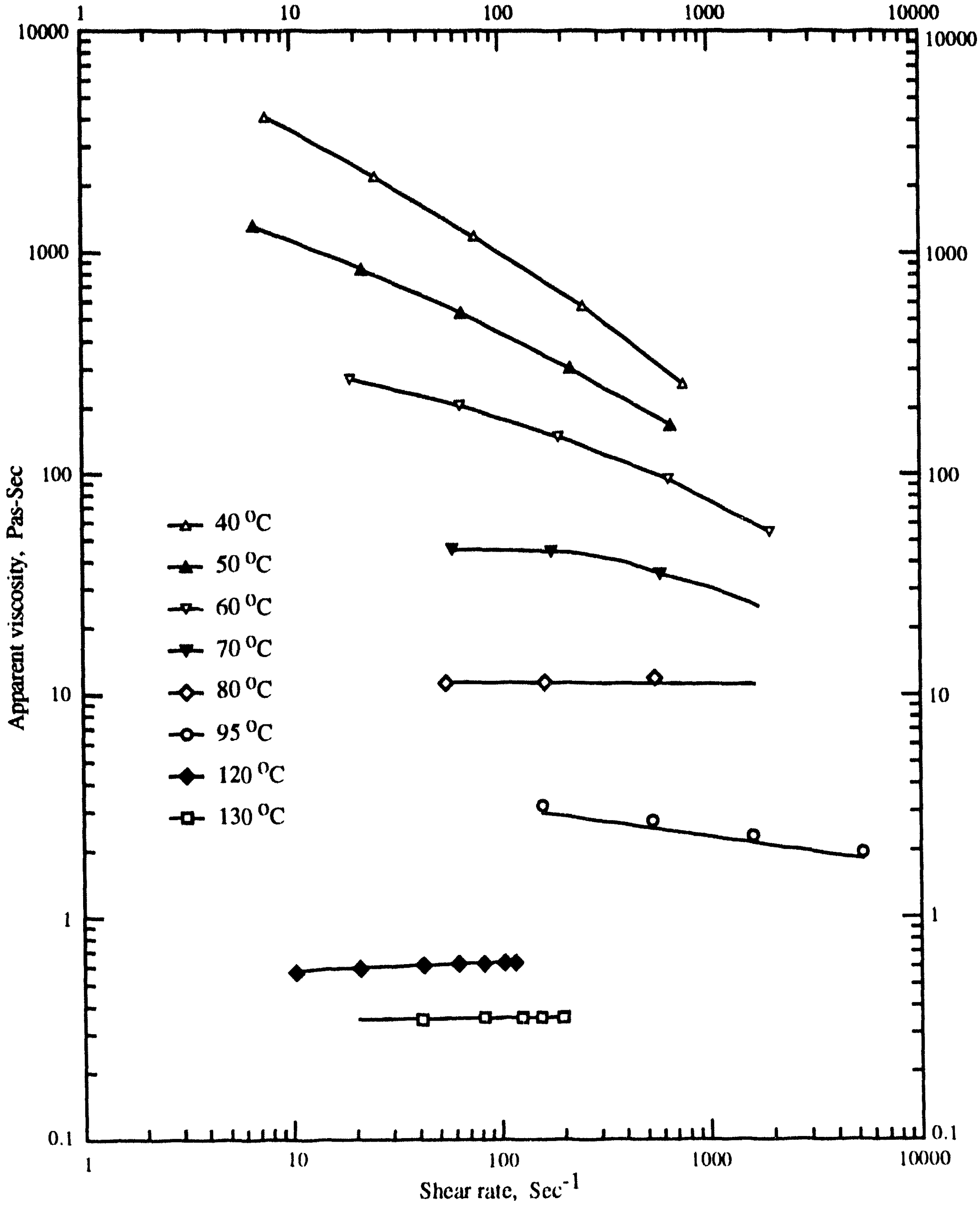
Dependence of zero shear rate viscosity on shear rate
for 73.94% solid blak liquor AXAGB001

FIGURE 27. Viscosity of Softwood Kraft Black Liquor AXAGB001 at 73.94% Solids and Low Shear Rates



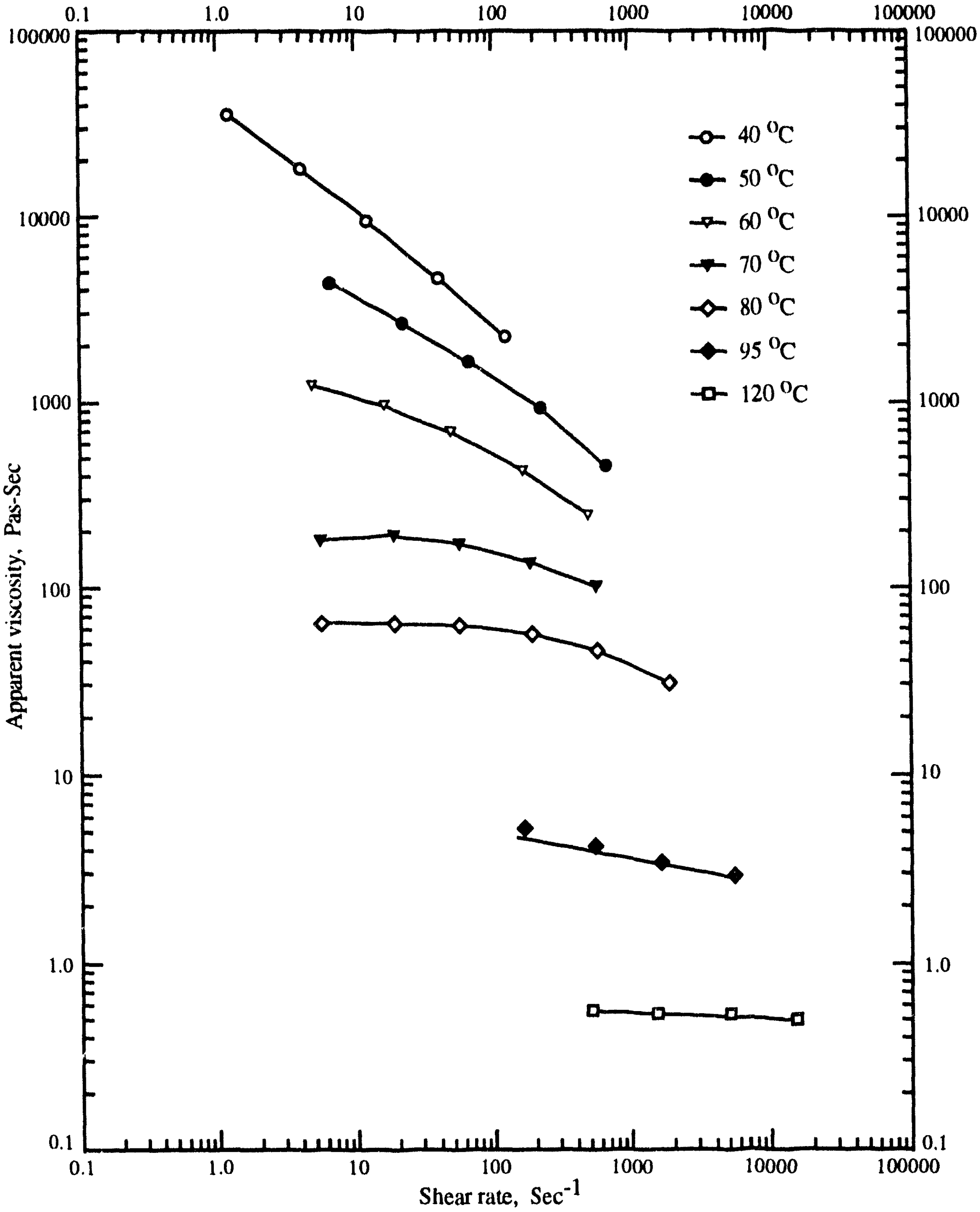
Viscosity vs. shear rate for 73.94% solid blak liquor AXAGB001

FIGURE 28. Viscosity of Kraft Black Liquor AXAGB001 at 73.94% Solids and High Shear Rates



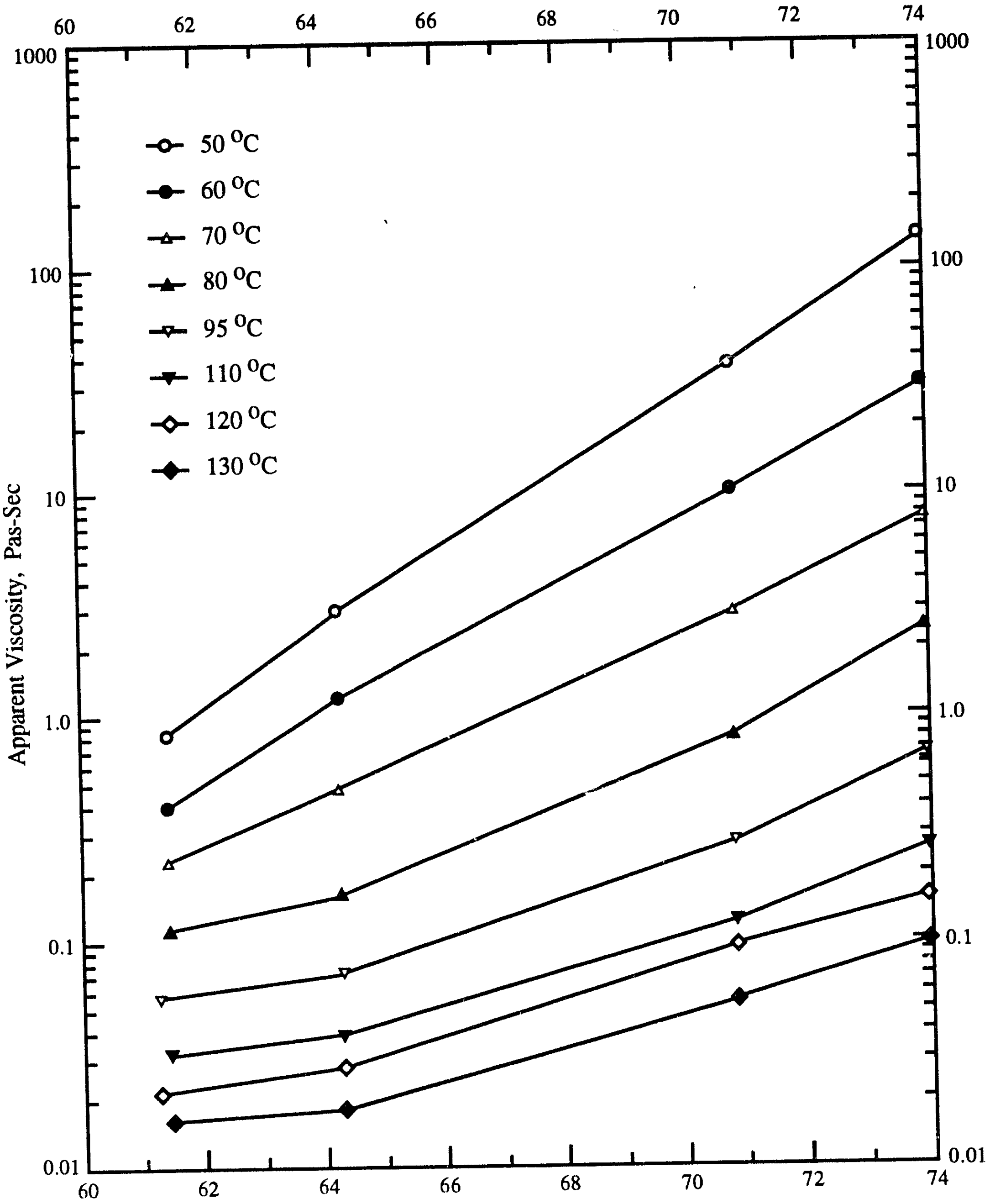
Dependence of viscosity on shear rate for 77.87% solid black liquor AXAGB001

FIGURE 28a. Viscosity of Kraft Black Liquor AXAGB001 at 77.87% Solids



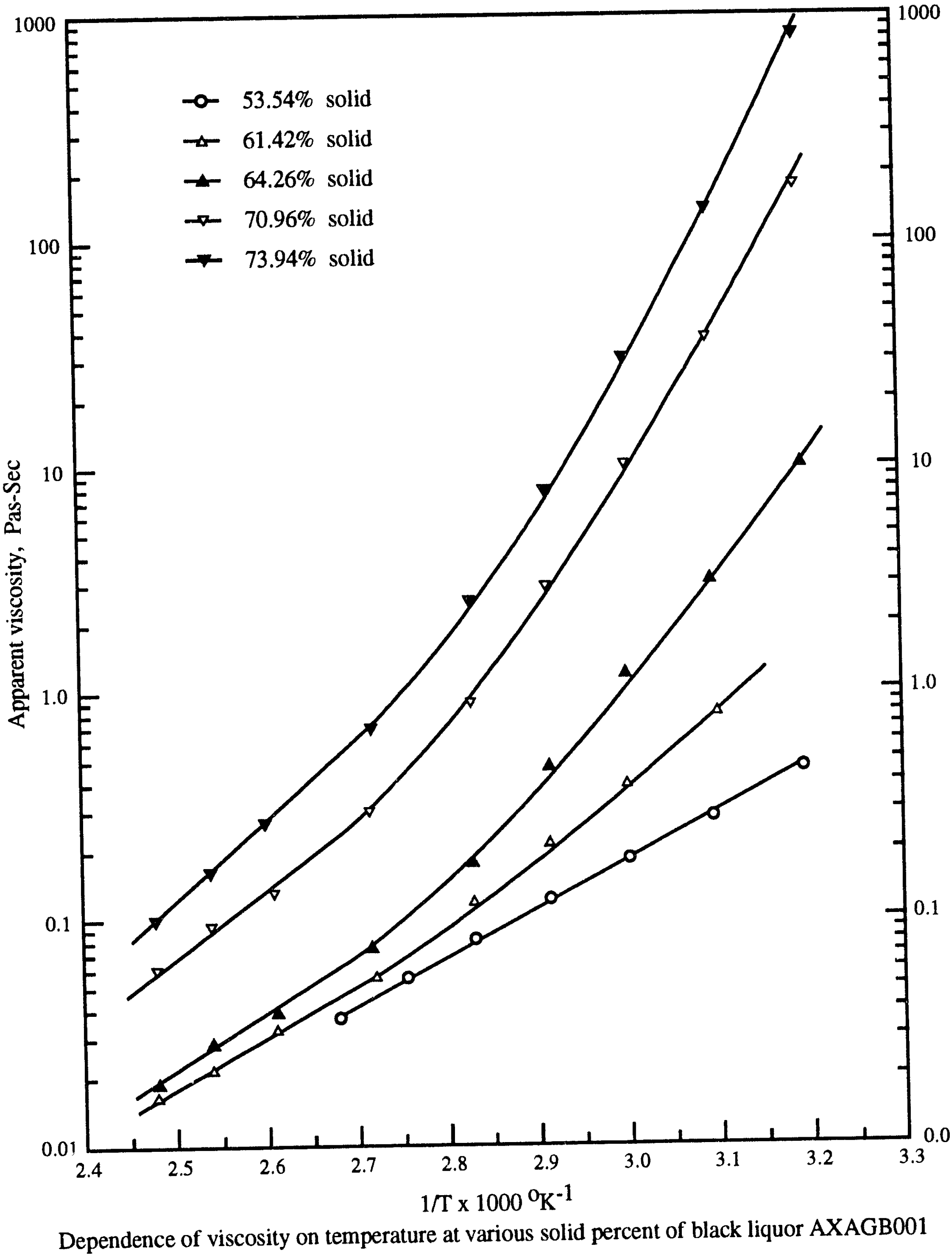
Dependence of viscosity on shear rate for 83.33% solid black liquor AXAGB001

FIGURE 29. Viscosity of Kraft Black Liquor AXAGB001 at 83.33% Solids



Dependence of viscosity on solid percent for black liquor AXAGB001

FIGURE 30. Effect of Solids Concentration on Zero Shear Rate Viscosity of Kraft Black Liquor AXAGB001 at Various Temperatures



Dependence of viscosity on temperature at various solid percent of black liquor AXAGB001

FIGURE 31. Effect of Temperature on Zero Shear Rate Viscosity of Kraft Black Liquor AXAGB001 at Various High Solids Concentrations

viscosity over the range of present or future practical interest can be determined experimentally. Data reduction and correlation programs are under development. It is now a matter of time and effort to collect data and develop final correlations.

PLANS AND ALLOCATION OF RESOURCES

With the few exceptions cited--installation of a second small scale evaporator, installation of a new column and a UV-visible detector on the HTHPLC, and construction of a thermal conductivity cell--all necessary capital items have been installed, and funds are currently available for all but the thermal conductivity cell. Furthermore, with few exceptions, all instruments are performing well and all necessary experimental procedures have been developed to a satisfactory level. The SEC is still not providing us with useful information on lignin MWD; this is important and is going to require additional work, most likely with NaOH solution as a solvent. Work must be done to improve density measurements at concentrations above 65% solids. Some improvement in techniques for loading the dual chamber viscometer must be made. Except for SEC work, however, little more needs to be done on developing or improving experimental procedures or techniques.

Emphasis has shifted almost entirely to data collection and data reduction. Pulping, liquor concentration, and liquor compositional analysis are now proceeding in a routine, planned manner. Thermal and rheological data collection and characterization of lignin are proceeding with individual work by graduate students and technicians. Programs have been or are being written for routinely calculating results, regressing data, and storing results. Where necessary, data reduction and correlation models are being programmed and data used for testing. In the near future, correlation models will be fully systemitized in time to use to develop final general correlations for physical properties.

Over the past fifteen months, most of our effort has been spent in improving methods or equipment, installing and calibrating instruments and systems, checking precision and reproducibility of methods, and repairing equipment. It has been virtually impossible to plan work systematically or to develop a realistic schedule. This has now changed. The last few months have been concentrated upon isolating the few remaining problems, evaluating and eliminating bottlenecks, and developing time estimates for each part of the overall program.

Our major problem at this time is manpower. Our staffing of two technicians and four graduate students is adequate only for evaluation of a total of about 40-50 additional liquors over the next two years. The capacity of the system appears to be about 80-95 additional liquors over the next two years, but this would require two additional technicians and at least one additional graduate student, which would cost an additional estimated $93,000 per year for two years, or a 25% increase in the current level of funding. A reasonable compromise between present level of effort and full capacity of the system would be the addition of one technician and one graduate student, which would cost an additional $57,700, or a 15% increase in the current level of funding. This compromise level should permit us to evaluate an additional 50-65 liquors over the next two years.

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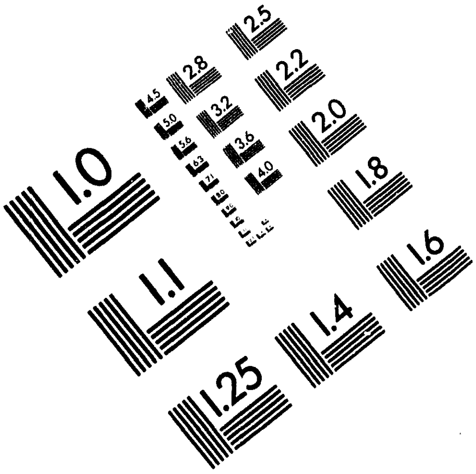

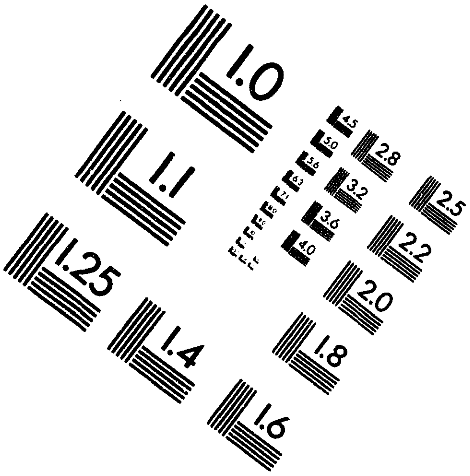

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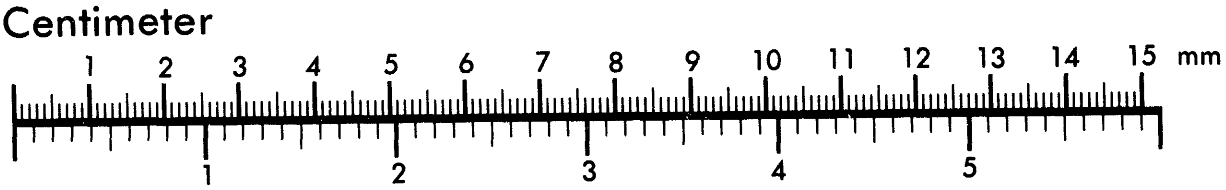

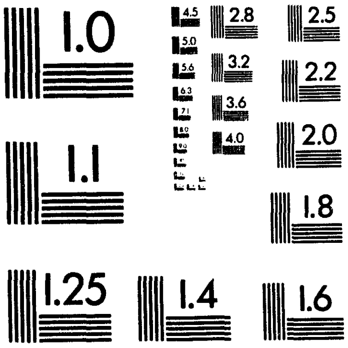

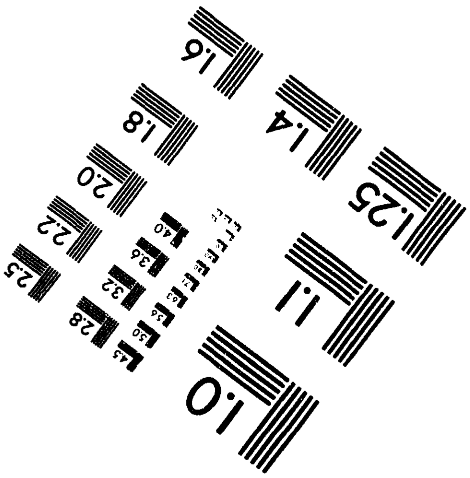

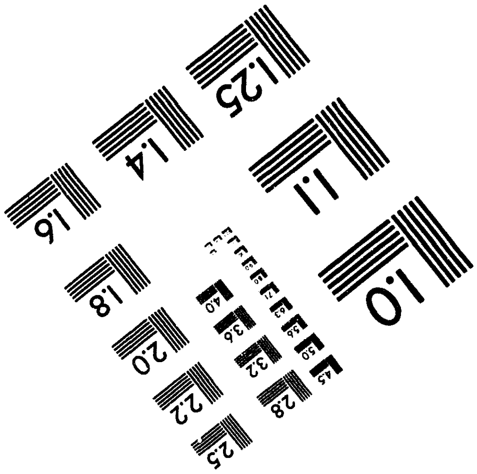

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