

COAL PRECURSORS FOR PRODUCTION OF CARBON AND GRAPHITE PRODUCTS

FINAL REPORT

April 8, 1996

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under Subcontract 62X-SR928C, WBS Element-UCAR-3

for
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
Managed by
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
for the
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I. SUMMARY

Chemical and analytical characterization data were obtained for NMP extracts of hydrotreated coal prepared by the West Virginia University (WVU) Group. Initial evaluation of small-scale samples produced by varying coal hydrotreating time, temperature, and catalyst type were used to define the conditions that would produce material suitable as binder, impregnant, C/C matrix pitches and precursors for needle coke, anode coke, and mesophase pitch fibers. In addition to analytical characterization, mesophase formation studies were used to assess the coal extract quality.

Based on the small-scale testing, specific extracts derived from hydrotreating coal at 450°C were recommended for scaleup. Evaluation of the 450°C - 2-hour hydrotreated coal extract showed that it should be suitable as an impregnant or binder pitch and as a precursor for needle coke and mesophase pitch. This material formed a large-domain mesophase, despite a high oxygen and nitrogen content.

A small graphite artifact was produced using coke derived from the extract as the filler and the extract itself as the binder. The coefficient of thermal expansion (CTE) of $0.26 \times 10^{-6}/\text{C}^\circ$, measured for the artifact is in the range found for electrode type graphite.

Coal extraction residues were steam activated to produce active carbons with surface areas from 400-700 m^2/gm . The program has demonstrated that the coal extraction process coupled with hydrotreatment, has the potential for providing a broad range of carbon and graphite products.

II. INTRODUCTION

The main goal of the overall program on "Coal-Based Precursors for Carbon Products" was to demonstrate the utility of coal extracts from the WVU extraction process as suitable base raw materials for the carbon products encompassed by the Carbon Products Consortium (CPC) team. These include binder and impregnating pitch, coke for graphite electrodes, cokes for anodes and specialty graphite, matrices for C/C composites and raw material for mesophase pitch fibers. Each of these products has unique requirements for properties of a suitable precursor. Our previous work on the Coal Precursor for Graphite Program⁽¹⁾ has shown that the WVU coal extraction process coupled with hydrotreatment, does have the potential for achieving this objective. Our current effort, therefore, involved the screening and evaluation of extracts produced by the WVU Group and recommending appropriate materials for scaleup for subsequent evaluation by Consortium Team members.

Our program involved an initial characterization of small-scale extracts using standard analytical methods and mesophase formation studies. This was followed by feedback to the WVU Group and to the CPC partners (Koppers, ALCOA, FMI, and APPI) with recommendation of material for scaleup. We also performed similar analytical and mesophase studies on some of the scaled-up extracts.

⁽¹⁾Research sponsored by the U.S. Department of Energy, Fossil Energy Advanced Research and Technology Development Materials Program, DOE/FE AA 15 10 10 0, Work Breakdown Structure Element UCAR-3"

As part of our program, we investigated the activation of the coal extraction residues for the purpose of producing a useful active carbon. A further task, which was started towards the end of the program, was to fabricate a small graphite artifact using coke derived from coal extract as the filler and the coal extract itself as a binder. The results of our studies are summarized in the following sections of this report.

III. EXPERIMENTAL PROCEDURES

A. Analytical Methods

1. Elemental Analysis - Elemental C, H, N, and O data were measured using a LECO CHN 1000 Analyzer. Elemental sulfur was measured using a LECO SC-132 carbon analyzer.
2. Thermogravimetric Analysis (TGA) - The data were obtained using TA Instruments 951 TGA module. Samples were heated at a rate of 10°C/minute in an inert atmosphere.
3. Nuclear Magnetic Resonance (NMR) - The NMR spectra were measured for CS₂ solutions using a Varian A-60 spectrometer. In order to increase solubility, the solutions were prepared by either refluxing with solvent or by ultrasonic mixing.
4. Toluene and Trichlorobenzene (TCB) Solubility - The insoluble contents in toluene and TCB were determined using procedures in ASTM D-4072.
5. Mettler Softening Point (SP) - The softening points were measured using a Mettler FP83HT SP apparatus following the standard procedures in ASTM D-3104.
6. Modified Conradson Carbon (MCC) - The MCC data (carbon yields) were obtained using procedures in ASTM D-2146.
7. Gel Permeation Chromatography (GPC) - Molecular weight determinations were obtained from GPC measurements using a Dupont 850 Liquid Chromatographic System coupled with a Knauer High Temperature Differential Refractometer. The column configuration and calibration have been described elsewhere⁽²⁾. The GPC data were obtained for the portion soluble in TCB solvent at 90°C.

B. Mesophase Formation Studies

1. Test-Tube Evaluations

The small-scale extracts were evaluated initially for mesophase quality by heating 0.7-1.3 gm samples in pyrex test tubes for six hours at 400°C in an inert gas environment. The objective was to produce a 15-40% mesophase content in the heat-treated residue, with most of the mesophase concentrated at the bottom of the test tube. After heat treatment, the pyrex test tubes were dissolved in aqueous HF, and the residues were mounted and polished by standard metallurgical procedures to show a midline vertical cross-section. Polarized light microscopy techniques were used to make a qualitative assessment of the amount and quality of the mesophase and the presence, if any, of insoluble solid contaminants in the extracts.

2. Mesophase Domain Size

Specimens for automated image analysis were prepared by heat treating the coal extracts in an inert atmosphere at 400°C in ceramic boats and then preparing "annealed" samples for the mesophase domain size measurements using procedures described elsewhere⁽³⁾.

3. Hot-Stage Microscopy

Direct observations of the melting behavior, gas evolution characteristics, mesophase formation rate, and mesophase quality were made while heating the coal extracts up to 400°C at 6-10°C/min. and holding at 400°C for several hours. Details of the cover glass "sandwich" configuration used to contain the sample, the modified Kofler hot stage and the polarized light microscope have been reported previously⁽⁴⁾.

A simple CCD video camera and color monitor/VCR system were acquired late in the contract period to facilitate direct recording of the dynamic behavior of the coal extracts when they were heated on the hot-stage microscope.

C. Steam Activations

Activation experiments were carried out on powdered coal extraction residues using a specially designed tumbling furnace. The activations were performed by passing a mixture of steam and N₂ over the sample maintained at a constant temperature of 900°C. The treatment was interrupted intermittently and the sample weighed to determine percent burn-off.

D. Graphite Fabrication

Small 19mm-diameter graphite electrodes were fabricated using calcined coke produced from hydrotreated coal extract as filler and the hydrotreated extract as the binder. The binder and filler were mixed and extruded using standard procedures. The formed rods were then baked and graphitized to 3,000°C.

IV. EXPERIMENTAL RESULTS

A. Small-Scale Coal Extracts

1. Sample Preparations

The WVU Group initially carried out a series of small-scale extractions on a hydrotreated bituminous coal, WVGS-13421. The coal was hydrotreated at three different temperatures 350°C, 400°C, and 450°C for a period of 1 hour in 800 psig H₂. An additional set of hydrotreatments was carried out at 450°C for 2 hours. For each temperature, the hydrotreatments were performed using tetralin as a hydrogen donor without a catalyst, and with the use of a Fe₂S₃ catalyst or a sulfided Mo catalyst. The NMP extractions were performed on the hydrotreated products.

Initial characterization data from the WVU Group showed that the softening temperatures of the 350°C and 400°C extracts were much too high to make them useful for most of the proposed applications of the Team. We therefore agreed to fully characterize only the 450°C-treated materials.

Our characterization results for the extracts from the WVGS-13421 coal hydrotreated at 450°C for 1 and 2 hours follow.

2. Analytical Characterization of 450°C - 1-Hour Samples

The analytical characterization data for the 3 different materials prepared from hydrotreated coal at 450°C for 1 hour are presented in Table I. The Mettler softening points (measured at WVU) range from 156° to 190°C which are too high for use as conventional binder and impregnant pitches.

Table I
Characterization Data for Extracts from Hydrotreated Coal, WVGS-13421, 450°C - 1 Hour

	C-269-2 Thermal	C-279-1 Fe ₂ S ₃	C-288-2 Mo(S)
SP°C	190	156	158
%C	85.2	84.5	81.9
%H	5.51	5.63	5.82
C/H atomic ratio	1.30	1.26	1.18
%N	3.08	2.89	3.73
%O	4.73	4.60	6.07
%S	0.49	0.57	0.43
TGA Yd%	49	46	42
%TI	28.9	-----	-----
%Arom. H.	38	36	33
GPC - MW (Mn)	415	395	371
%TCB Insoluble	40.6	26.0	19.7
%NMP	0	0.1	5

All the extracts show very high N and O contents. The Mo(S)-treated coal extract showed the highest N content as a result of retained NMP. The low C/H ratios are expected for the hydrotreated extracts.

The proton NMR spectra obtained in CS₂ solution are presented in Figures 1-3. The extracts were incompletely soluble in CS₂. We were able to obtain essentially complete solution in pyridine D-5; however, the residual hydrogen or water in the solvent interfered with the analysis. The extracts all show extremely high aliphatic hydrogen contents resulting from the hydrogenation of aromatic rings. The NMR results are also summarized in Table I. For comparison, a spectrum for coal tar binder pitch exhibits about 85% aromatic hydrogen compared to the 33-38% range for the extracts. From the NMR data as well as the C/H ratios, it appears that the catalytically treated materials may have been slightly more hydrogenated.

The TGA data for the 3 extracts are presented in Figures 4-6. The TGA carbon yields of 42-49% are quite acceptable for a pitch-type material. The low-temperature weight loss occurring from about 150-250°C is attributed to evolution of retained NMP solvent. This is particularly apparent in the TGA result for the Mo(S) product in Figure 6.

The GPC curves for the three 450°C - 1-hr. samples are shown in Figures 7-9. They are all similar, except for a resolved doublet in the Fe₂S₃

catalyzed material. They all show a broad symmetrical molecular weight distribution (MWD) with an apparent molecular weight range of about 250-900. The negative peaks in the GPC spectra are attributed to retained NMP. An estimate of the amount of NMP present was made by integrating these peaks and the results are summarized in the last line of Table I. Also shown in Table I are the toluene insolubles (TI) content and the measured insolubles in TCB.

3. Analytical Characterization of 450°C - 2-Hour Samples

The analytical data for the small-scale extracts obtained from coal hydrotreated at 450°C for 2 hours are summarized in Table II. The softening points are all considerably lower than those for the samples produced by hydrotreating for 450°C for 1 hour. Like the 450°C - 1-hour samples, the products in Table II exhibit very high N and O contents. The H contents, however, are higher, for the 2-hour samples reflecting the greater degree of hydrogenation. The 2-hour materials also showed a higher solubility in TCB than the 1-hour samples.

Table II
Characterization Data for Extracts from Hydrotreated Coal,
WVGS-13421, 450°C - 2 Hours

	C-300-3 Thermal	C-300-6 Fe ₂ S ₃	C-300-9 Mo(S)
SP°C	126	123	131
%C	84.2	83.9	86.1
%H	5.74	5.75	5.82
C/H atomic ratio	1.23	1.23	1.27
%N	3.65	3.60	3.22
%O	5.53	5.66	4.61
%S	0.35	0.42	0.41
TGA Yd%	40	41	42
%Arom. H	40	40	43
GPC - Mn	421	426	416
%TCB Insoluble	21.9	22.3	18.1
%NMP	2	2	1

The proton NMR data for the extracts in Figures 10-12 show a lower content of long chain aliphatic protons than for the 1-hour treated samples, indicative of more selective hydrogenation of aromatic rings. The TGA results in Figures 13-15 demonstrate a reduced carbon yield for the

450°C - 2-hour materials as compared to the 1-hour samples. The presence of retained NMP is evident from the weight loss occurring below 300°C. The GPC curves for the 450°C - 2-hour samples in Figures 16-18 exhibit somewhat broader MWD's when compared to the 1-hour extracts, which could account for the lower softening points. The amounts of NMP solvent present in the extracts, as measured from integrating the negative GPC peaks, are also summarized in Table II. From the measured properties, there appears to be no advantage for the use of a catalyst during the hydrotreatment.

4. Mesophase Formation Studies of 450°C - 1-Hour and 2-Hour Samples

Hot-stage microscopy examinations were carried out on all three of the small-scale 450°C - 1-hour samples. The primary results from the heat-up and hold period at 400°C are summarized in Table III. The initial softening temperatures from visual observations on the hot-stage were reasonably consistent with the Mettler S. P. results in Table I. The most unusual feature of the hot-stage microscopy observations was the onset of vigorous bubbling, presumably gas evolution, at temperatures in the 250° to 275°C range. Conventional coal tar and petroleum pitches do not show this vigorous bubbling behavior below 300°C. Evolution of residual NMP (202°C Boiling Point) could be responsible for a portion of the low-temperature gas evolution from the extracts, but certainly not all of it, because the vigorous gas evolution continued throughout the 300°-400°C range. Dehydrogenation and/or decomposition reactions are suspected to be the origin of the gas evolution in these initial 450°C - 1-hour extracts, but an attempt to confirm evolution of H₂, H₂O, or other low MW gases in this temperature range was not successful⁽⁵⁾.

Mesophase spheres were detected at the edge of the cover glass sandwich in all three 450°C - 1-hour samples after ~20 min. at 400°C, indicating that all of them had comparable mesophase formation rates. The mesophase viscosity appeared to be reasonably low, based on bubble deformation behavior, and was essentially equivalent in the 3 samples. The overall mesophase quality was estimated to be borderline for a needle coke precursor.

All of the samples contained a small amount of finely divided solids, but none had a concentration judged high enough to have a significant effect on coke quality or performance as an impregnant. However, these finely divided solids would be expected to degrade the performance of these extracts as a mesophase pitch fiber precursor.

All of the 450°C - 1-hour and 450°C - 2-hour samples were evaluated by the test-tube method. Measured yields after heat treatment at 400°C for six hours were in the 72 to 85% range. However, all of these samples foamed extensively during the heat treatment, so some material may have been lost. The extensive foaming during the test-tube heat treatments of the 450°C - 1-hour samples is consistent with the vigorous low-temperature bubbling behavior noted during the hot-stage microscopy observations. The 450°C - 2-hour samples foamed as much as the 450°C - 1-hour samples in the test-tube heat treatments, so the additional reaction time at 450°C did not seem to have any significant effect on this characteristic of the small-scale extracts.

Examination of the domain size in the coalesced mesophase layer, which collects at the bottom of the test tube for conventional coal tar and petroleum pitches, can be used as an indicator of overall mesophase quality. Unfortunately, gas evolution from all of the small-scale extracts was so copious and disruptive that no well-defined coalesced mesophase formed at the bottom of the test tube. The actual appearance of all of the residues from test-tube heat treatments of the extracts is shown schematically in Figure 19. Because of the effects of gas evolution, we were not able to obtain a definitive evaluation of the uniformity and quality of the mesophase formed in the small-scale extract by the test-tube method. However, based on appearance, the overall mesophase quality was judged to be borderline for a needle coke precursor. The true mesophase quality may have been somewhat better, but the effects from the gas evolution precluded obtaining a definitive answer.

Finely divided solids were detected around the perimeter of most of the coalesced mesophase regions and many of the larger mesophase spheres in all of the test-tube residues. These solids provided a local, short-range decrease in the mesophase domain size, but the effect on the overall quality was minor.

Qualitative SEM/EDX analyses were carried out on the finely divided solids in the C-296-2 (Thermal, 450°C - 1-hour) extract. Most appeared to be carbonaceous, some contained high Si, Al, O levels ($\text{SiO}_2 + \text{Al}_2\text{O}_3$?), and some contained high Cu, Fe, S, and O levels (possibly a mixed copper and iron sulfate). The WVU Group suggested that the high Cu content in the last type of solid may have originated via attack of a copper gasket by the hot reactant mixture in the small-scale apparatus.

Table III
Summary of Hot-Stage Microscopy Observations on 450°C - 1-Hour Samples

SAMPLE	INITIAL SOFTENING TEMP., °C	ONSET OF VIGOROUS BUBBLING, °C	INITIAL DETECTION OF MESOPHASE, TIME AT 400°C
C269-2 Thermal	198	255-275	21 min.
C279-1 CF-1, Fe ₂ S ₃	155	250	16
C288-2 CF-2, Mo(S)	125	235	24

B. Large-Scale Extracts from Hydrogenated Coal

1. Sample Preparation

Following our evaluation of the small-scale extracts, we recommended that the 450°C hydrotreated coal materials be scaled up for evaluation by the Team. The extracts produced without the use of any catalyst appeared suitable for testing as a binder and impregnating pitch and as a precursor for needle coke and mesophase pitch for fibers.

Scaleup of the hydrotreated coal extracts was performed at WVU by hydrotreating 600 grams of powdered coal in 1-gallon batch reactors. They investigated 2 different coals using hydrotreatment times of 1 and 2 hours at 450°C. A description of the 4 materials produced (A066, A076, A075, and A073) and the properties measured at WVU are summarized in Table IV. The materials were also vacuum dried for an extended time in order to remove all of the retained NMP. We received about 200 gms of each material for further characterization.

Table IV
Large-Scale, Hydrotreated Coal Extracts

Prepared Conditions	A066 Coal 13421 450°C - 1 hr.	A076 Coal 13421 450°C - 2 hr.	A075 Coal 13423 450°C - 1 hr.	A073 Coal 13423 450°C - 2 hr.
SP, °C	155.8	101.7	129.3	112.5
Density, g/cc	1.264	1.227	1.220	1.223
TI, Wt %	22.3	12.1	19.8	20.9
Coke Yield, Wt %	62.4	54.0	54.7	52.6

2. Analytical Data for Large-Scale 450°C Hydrotreated Coal Extracts

The data and properties obtained for the four large-scale coal extracts are summarized in Table V. We fully characterized the more extensively hydrotreated (2-hour) samples because these had the lowest softening points, making them more suitable for use as binder or impregnating pitch. In general, these larger scale products were superior in behavior to the small-scale samples discussed previously. One major characteristic was the essentially complete absence of any retained NMP. The N and O contents were therefore substantially reduced, but they were still much higher than those found in conventional coal tar pitches. The C/H ratios are similar to those in the comparably treated small-scale extracts.

Only the 2-hour products had softening points in the range of those for conventional carbon binder and impregnant pitches. The carbon yields of 52% for these materials are similar to those for commercial solids-free pitches of comparable softening point.

Table V
Properties of Large-Scale WVU Coal Extracts

	A076 450°C - 2 Hrs. Coal 13421	A066 450°C - 1 Hr. Coal 13421	A073 450°C - 2 Hrs. Coal 13423	A075 450°C - 1 Hr. Coal 13423
SP, °C	104.7	160.7	115.3	134.5
MCC %	52.9	63.0	51.7	53.7
TGA Yd%	34	45	31	36
C, %	88.9	-----	89.6	-----
H, %	5.85	-----	5.78	-----
C/H Ratio	1.28	-----	1.30	-----
N, %	2.20	-----	1.90	-----
O, %	2.74	2.27	2.49	3.33
S, %	0.45	-----	0.33	-----
Ar H %	45	44	48	39
Mn (GPC)	367	417	389	388
Mesophase (μ)	272	166	136	78

The proton NMR spectra for the four materials in Table V are presented in Figures 20-23. All the extracts show substantial contents of hydrogenated ring systems. The decrease in the long chain aliphatic hydrogen peak at about 1.3 ppm, with extended hydrogenation, is particularly noticeable for the WVGS-13423 coal. The TGA curves for these large-scale extracts are shown in Figures 24-27. It is evident that the improved sample-drying procedure has removed any retained NMP. As expected, the total TGA weight losses increase for the more severely hydrotreated samples. The GPC curves for the four materials shown in Figures 28-31 do not exhibit any negative peaks due to NMP. The more severely hydrotreated coals show a broader molecular weight distribution (MWD) and the presence of an unresolved component at 280 a.m.u. when compared to the 1-hour samples.

3. Characterization of Extract Distillation Residues

We also received 3 distillation residues prepared by vacuum stripping of Sample A073 at temperatures of 250°C, 350°C, and 400°C. The materials are described in Table VI. The samples were prepared to determine whether we could detect any chemical changes resulting from heat treating at these temperatures.

Table VI
Vacuum Distillation Residues from Sample A073 (WVGS 13423 - 450°C - 2 Hours)

SAMPLE	DISTILLATION TEMP., °C	YIELD, %
D035-1	250	76
D035-2	350	70
D035-3	400	68

We obtained NMR and TGA data for these residues and the results are summarized in Table VII. The NMR results show an increasing aromaticity with increasing depth of distillation. It is not possible to determine whether this effect is due to removal of volatile hydrogenated components during distillation or to low-temperature cracking reactions. The NMR data for the distillation residues are presented in Figures 32-34 while the TGA data are shown in Figures 35-37.

Table VII
Characterization of Hydrotreated Coal Extract Distillation Residues

SAMPLE	% AROM H	% LONG CHAIN*	TGA Yd. %
D035-1	52	21	43
D035-2	55	22	58
D035-3	60	15	57

* % of aliphatic H that is long chain

4. Mesophase Evaluations of Large-Scale Extracts

Hot-stage microscopy examinations were carried out on both of the 450°C - 2-hour extracts in the same run. The A073 extract began to soften visibly at 94°C, and the A076 extract had slumped noticeably by 104°C while they were being heated at 6°C/min. to 400°C. The low initial visible softening temperatures on the hot-stage are consistent with the low Mettler S. P.'s given in Tables IV and V for these two extracts.

Both of these large-scale extracts evolved much less gas between 250°C - 350°C as compared to the levels seen with all of the small-scale extracts. They behaved much more like conventional petroleum and coal tar pitches in their low-temperature gas evolution characteristics. Apparently, the combined effects of more stringent drying conditions to remove residual NMP and the somewhat more severe reaction conditions

employed by the WVU Group for the large-scale extracts had nearly eliminated the severe gas evolution problem detected with the small-scale extracts.

Small amounts of mesophase spheres were detected at the edges of the cover glass sandwiches in both A073 and A076 extracts after ~25 min. at 400°C, indicating that they had comparable initial mesophase formation rates. These onset times are only marginally longer than those noted for the 450°C - 1-hour, small-scale samples.

A hot-stage microscopy run carried out with both of the 450°C - 1-hour samples showed an initial softening temperature of 114°C for A066 extract and 146°C for A075 extract. These results are reasonably consistent with the Mettler S. P. data in Tables IV and V.

The A066 and A075 extracts also evolved much less gas in the 250°-350°C range than the small-scale extracts. Clearly, the beneficial effects from the more stringent drying conditions and the somewhat different reaction conditions employed by the WVU Group were realized after only 1 hour at a nominal reaction temperature of 450°C.

Small amounts of mesophase were detected at the perimeter of the cover glass sandwiches for both A066 and A075 extracts after 21-22 min. at 400°C on the hot-stage microscope. Hence, the mesophase formation rates of these large-scale 450°C - 1-hour samples were comparable to each other and to those for both the 450°C - 1 hour large-scale and small-scale extracts. Both of the 450°C - 1-hour samples appeared to generate slightly more true pyrolysis gas during the hold period at 400°C than the 450°C - 2-hour samples. This is an indication that the 450°C - 1-hour samples had a slightly higher initial rate for cracking reactions.

All of the large-scale extracts were heat treated in boats at 400°C to produce approximately 50% mesophase and then subjected to the "annealing" process for measurement of mesophase domain size. Polarized light (crossed polars) micrographs taken at 50X and 250X magnification of the derived mesophase are shown in Figures 38-41. It is apparent that the more extensively hydrotreated extracts give larger domain size mesophase than the less-treated 1-hour samples. It is also evident that the mesophase derived from the WVGS-13421 coal extract has a larger domain size than that from WVGS-13423 coal for the same hydrotreatment severity. The A076 extract from WVGS coal 13421 hydrotreated 2 hours at 450°C gave the largest mesophase domain size of any of the large-scale extracts. Mesophase domain sizes were obtained by image analysis and are reported in Table V. It is apparent that the domain sizes of the extracts from the

WVGS-13423 coal are significantly smaller than the corresponding extract from the WVGS-13421 coal. The measured domain size of 272 μ m for the A076 extract is in the range found for excellent needle coke precursors.

The presence of solid particles in the coalesced mesophase and at the mesophase/isotropic phase boundary was noted to some extent in the annealed samples from all of the large-scale extracts. The WVGS-13421 extracts had more of this finely divided material than those derived from WVGS-13423. Figure 42 shows an area where the solids have collected or segregated in a small region near the edge of the coalesced mesophase from the A076 extract sample from WVGS-13421. SEM/EDX analyses of the particles in this cluster showed that several different materials were present. Carbonaceous particles with very high C and modest S levels were numerous, presumably coke-like material from the original coal which had not reacted during hydrotreatment. Particles with high Si, Al, and O contents were also prevalent, presumably very small ash particles from the original coal which had not been removed completely during the filtration step after hydrotreatment and NMP extraction. There was also a significant number of particles with high Fe, Cr, S, and possibly O contents, presumably iron and chromium sulfates. A few particles with high Ti and O contents (TiO_2 ?) or high Cu, K, and small O contents (calcium and potassium sulfides or sulfates?) were also detected. As expected, most of these finely divided solids originate in the coal. Presumably, their removal would be more complete in larger scale equipment.

C. Additional Extract Samples

Small quantities of three additional extract materials were received from the WVU Group toward the end of the contract period. Two of the samples were the toluene soluble (TS) portions from hydrotreated coal extracts. D065-2 was the TS portion from a 450°C - 1-hour hydrotreatment of the WVGS-13423 coal, and D054 was TS from a 450°C - 2-hour hydrotreatment of WVGS-13421 coal. Both of these extracts melted in the 90°-100°C range on the hot-stage microscope and had low yields after heating to 400°C at 6°C/min. Both were also very refractory during the hold period at 400°C and required 1.5-2.0 hours to produce detectable mesophase spheres. An attempt to evaluate their mesophase domain size was unsuccessful because these TS materials were so unreactive under the normal heat treatment conditions and had low yields. The low softening point behavior and low yield upon heat treatment are consistent with the low MW range encompassed by toluene soluble material.

A third extract (A122) was prepared at WVU by carrying out a 450°C - 1-hour hydrotreatment on the toluene insoluble (TI) fraction from a large-scale NMP extract from an initial 450°C - 2-hour hydrotreatment of WVGS-13423 coal. This double-hydrotreated material had an initial softening temperature of 188°C and formed mesophase spheres quite rapidly at 400°C, probably due to distillation of volatiles. Additional mesophase formed at a normal rate for

thermal processing of good feedstocks at 400°C. The mesophase quality appeared excellent on the hot stage. A standard mesophase evaluation showed that A122 had a domain size of approximately 200 μ m by visual observation on the annealed sample. Quantitative image analysis was not reliable on this sample because the mesophase in the annealed specimen had so many cracks. The oxygen content of the double-hydrotreated A122 material was still 1.88%, indicating that the O heteroatom structures in these coal extracts are very resistant to removal by hydrogenation. Even with this high oxygen content, the A122 extract still formed a high-quality mesophase.

D. Activation of Coal Extraction Residues

The economics of the coal extraction process would be improved if the extraction residues also had some value. For this purpose, we attempted to activate these materials to produce a high surface area carbon. We obtained samples of the NMP extraction residue of raw coal WVGS-13421, as well as the extraction residue of a coal hydrotreated at 450°C for 2 hours (A-67).

Both materials were activated in a H₂O/N₂ mixture at 900°C using a tumbling furnace. The hydrotreated (A-67) residue was very refractory and after about 81 hours of treatment gave a 64% burn-off. The raw coal residue was much more reactive and gave about 85% burn-off after 48 hours.

The surface areas and pore characteristics were determined for both materials at the Oak Ridge Laboratory by T. Burchell and E. L. Fuller. The measured surface area for the activated residue from the untreated coal was 770 m²/gm while that for the hydrotreated coal was 212 m²/gm. The lower surface area and refractory nature of the hydrotreated residue is expected since it would have a greater ash content than the residue from the untreated coal. Since hydrotreatment increases the extraction yield, it would also lead to a higher ash content in the insoluble residue.

In a subsequent study, we obtained a second sample of the extraction residue from untreated coal and attempted to produce active carbons using different amounts of burn-off. We prepared 3 materials with active carbon yields of 50, 65, and 68%. These samples were also submitted to T. Burchell for surface area measurement. The results are summarized in Table VIII along with our measured ash analysis for these activated carbons. The results show that surface area does increase with increasing burn-off. However, more detailed studies would be needed to determine the optimum activation that can be achieved for these residues.

Table VIII
Active Carbons from Coal Extraction Residue (Activated at 900°C, H₂O)

SAMPLE	ACTIVE CARBON Yd. %	SURFACE AREA m ² /gm	% ASH
65-1	50	464	4.6
65-3	65	410	4.3
65-2	68	332	4.2

E. Fabrication of Graphite Artifacts from Hydrotreated Coal Extracts

We produced a graphite artifact using coal extract-derived coke as the filler and the coal extract itself as the binder. The coal extract coke was produced from WVGS-13421 coal hydrotreated for 450°C for 2 hours. The raw coke was prepared at WVU and then calcined to 1,100°C by T. Burchell at the Oak Ridge Laboratory. The same coal NMP extract was used as the binder for graphite fabrication. The extract (D-085) had a 113°C Mettler softening point and a 52.6% MCC value. After milling, the calcined coke was mixed with 1/3 by weight of the coal extract binder and then extruded to produce 19mm-diameter rods. The rods were baked and graphitized to 3,000°C. The properties measured for the graphitized rods were the following:

Coefficient of Thermal Expansion (CTE) = $0.26 \times 10^{-6}/^{\circ}\text{C}$

Specific Resistance = 9.55 micro-ohm-meters

Density = 1.376 g/cc

The very low CTE value of 0.26 is similar to that measured for electrode graphite derived from petroleum needle coke. The relatively low density for the fabricated artifact could be due to an inappropriate binder level or to a puffing effect from the nitrogen in the coke.

V. DISCUSSION

Our screening evaluation studies have demonstrated that the coal extraction process has the potential for producing acceptable products for all the applications anticipated for the program. However, hydrotreatment is necessary to produce materials that are suitable for use as pitches, coke precursors, or mesophase raw materials.

The extract from the hydrotreated coal WVGS-13421, 450° - 2 hours appears to be acceptable as either a carbon binder or impregnation pitch. Summarized in Table IX is a comparison of the properties for the A076 extract with those for commercial coal tar binder and petroleum impregnant pitches. The carbon yield (MCC) for the extract is quite high for a solids-free pitch with a softening point of 105°C. Some of the analytical characteristics of the extract are quite unusual in comparison to those for the commercial pitches. The low aromatic

hydrogen content reflects the effects of hydrotreatment of the precursor coal. The high N and O contents are also unusual for a binder or impregnant pitch material.

Our mesophase evaluation studies show that a material, such as the NMP extract of the WVGS-13421 coal hydrotreated for 450°C for 2 hours, is capable of forming a very large domain mesophase. This extract could therefore be used to produce a mesophase pitch which may be acceptable for fibers. The mesophase quality is comparable to that for precursors of needle coke. The high nitrogen content would be a drawback for processing of such a coke. The excellent mesophase development for a pitch such as the A076 extract is surprising because of its very high oxygen content. A high oxygen content in coal conversion materials has been previously associated with a high reactivity and a poor mesophase quality. Obviously, the form of oxygen in these hydrotreated coal extracts is different from that in typical coal conversion products and does not lead to a fast coking reactivity.

Our results have shown that a hydrotreated coal extract such as the A076 can be used directly as a binder pitch without any subsequent processing. The direct production of pitches by the extraction process could have advantages over the current commercial coal tar binder pitch processes which involve the distillation of coal tar. The need for coke oven processing for tar generation and the handling of by-products from tar distillation would be avoided. It is likely that pitches with different properties could be obtained by controlling the hydrotreatment and extraction conditions.

We have demonstrated that coke derived from hydrotreated coal extract can be used to produce graphite with a low coefficient of thermal expansion, a requisite for graphite electrodes. By altering the processing conditions and the use of blends, it would be possible to produce graphites with varying degrees of anisotropy. We had shown previously that isotropic graphite can be produced from the coal extract⁽¹⁾. No other process has the flexibility for producing this range of carbon materials. The high nitrogen contents of the extracts could, however, be a drawback for the use of these materials for some graphite products.

Finally, the extraction residue can be activated to produce an activated carbon. The best procedure for achieving an optimum active carbon still needs to be defined. However, the use of the residue for a commercial applications would definitely improve total process economics.

Table XI
Properties of Coal Extract and Commercial Pitches

	EXTRACT A076	COAL BINDER	PETROLEUM IMPREGNANT
SP, °C	105	112	120
MCC %	53	58	52
C, %	88.9	93.8	91.5
H, %	5.85	3.92	5.0
N, %	2.20	0.70	0.6
O, %	2.74	0.93	0.5
S, %	0.45	0.56	2.5
ArH %	45	85	55
Mol Wt.	370	410	500

References:

- (1) "Coal-Based Nuclear Graphites for the New Production Gas-Cooled Reactor" DOE Grant DE FG02-91 NP00159, Final Report, May 31, 1994
- (2) R. A. Greinke and L. H. O'Connor, *Anal. Chem.* 52, 1877 (1980)
- (3) R. T. Lewis, I. C. Lewis, R. A. Greinke, S. L. Strong, *Carbon* 25, 289 (1987)
- (4) R. T. Lewis, Extended Abstract for 12th Biennial Carbon Conference, Pittsburgh, PA, p. 215, 1975
- (5) E. L. Fuller, ORNL, personal communication

Figures

- Figure 1: Proton NMR in CS₂ Solution for C-269-2, Hydrotreated Coal 450°C - 1 Hour, No Catalyst
- Figure 2: Proton NMR in CS₂ Solution for C-279-1, Hydrotreated Coal 450°C - 1 Hour, Fe₂S₃ Catalyst
- Figure 3: Proton NMR in CS₂ Solution for C-288-2, Hydrotreated Coal 450°C - 1 Hour, Mo(S) Catalyst
- Figure 4: TGA Curve for C-269-2, Hydrotreated Coal 450°C - 1 Hour, No Catalyst
- Figure 5: TGA Curve for C-279-1, Hydrotreated Coal 450°C - 1 Hour, Fe₂S₃ Catalyst
- Figure 6: TGA Curve for C-288-2, Hydrotreated Coal 450°C - 1 Hour, Mo(S) Catalyst
- Figure 7: Gel Permeation Chromatography (GPC) Curve for C-269-2, Hydrotreated Coal 450°C - 1 Hour, No Catalyst
- Figure 8: Gel Permeation Chromatography (GPC) Curve for C-279-1, Hydrotreated Coal 450°C - 1 Hour, Fe₂S₃ Catalyst
- Figure 9: Gel Permeation Chromatography (GPC) Curve for C-288-2, Hydrotreated Coal 450°C - 1 Hour, Mo(S) Catalyst
- Figure 10: Proton NMR in CS₂ for C-300-3, Hydrotreated Coal 450°C - 2 Hours, No Catalyst

Figure 11: Proton NMR in CS₂ for C-300-6, Hydrotreated Coal 450°C - 2 Hours, Fe₂S₃ Catalyst

Figure 12: Proton NMR in CS₂ for C-300-9, Hydrotreated Coal 450°C - 2 Hours, Mo(S) Catalyst

Figure 13: TGA Curve for C-300-3, Hydrotreated Coal 450°C - 2 Hours, No Catalyst

Figure 14: TGA Curve for C-300-6, Hydrotreated Coal 450°C - 2 Hours, Fe₂S₃ Catalyst

Figure 15: TGA Curve for C-300-9, Hydrotreated Coal 450°C - 2 Hours, Mo(S) Catalyst

Figure 16: Gel Permeation Chromatography Curve for C-300-3, Hydrotreated Coal 450°C - 2 Hours, No Catalyst

Figure 17: Gel Permeation Chromatography Curve for C-300-6, Hydrotreated Coal 450°C - 2 Hours, Fe₂S₃ Catalyst

Figure 18: Gel Permeation Chromatography Curve for C-300-9, Hydrotreated Coal 450°C - 2 Hours, Mo(S) Catalyst

Figure 19: Schematic Diagram of Test-Tube Heated Coal Extract

Figure 20: Proton NMR Spectrum for A076 from Hydrotreated Coal WVGS-13421 - 450°C, 2 Hours

Figure 21: Proton NMR Spectrum for A066 from Hydrotreated Coal WVGS-13421 - 450°C, 1 Hour

Figure 22: Proton NMR Spectrum for A073 from Hydrotreated Coal WVGS-13423 - 450°C, 2 Hours

Figure 23: Proton NMR Spectrum for A075 from Hydrotreated Coal WVGS-13423 - 450°C, 1 Hour

Figure 24: TGA Curve for A076 from Hydrotreated Coal WVGS-13421 - 450°C, 2 Hours

Figure 25: TGA Curve for A066 from Hydrotreated Coal WVGS-13421 - 450°C, 1 Hour

Figure 26: TGA Curve for A073 from Hydrotreated Coal WVGS-13423 - 450°C, 2 Hours

Figure 27: TGA Curve for A075 from Hydrotreated Coal WVGS-13423 - 450°C, 1 Hour

Figure 28: Gel Permeation Chromatogram for A076 from Hydrotreated Coal WVGS-13421 - 450°C, 2 Hours

Figure 29: Gel Permeation Chromatogram for A066 from Hydrotreated Coal
WVGS-13421 - 450°C, 1 Hour

Figure 30: Gel Permeation Chromatogram for A073 from Hydrotreated Coal
WVGS-13423 - 450°C, 2 Hours

Figure 31: Gel Permeation Chromatogram for A075 from Hydrotreated Coal
WVGS-13423 - 450°C, 1 Hour

Figure 32: Proton NMR Spectrum for 250°C Distillation Residue D035-1

Figure 33: Proton NMR Spectrum for 350°C Distillation Residue D035-2

Figure 34: Proton NMR Spectrum for 400°C Distillation Residue D035-3

Figure 35: TGA Curve for 250°C Distillation Residue D035-1

Figure 36: TGA Curve for 350°C Distillation Residue D035-2

Figure 37: TGA Curve for 400°C Distillation Residue D035-3

Figure 38: Annealed Mesophase Pitch from Sample A076

Figure 39: Annealed Mesophase Pitch from Sample A066

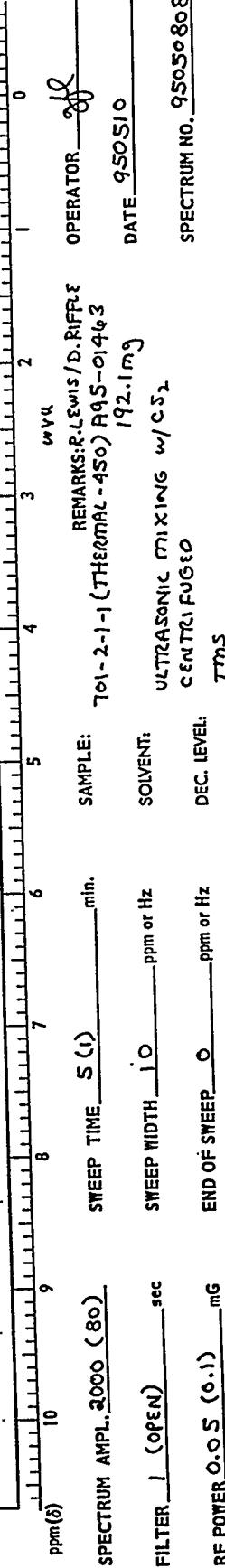
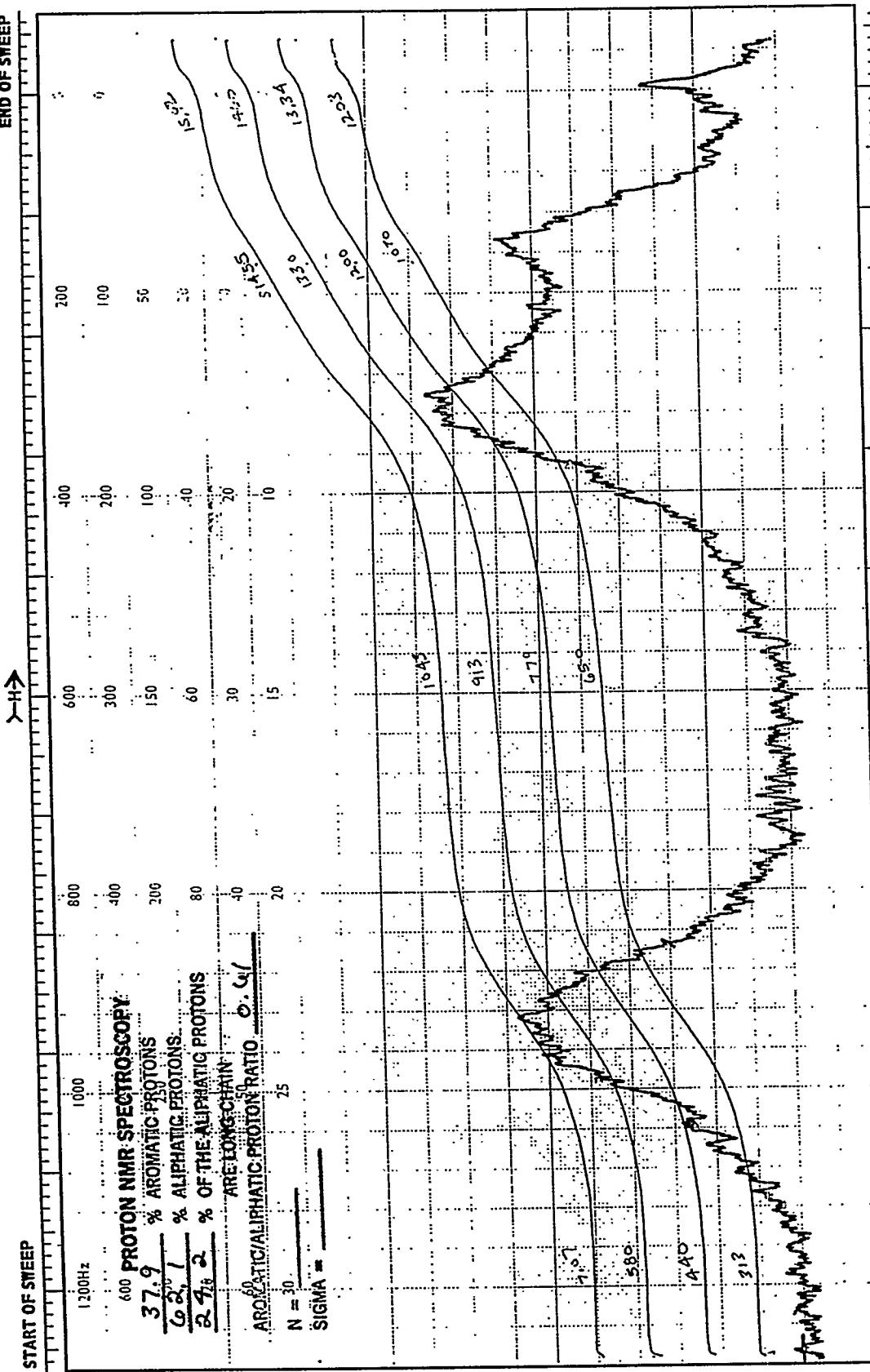
Figure 40: Annealed Mesophase Pitch from Sample A073

Figure 41: Annealed Mesophase Pitch from Sample A075

Figure 42: Area in Annealed Mesophase Pitch from Sample A076
Showing Clusters of Solid Particles

END OF SWEEP

START OF SWEEP



WILMAD GLASS CO., INC.
 WCV-360-K10-2
 U.S. Pat. No. 4,031,153
 1977-10-10
 WILMAD GLASS CO., INC.
 BUREAU, N.J. 07021 U.S.A.

Figure 1: Proton NMR in CS₂ Solution for C-269-2, Hydrotreated Coal
 450°C - 1 Hour, No Catalyst

Sample: 704-2-1-1 (THERMAL-450) A95-01463 TGA
Size: 26.3683 mg
Method: 100C/MIN
Comment: ARGON 100CC/MIN Pt PAN

File: 95050808A.08
Operator: gf1
Run Date: 18-May-95 16: 23

A95-01463 TGA

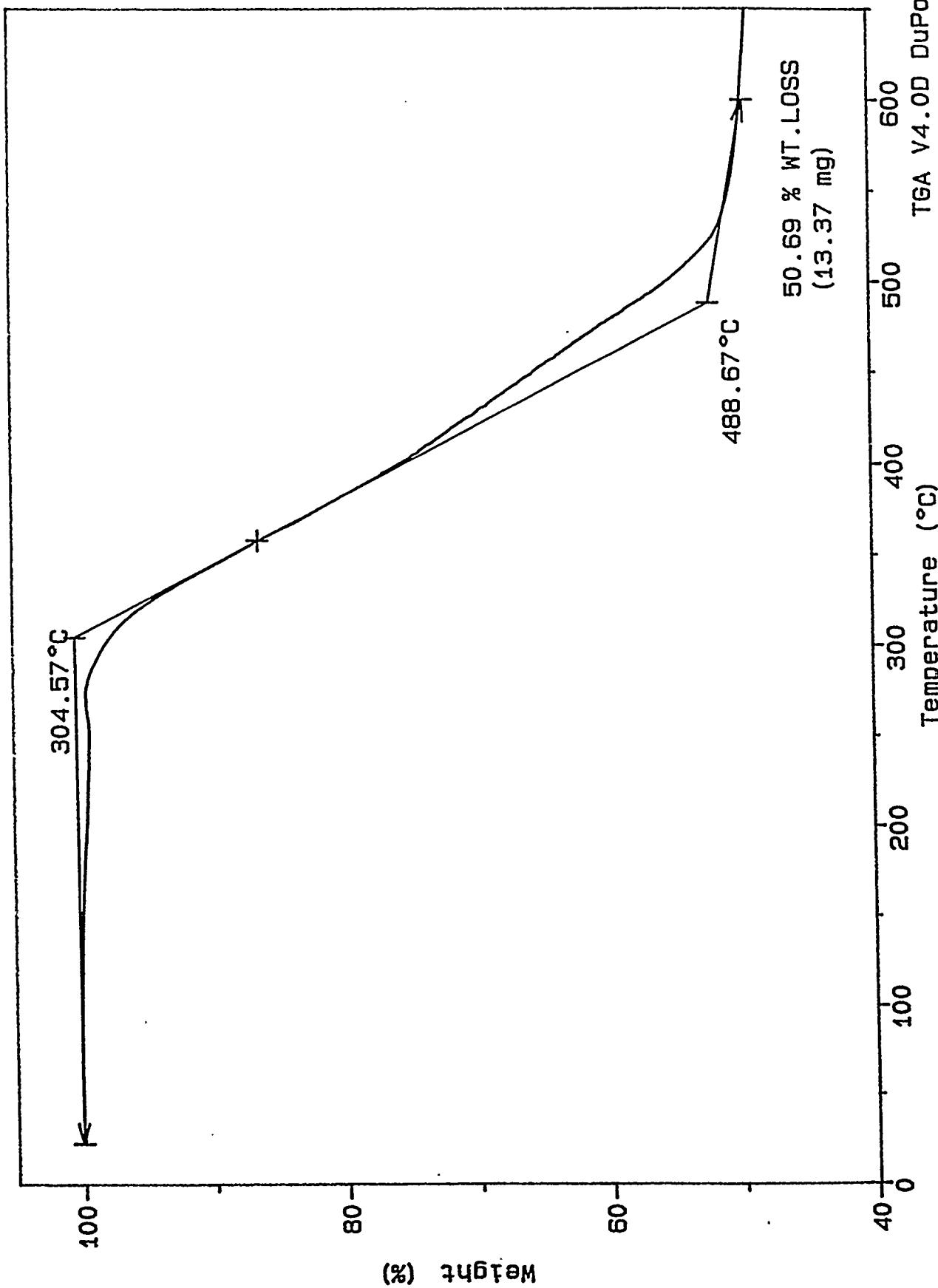


Figure 4: TGA Curve for C-269-2, Hydrotreated Coal 450°C - 1 Hour,
No Catalyst

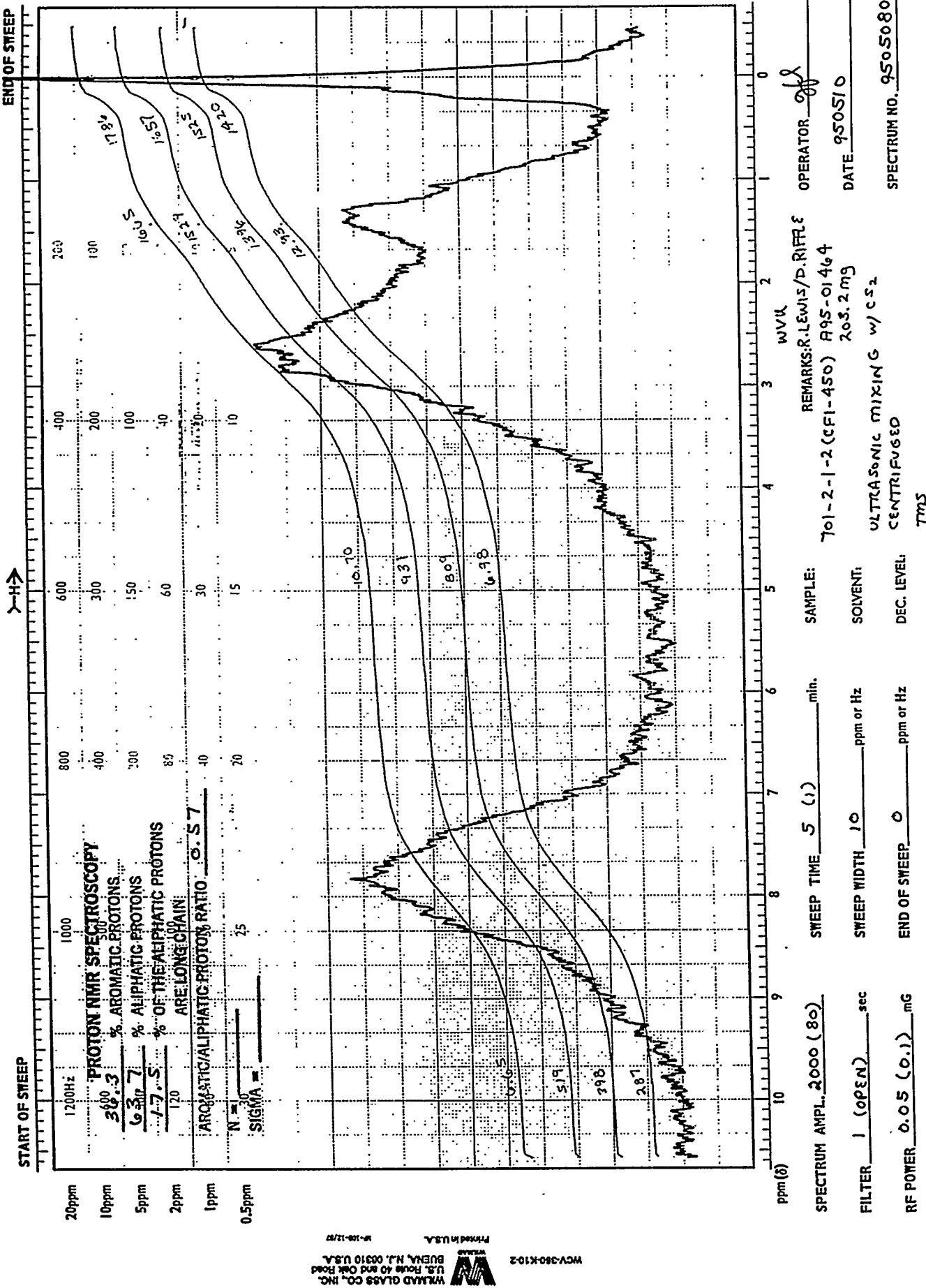


Figure 2: Proton NMR in CS₂ Solution for C-279-1, Hydrotreated Coal
 450°C - 1 Hour, Fe₂S₃ Catalyst

END OF SWEEP

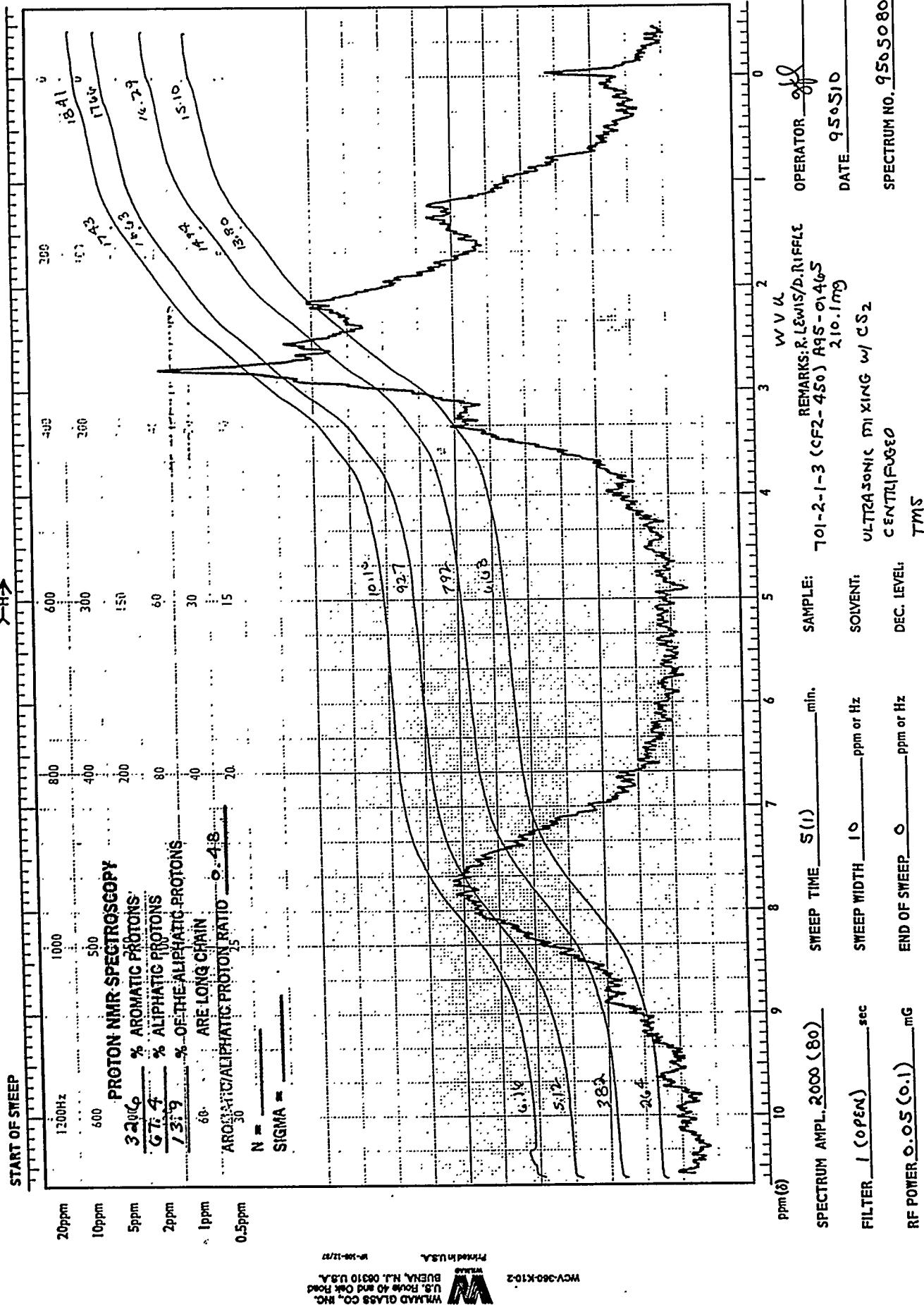


Figure 3: Proton NMR in CS₂ Solution for C-288-2, Hydrotreated Coal
450°C - 1 Hour, Mo(S) Catalyst

Samp1e: 701-2-1-2 (CF1-450)
Size: 25.5111 mg
Method: 10C/MIN
Comment: ARGON 100CC/MIN Pt PAN

File: 950508088.09
Operator: 9f1
Run Date: 18-May-95 13: 48

A95-01464 TGA

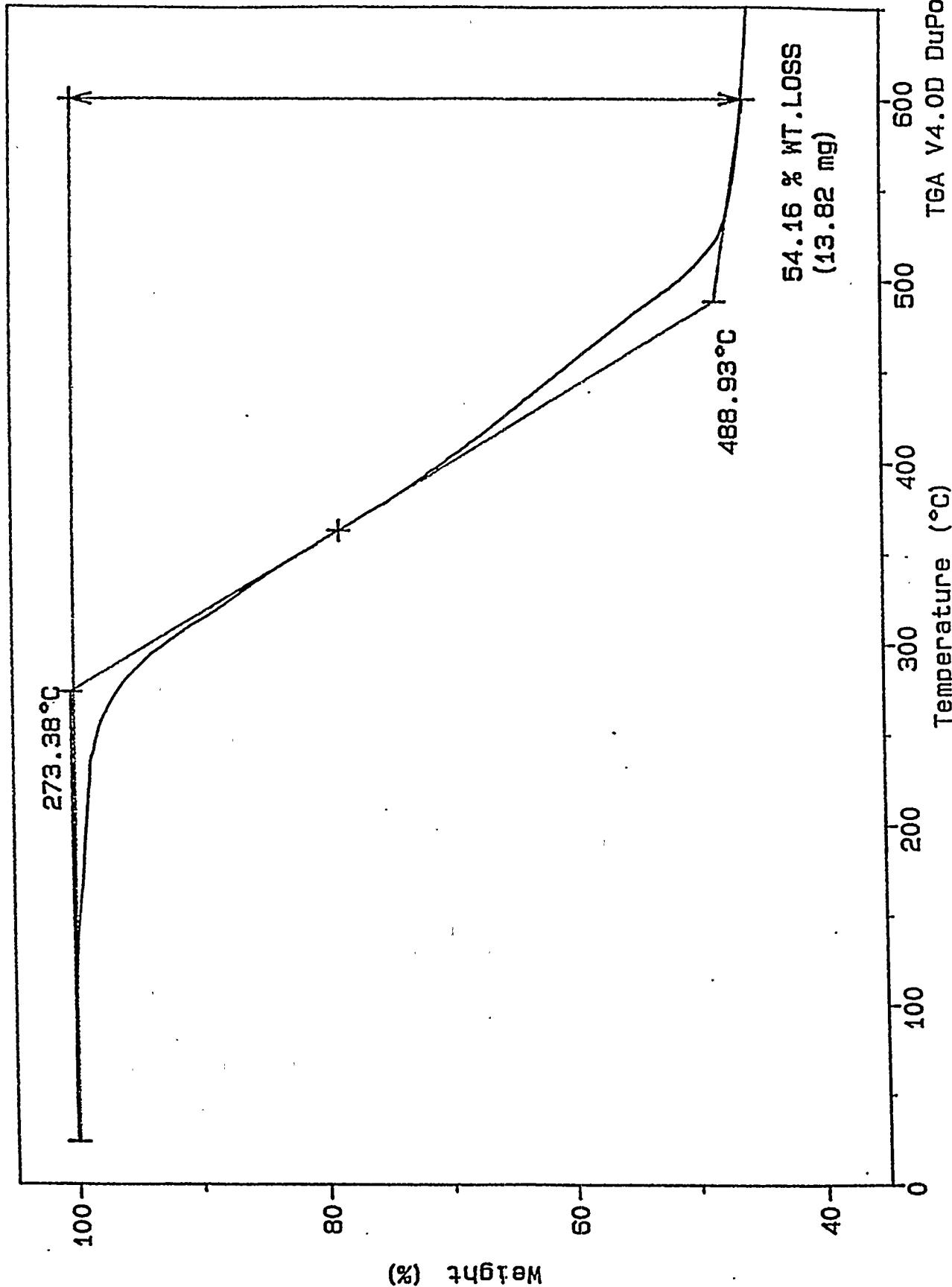


Figure 5: TGA Curve for C-279-1, Hydrotreated Coal 450°C - 1 Hour,
 Fe_2S_3 Catalyst

Samp16: 701-2-1-3 (CF2-450)
Size: 24.2128 mg
Method: 10C/MIN
Comment: ARGON 100CC/MIN Pt PAN

A95-01465 TGA

File: 95050808C.05
Operator: gf1
Run Date: 12-May-95 15:14

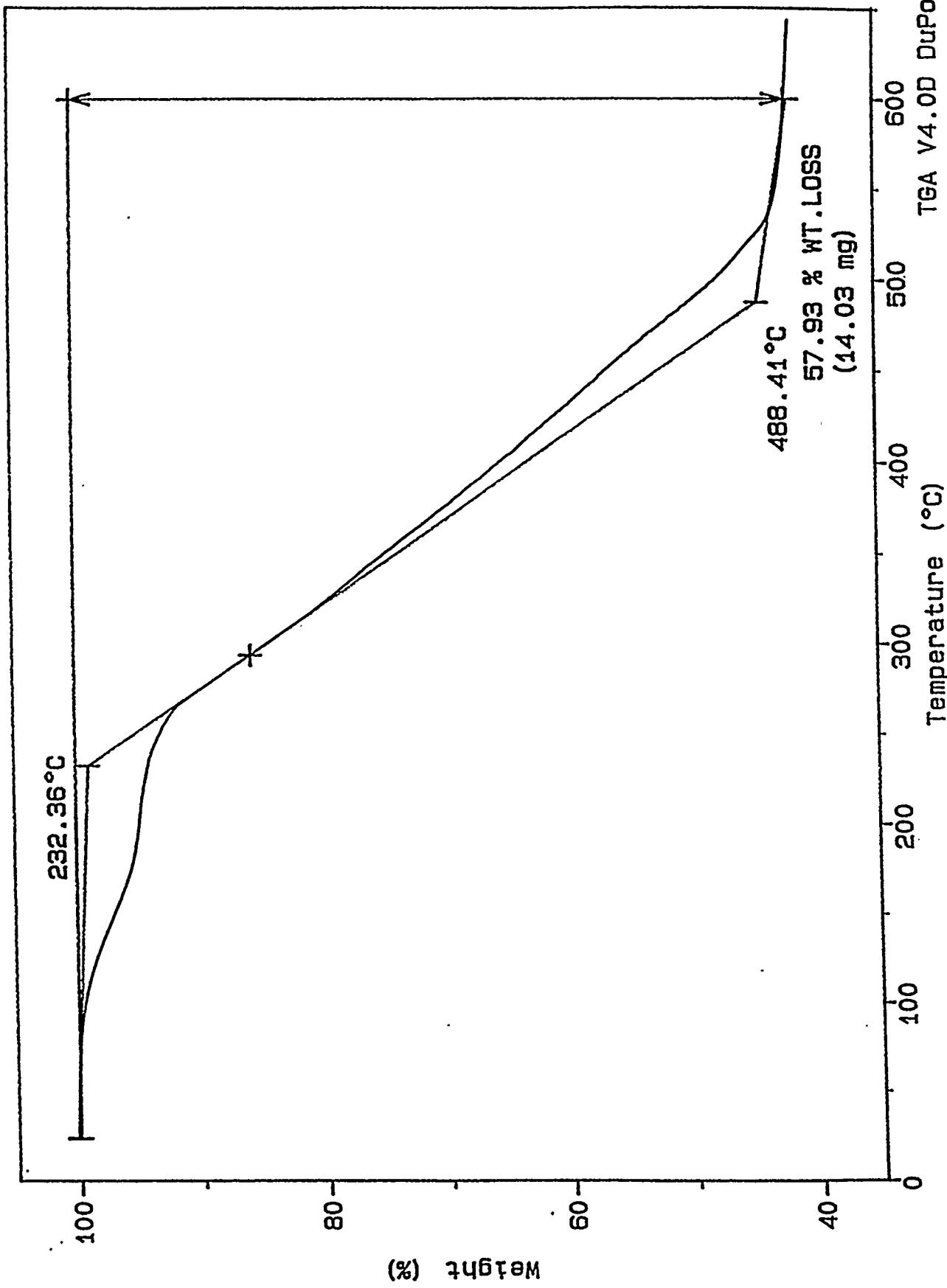
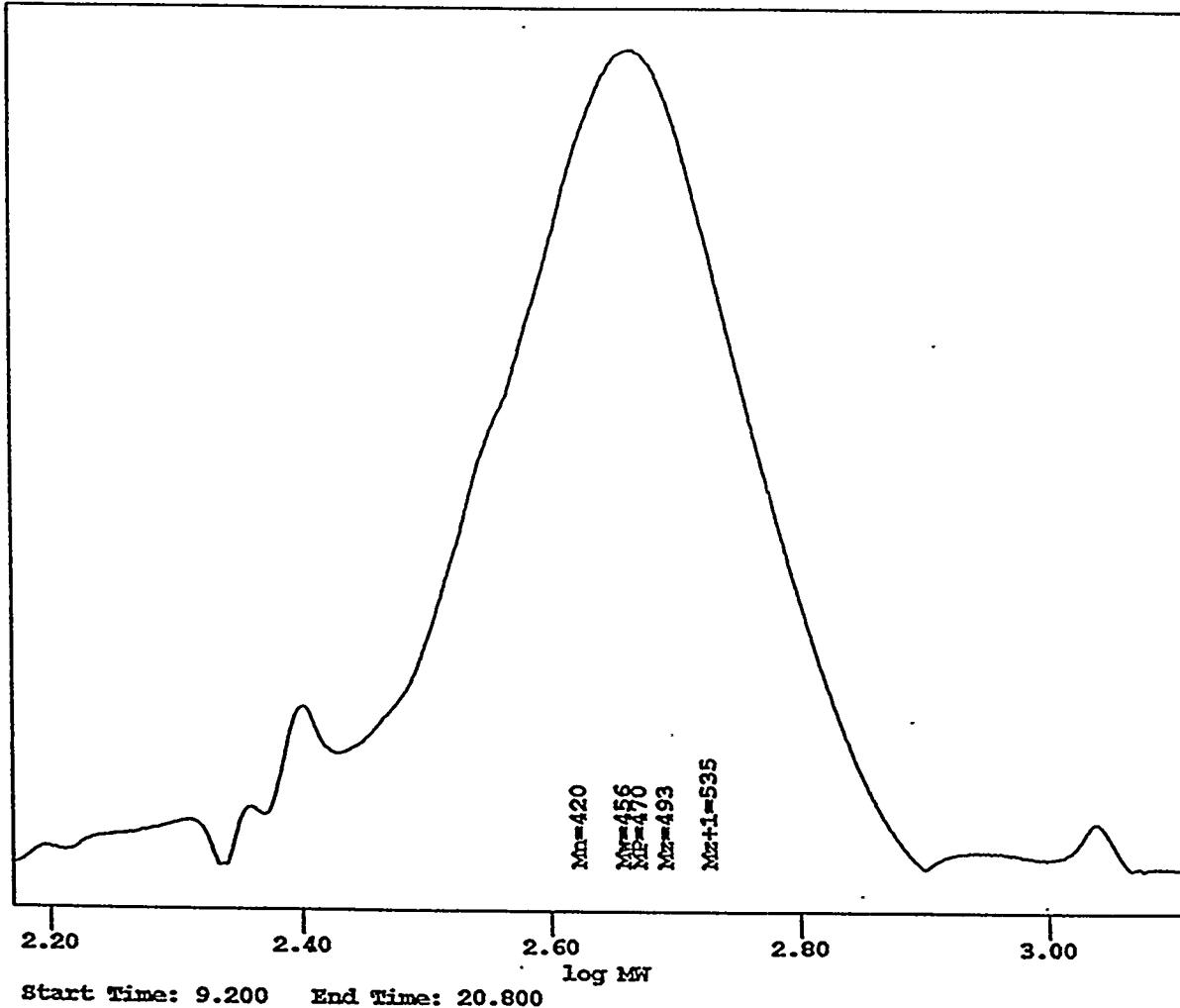


Figure 6: TGA Curve for C-288-2, Hydrotreated Coal 450°C - 1 Hour, Mo(S) Catalyst

Project Name: GPC Sample Type: Broad Unknown
Sample Name: 701-2-1-1 * Volume: 100.00
Vial: 2 Run Time: 30.0 min
Injection: 1 Date Processed: 06/23/95 10:02:42 AM
Date Acquired: 06/22/95 01:55:58 PM Pressure: 75
Processing Method: GPC Submitter: hkm
Comments: 95050808-1g3ml TCB Thermal - 450. prepped. 5/16/95

dw/d (log MW)



Peak Results

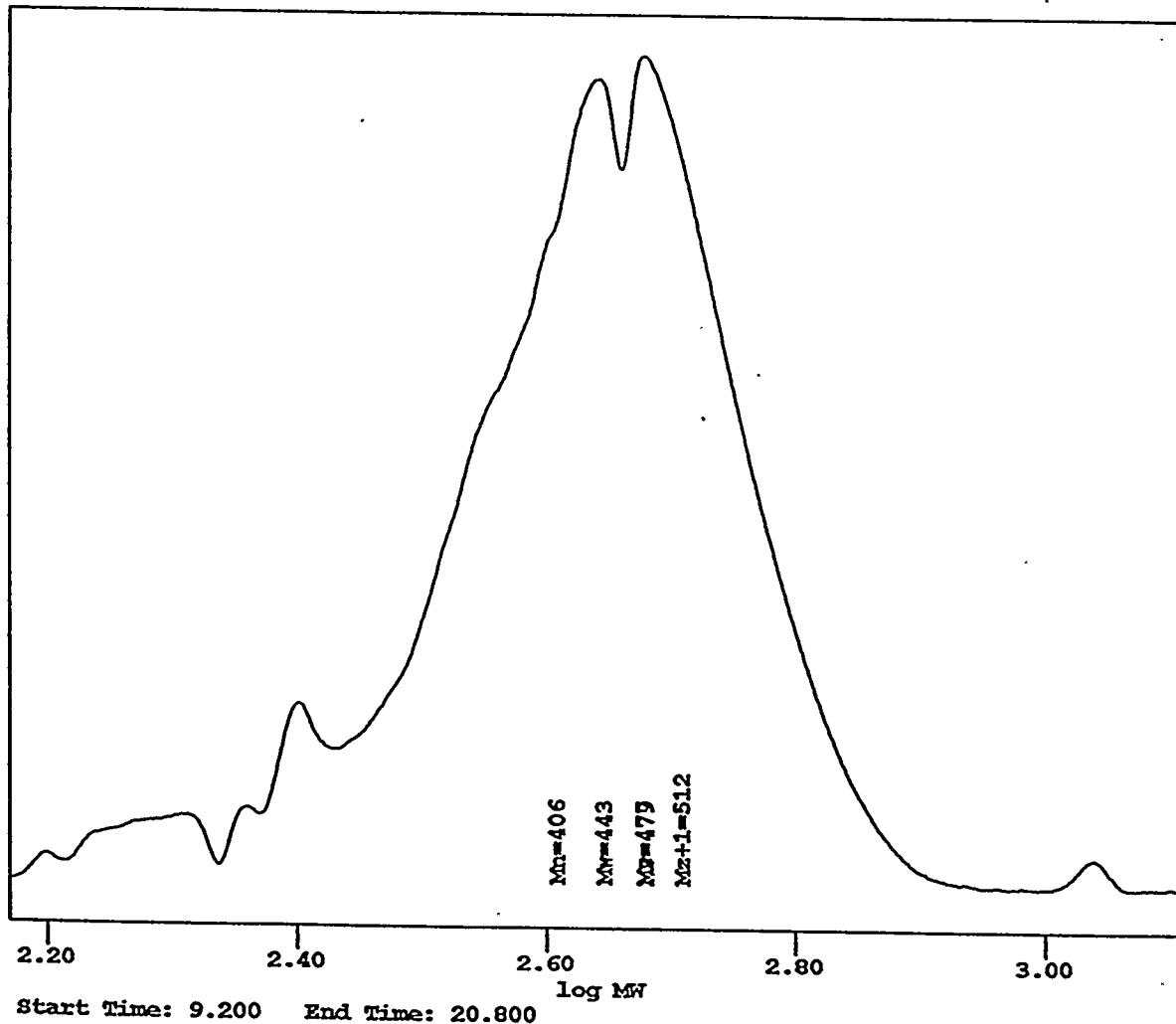
#	Ret Time (min)	Mn (Daltons)	Mp (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.617	420	470	456	493	535	1.086609

Figure 7: Gel Permeation Chromatography (GPC) Curve for C-269-2, Hydrotreated Coal 450°C - 1 Hour, No Catalyst

Project Name: GPC
Sample Name: 701-2-1-2
Vial: 3
Injection: 1
Date Acquired: 06/22/95 02:51:24 PM
Processing Method: GPC
Comments: 95050808 .1g3ml TCB CF-1- 450 prepped 5/16/95

Sample Type: Broad Unknown
Volume: 100.00
Run Time: 30.0 min
Date Processed: 06/23/95 10:02:13 AM
Pressure: 75
Submitter: hkm

dN/d(log MW)



Start Time: 9.200 End Time: 20.800

Peak Results

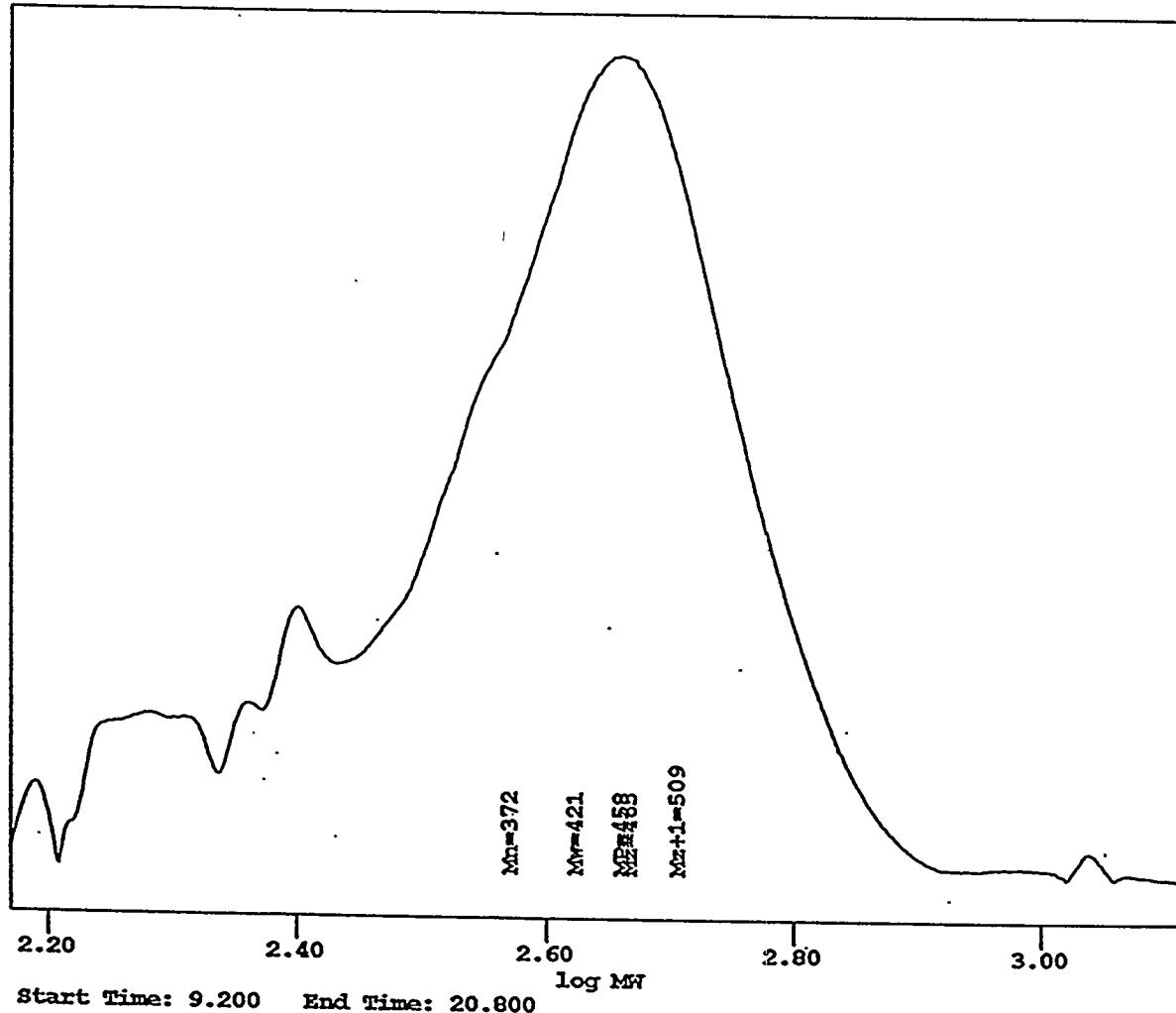
#	Ret Time (min)	Mn (Daltons)	Mp (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.517	406	479	443	477	512	1.090000

Figure 8: Gel Permeation Chromatography (GPC) Curve for C-279-1,
Hydrotreated Coal 450°C - 1 Hour, Fe_2S_3 Catalyst

Project Name: GPC
Sample Name: 701-2-1-3
Vial: 4
Injection: 1
Date Acquired: 06/22/95 03:32:41 PM
Processing Method: GPC
Comments: 95050808 .1g3ml TCB CF-2- 450 prepped 5/16/95*

Sample Type: Broad Unknown
Volume: 100.00
Run Time: 30.0 min
Date Processed: 06/23/95 10:01:31 AM
Pressure: 75
Submitter: hkm

dv/d(log MW)



Peak Results

#	Ret Time (min)	Mn (Daltons)	MP (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.750	372	458	421	465	509	1.129627

Figure 9: Gel Permeation Chromatography (GPC) Curve for C-288-2,
Hydrotreated Coal 450°C - 1 Hour, Mo(S) Catalyst

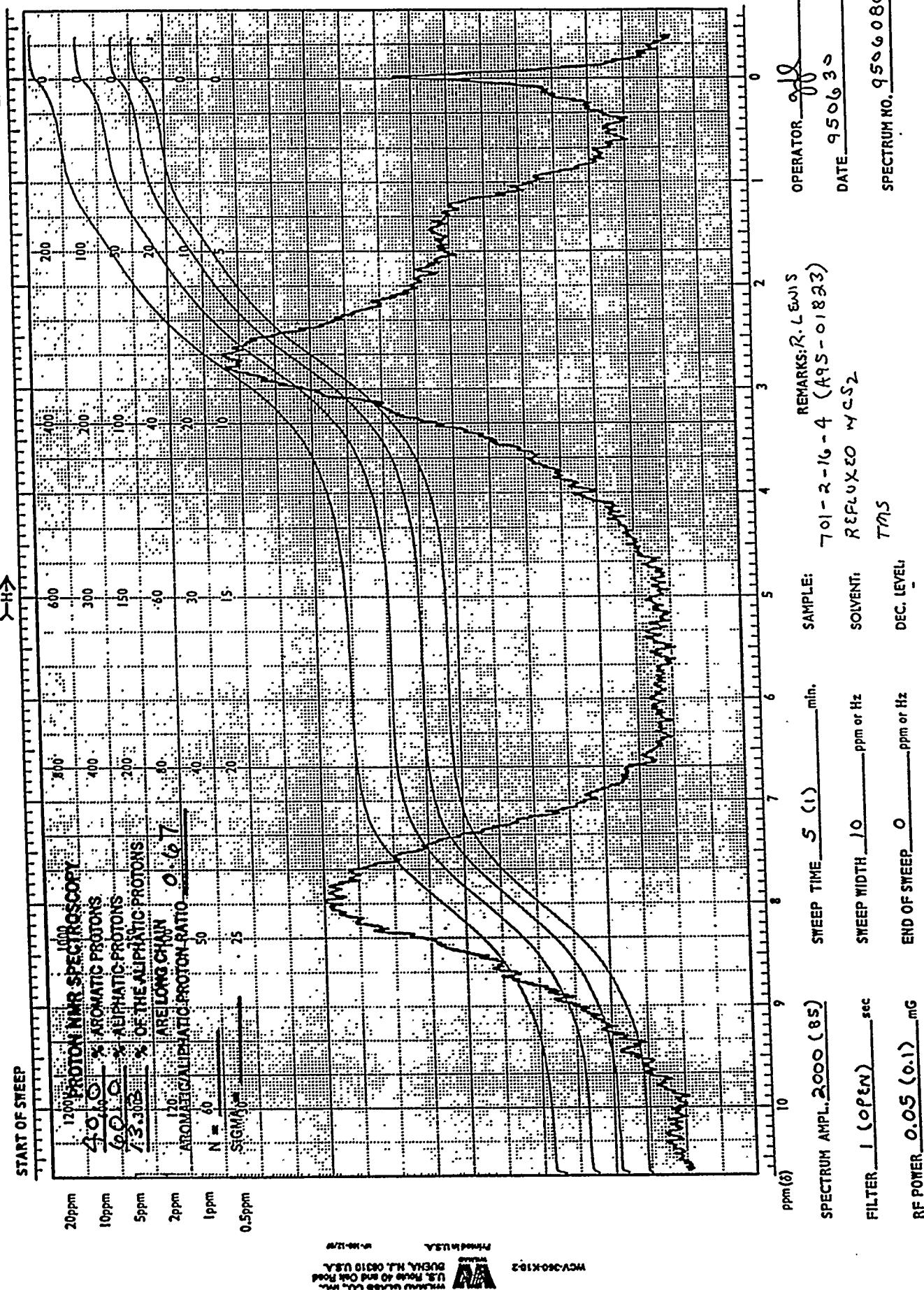


Figure 10: Proton NMR in CS_2 for C-300-3, Hydrotreated Coal
 450°C - 2 Hours, No Catalyst

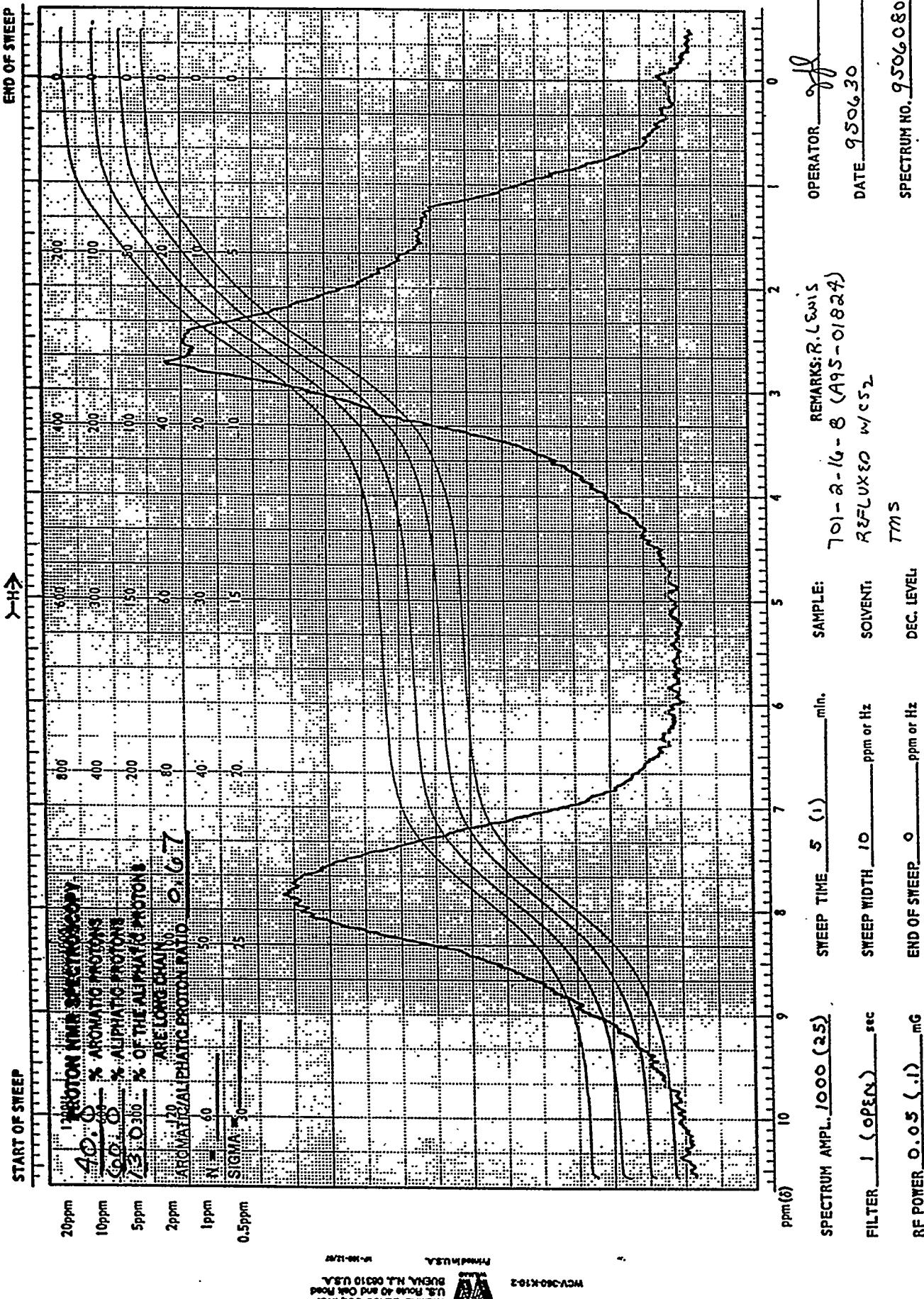


Figure 11: Proton NMR in CS_2 for C-300-6, Hydrotreated Coal
 450°C - 2 Hours, Fe_2S_3 Catalyst

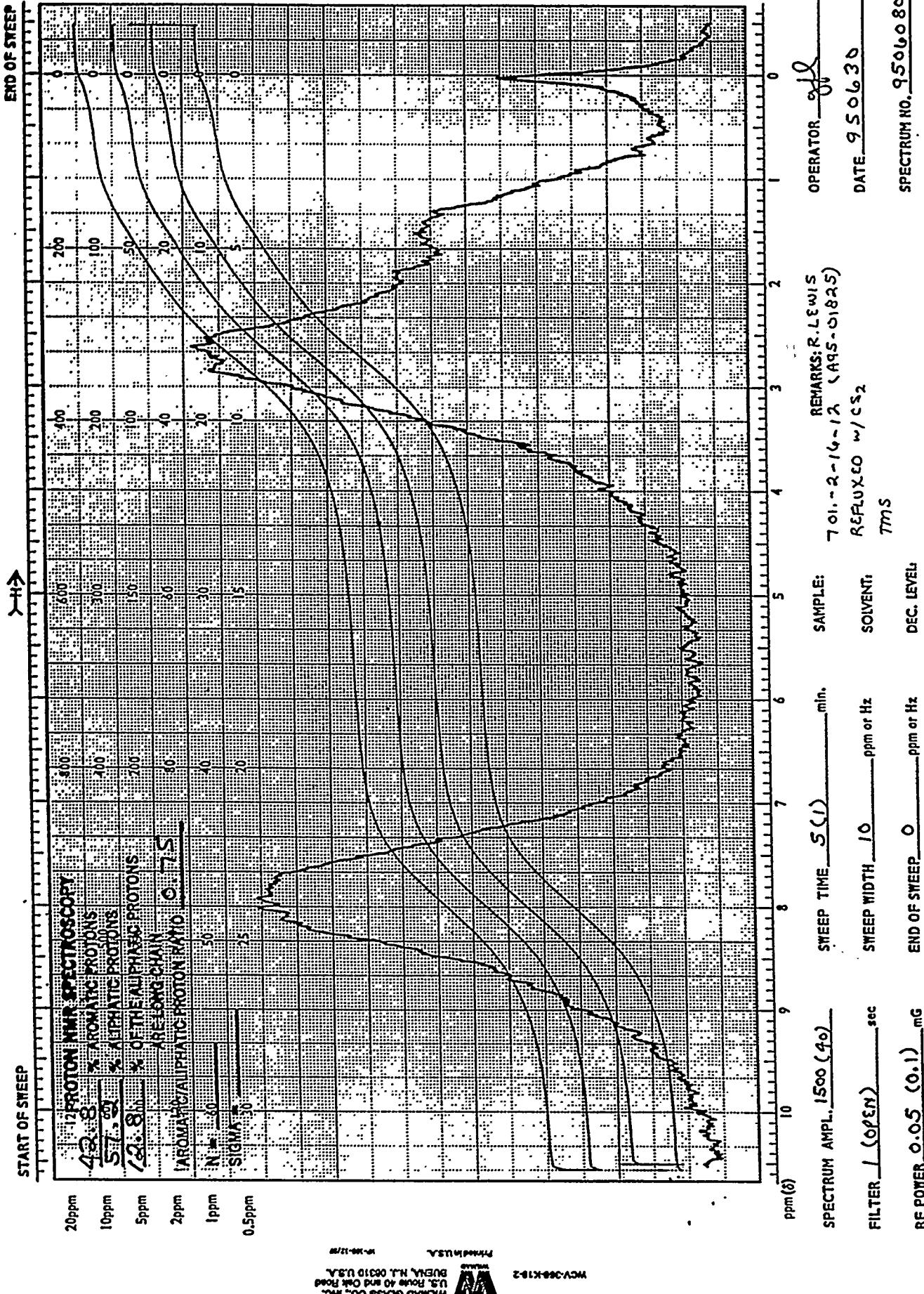


Figure 12: Proton NMR in CS_2 for C-300-9, Hydrotreated Coal
 450°C - 2 Hours, Mo(S) Catalyst

C-300-3
Sample: 701-2-16-4
Size: 24.8060 mg
Method: 10C/MIN
Comment: ARGON 100CC/MIN Pt PAN

A95-01823 TGA

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Operator: gf1
Run Date: 23-Jun-95 11:28

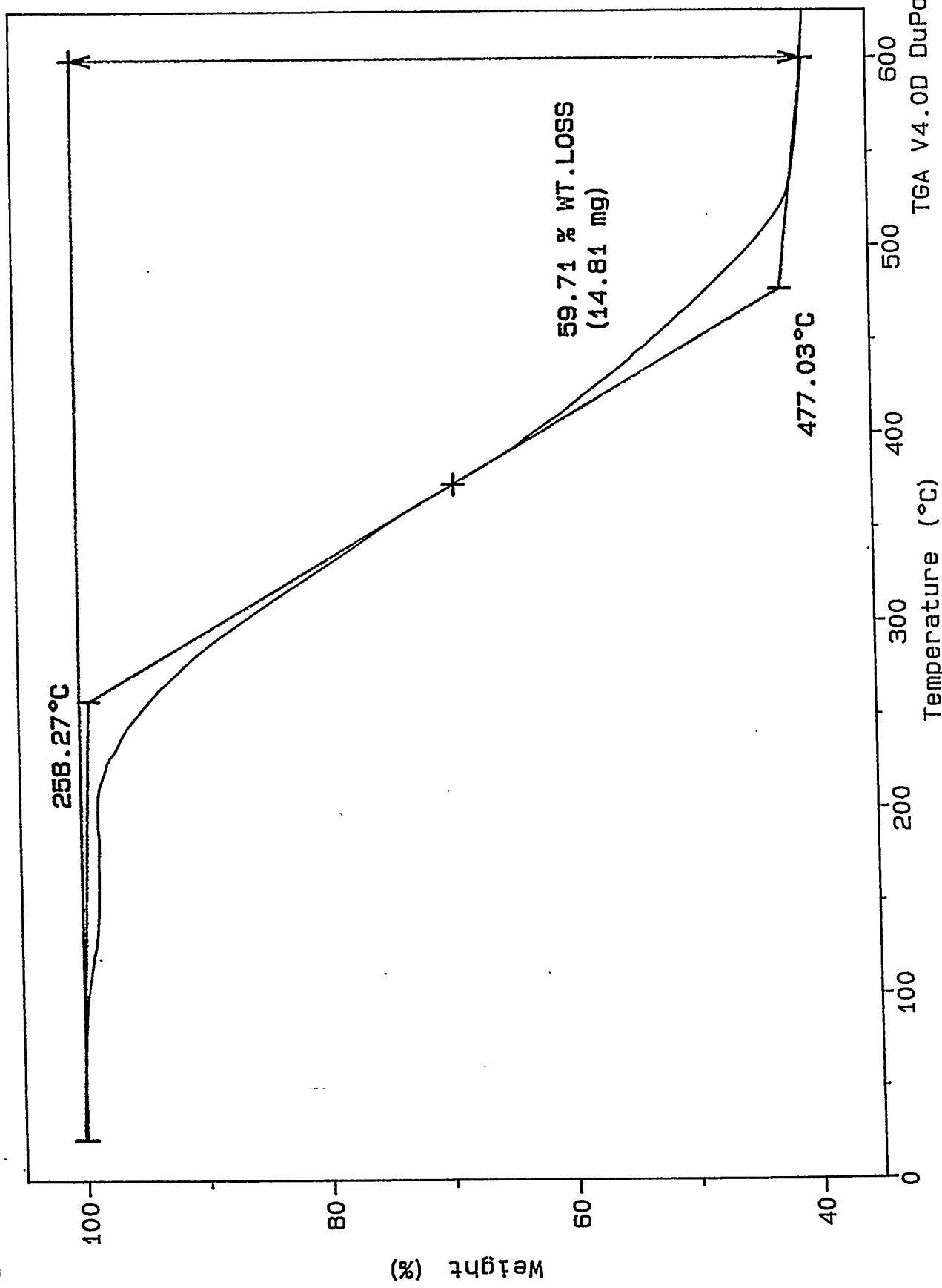


Figure 13: TGA Curve for C-300-3, Hydrotreated Coal
450°C - 2 Hours, No Catalyst

C-300-6

Sample: 701-2-16-8
Size: 24.4479 mg
Method: 10C/MIN
Comment: ARGON 100CC/MIN Pt PAN

A95-01824 TGA

File: 95060801B.01
Operator: gf1
Run Date: 23-Jun-95 08:34

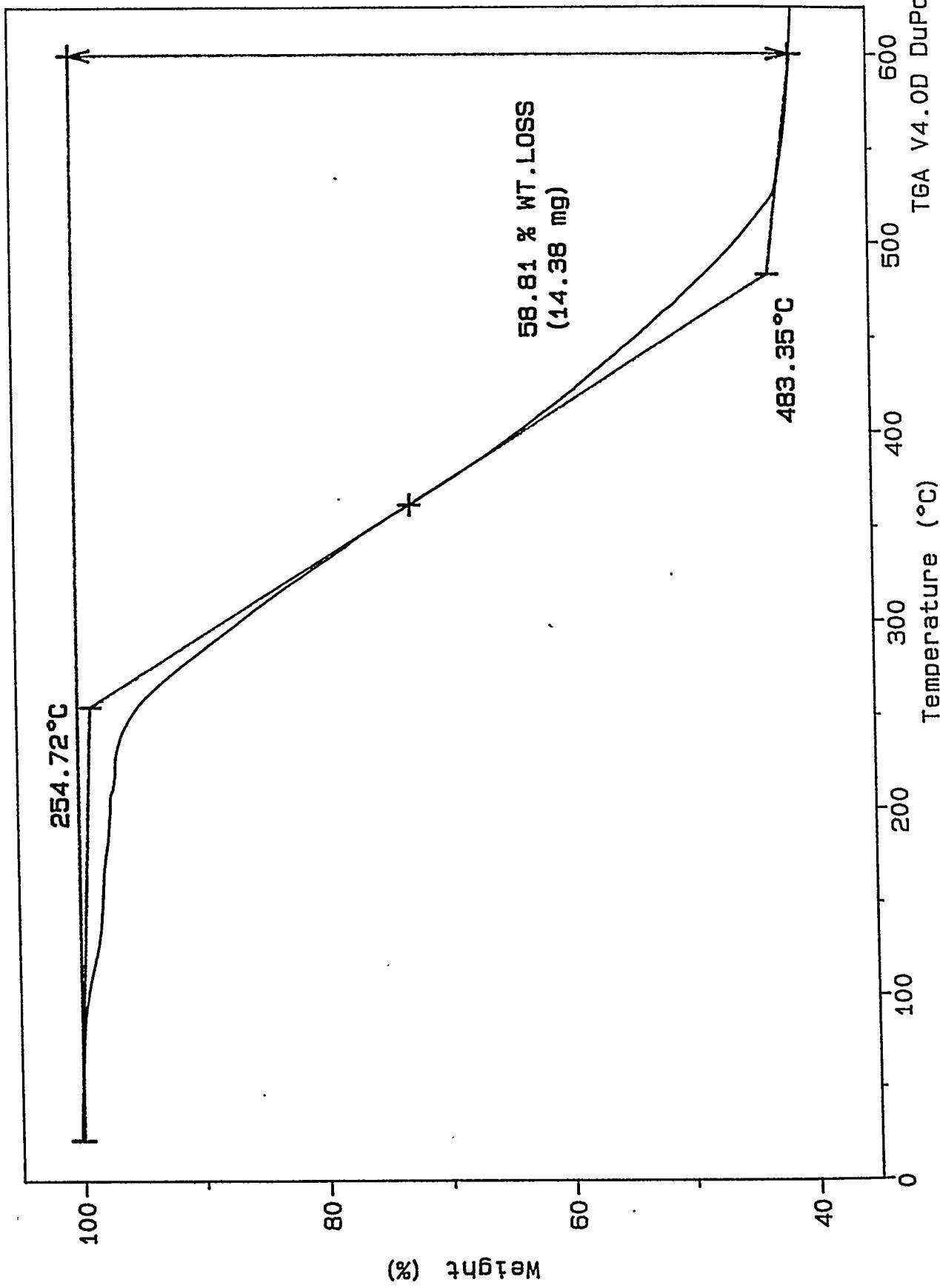


Figure 14: TGA Curve for C-300-6, Hydrotreated Coal
450°C - 2 Hours, Fe_2S_3 Catalyst

C-300-9

Sample: 704-2-16-12
Size: 25.1950 mg
Method: 10C/MIN
Comment: ARGON 100CC/MIN

File: 95060801C.01

Operator: gf1

Run Date: 22-Jun-95 16: 08

A95-04825 TGA

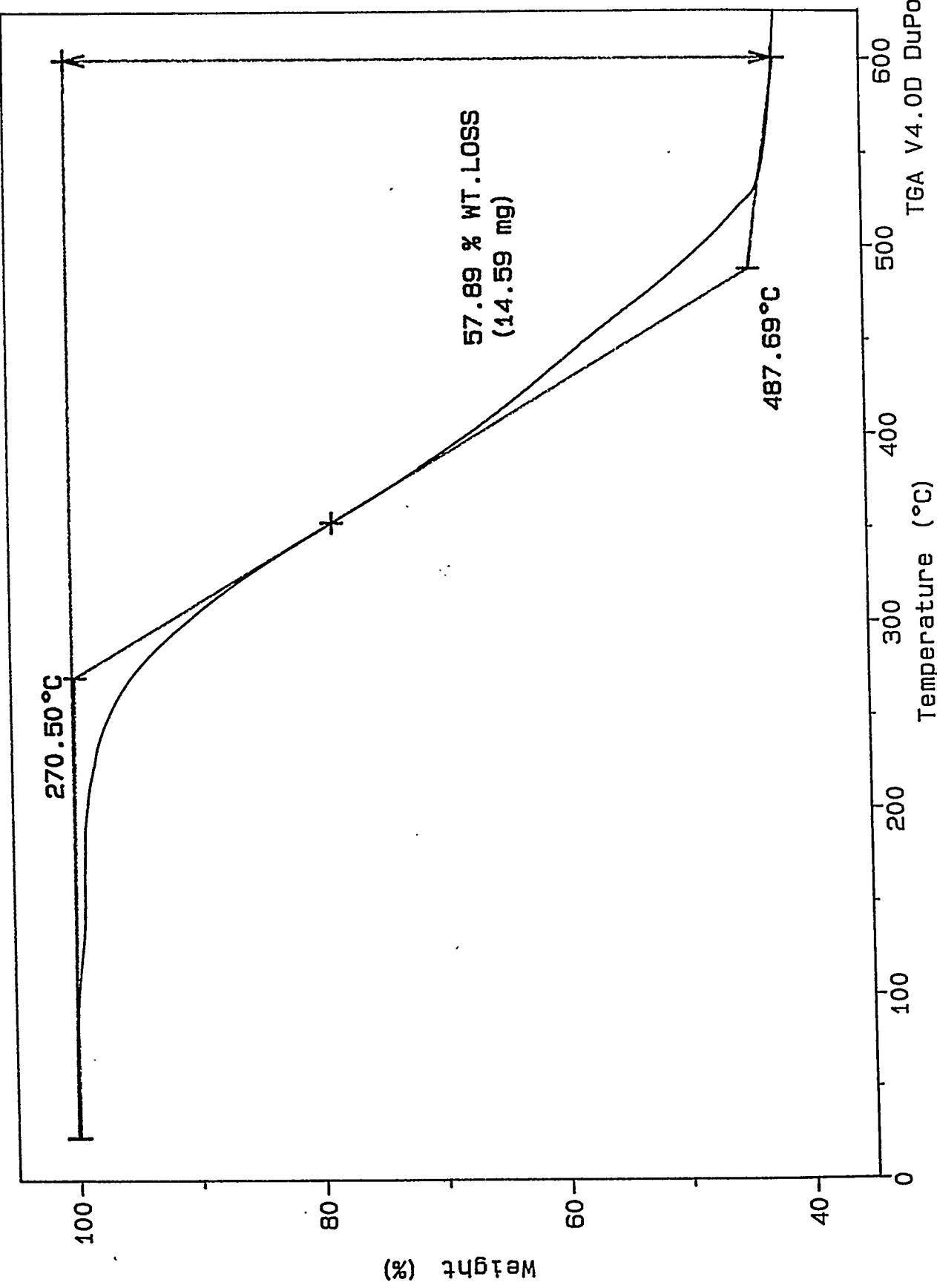
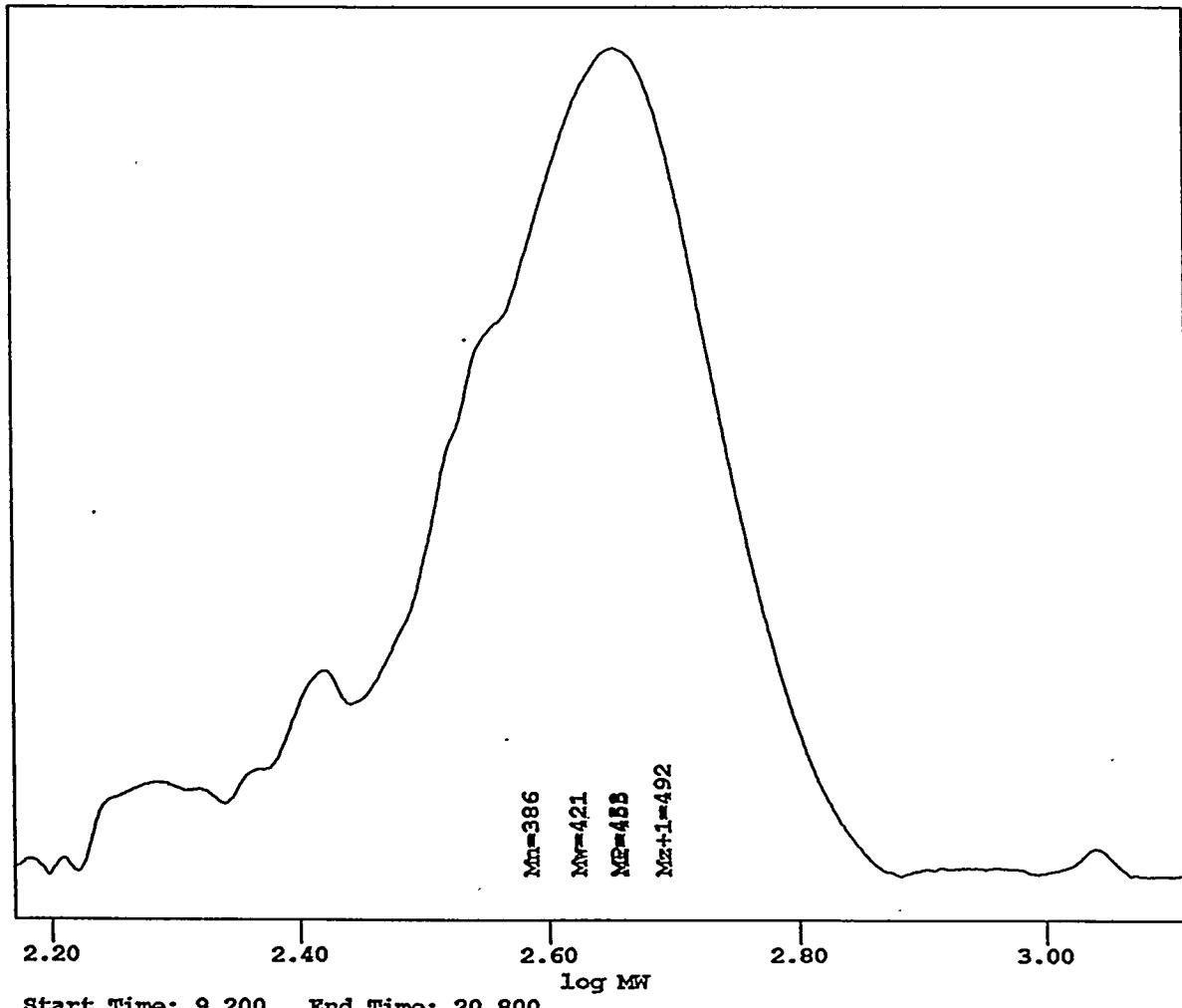


Figure 15: TGA Curve for C-300-9, Hydrotreated Coal
450°C - 2 Hours, Mo(S) Catalyst

Project Name: GPC Sample Type: Broad Unknown
Sample Name: 701-2-16-4 Volume: 100.00
Vial: 2 Run Time: 30.0 min
Injection: 1 Date Processed: 06/19/95 09:38:03 AM
Date Acquired: 06/16/95 12:43:30 PM Pressure: 75
Processing Method: GPC Submitter: RTL
Comments: C300-3, Thermal 450-2 prepped 6/15/95 .25g/7ml TCB no fl. rt. mkr. 95060801

dw/d(log MW)



Peak Results

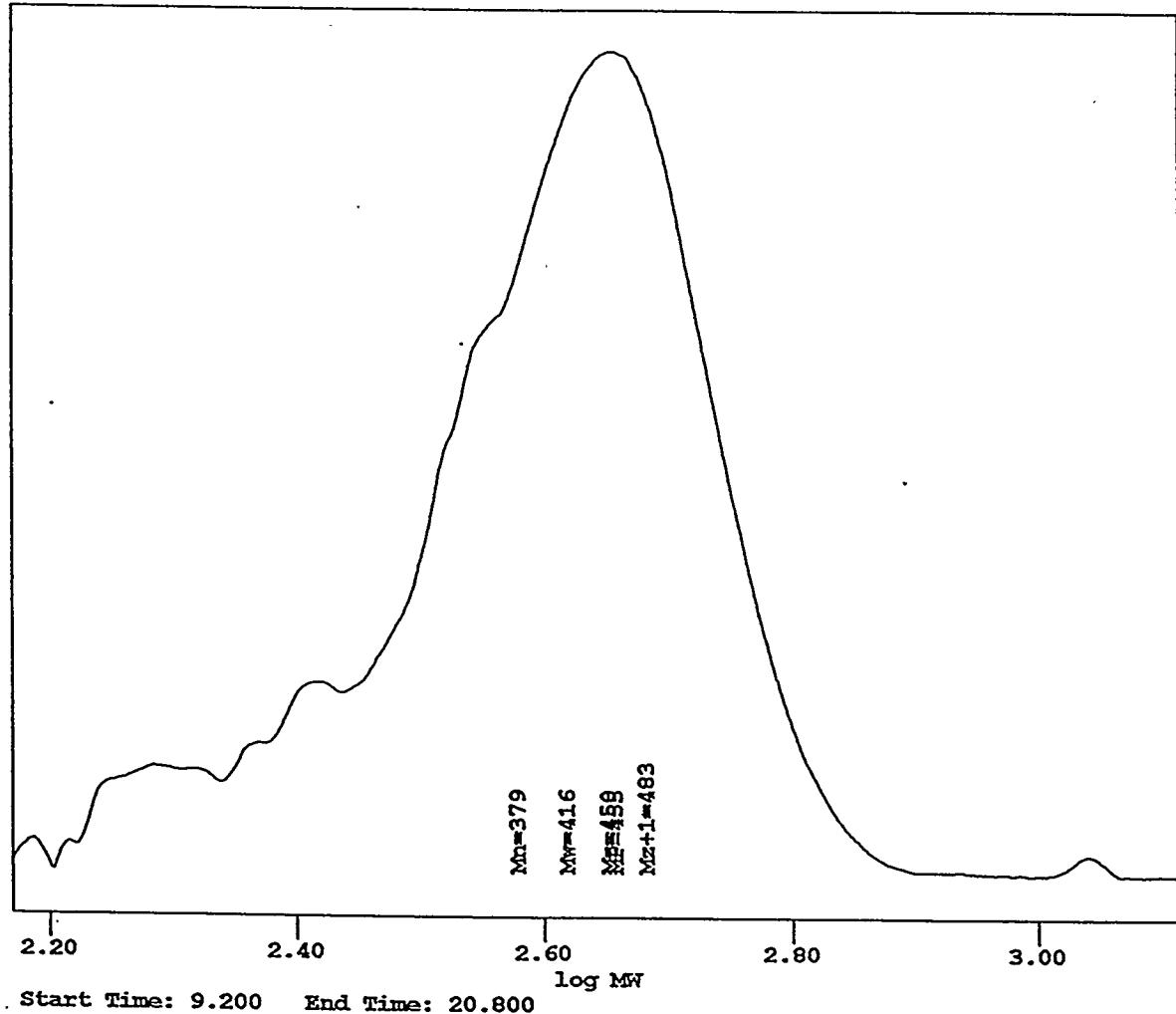
#	Ret Time (min)	Mn (Daltons)	MP (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.817	386	453	421	455	492	1.091709

Figure 16: Gel Permeation Chromatography Curve for C-300-3, Hydrotreated Coal 450°C - 2 Hours, No Catalyst

Project Name: GPC
 Sample Name: 701-2-16-8
 Vial: 3
 Injection: 1
 Date Acquired: 06/16/95 01:23:06 PM
 Processing Method: GPC
 Comments: C300-6, Fe Cat. 450-2 prepped 6/15/95 .25g/7ml TCB no fl. rt. mkr. 95060801

Sample Type: Broad Unknown
 Volume: 100.00
 Run Time: 30.0 min
 Date Processed: 06/19/95 09:37:30 AM
 Pressure: 75
 Submitter: RTL

dN/d(log MW)



Peak Results

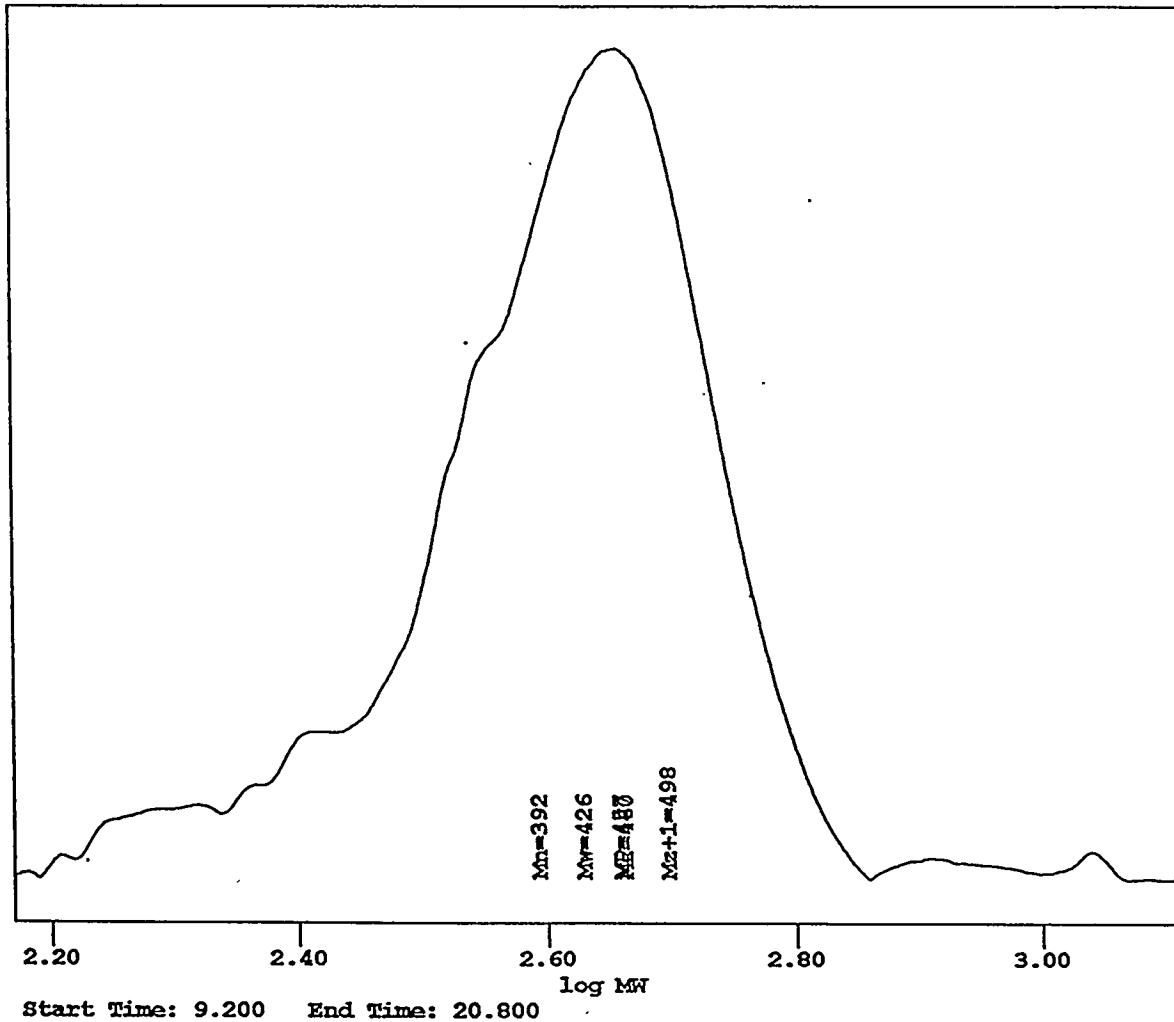
#	Ret Time (min)	Mn (Daltons)	MP (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.783	379	455	416	450	483	1.096545

Figure 17: Gel Permeation Chromatography Curve for C-300-6, Hydrotreated Coal 450°C - 2 Hours, Fe_2S_3 Catalyst

Project Name: GPC
Sample Name: 701-2-16-12
Vial: 4
Injection: 1
Date Acquired: 06/16/95 01:55:19 PM
Processing Method: GPC
Comments: C300-9, Mo Cat. 450-2 prepped 6/15/95 .25g/7ml TCB no fl. rt. mkr. 95060801

Sample Type: Broad Unknown
Volume: 100.00
Run Time: 30.0 min
Date Processed: 06/19/95 09:36:59 AM
Pressure: 75
Submitter: RTL

dw/d(log MW)



Peak Results

#	Ret Time (min)	Mn (Daltons)	Mp (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.767	392	457	426	460	498	1.087104

Figure 18: Gel Permeation Chromatography Curve for C-300-9,
Hydrotreated Coal 450°C - 2 Hours, Mo(S) Catalyst

PRODUCTS FROM 400°C-6 HR. HEAT TREATMENTS OF WVU COAL EXTRACTS

(Schematic Diagram)

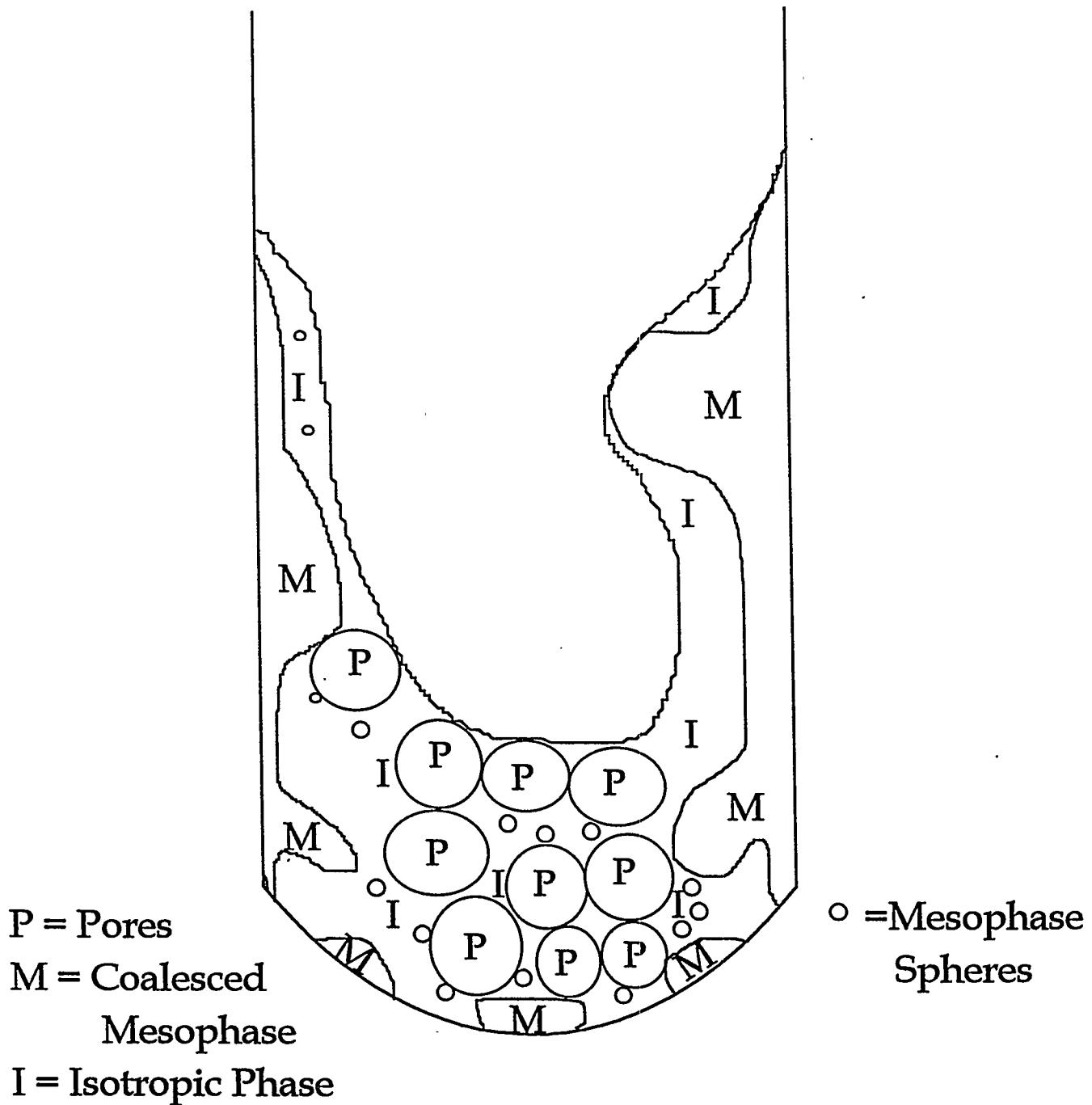
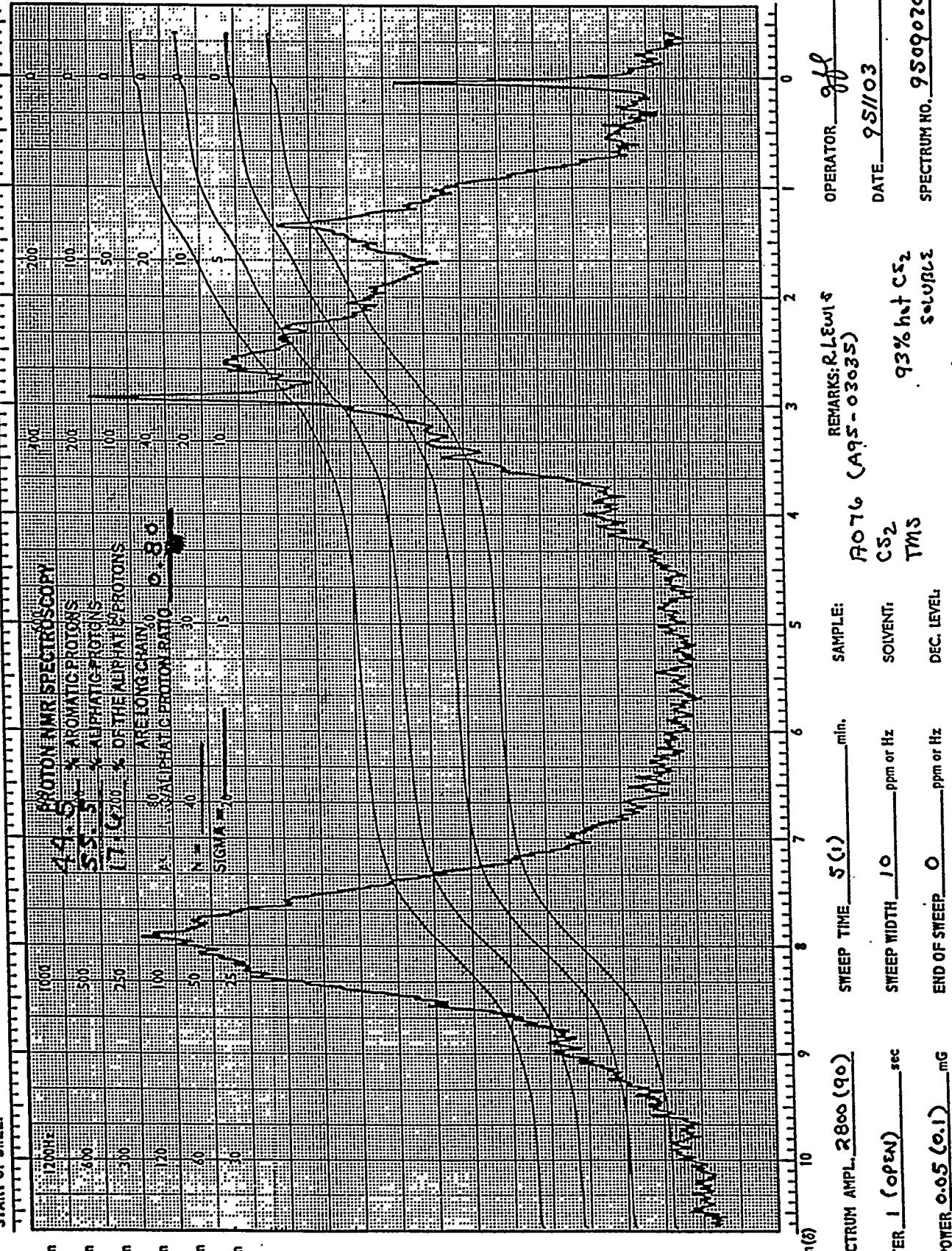


Figure 19

END OF SWEEP

START OF SWEEP



MCV-260-K102
WILKINSON GLASS CO., INC.
U.S. Route 102 and Old Quaker Road
BUREAU, N.H. 03010 U.S.A.
Patented in U.S.A.
10-106-1174

SPECTRUM NO. 95090204
DATE 95/03
OPERATOR Off
REMARKS: R. Lewis
A076 (A95-03035)
SAMPLE: A076
C52
TMS
SOLVENT:
DEC. LEVEL:
FILTER: 1 (OPEN) sec
SWEEP WIDTH 10 ppm or Hz
END OF SWEEP 0 ppm or Hz
RF POWER 0.05 (0.1) mG

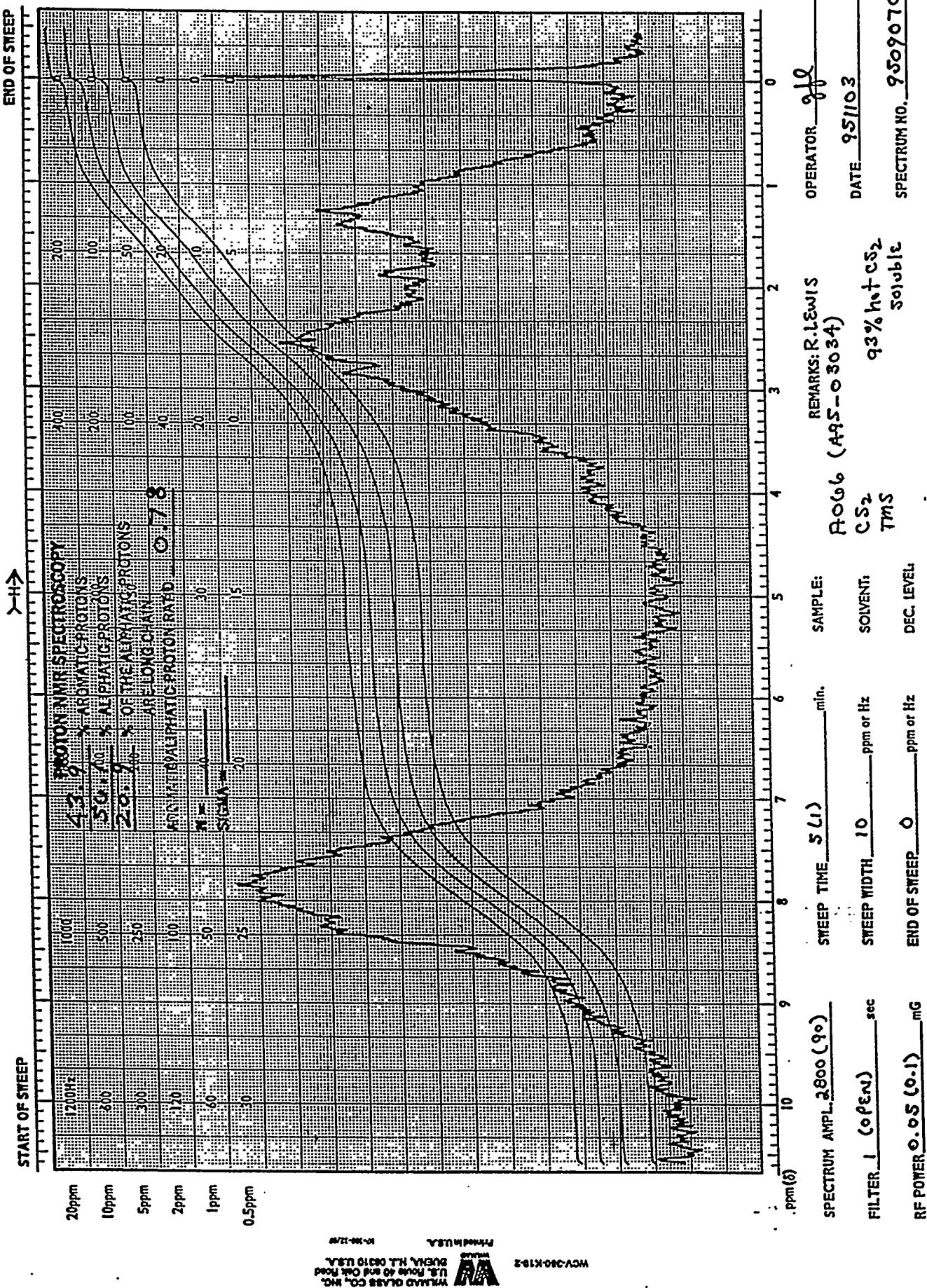


Figure 21: Proton NMR Spectrum for A066 from Hydrotreated Coal
WVGS-13421 - 450°C, 1 Hour

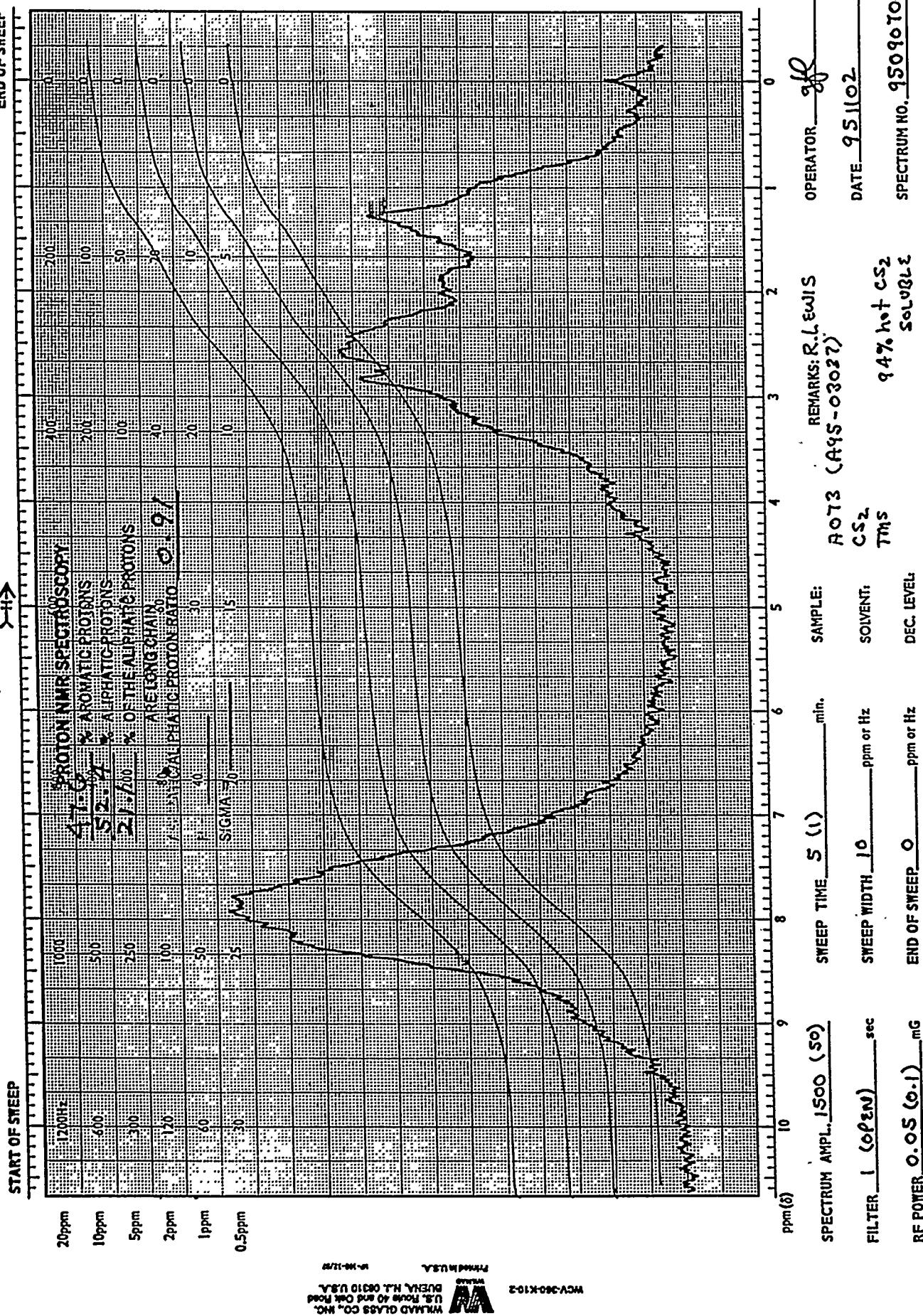


Figure 22: Proton NMR Spectrum for A073 from Hydrotreated Coal WVGS-13423 - 450°C, 2 Hours

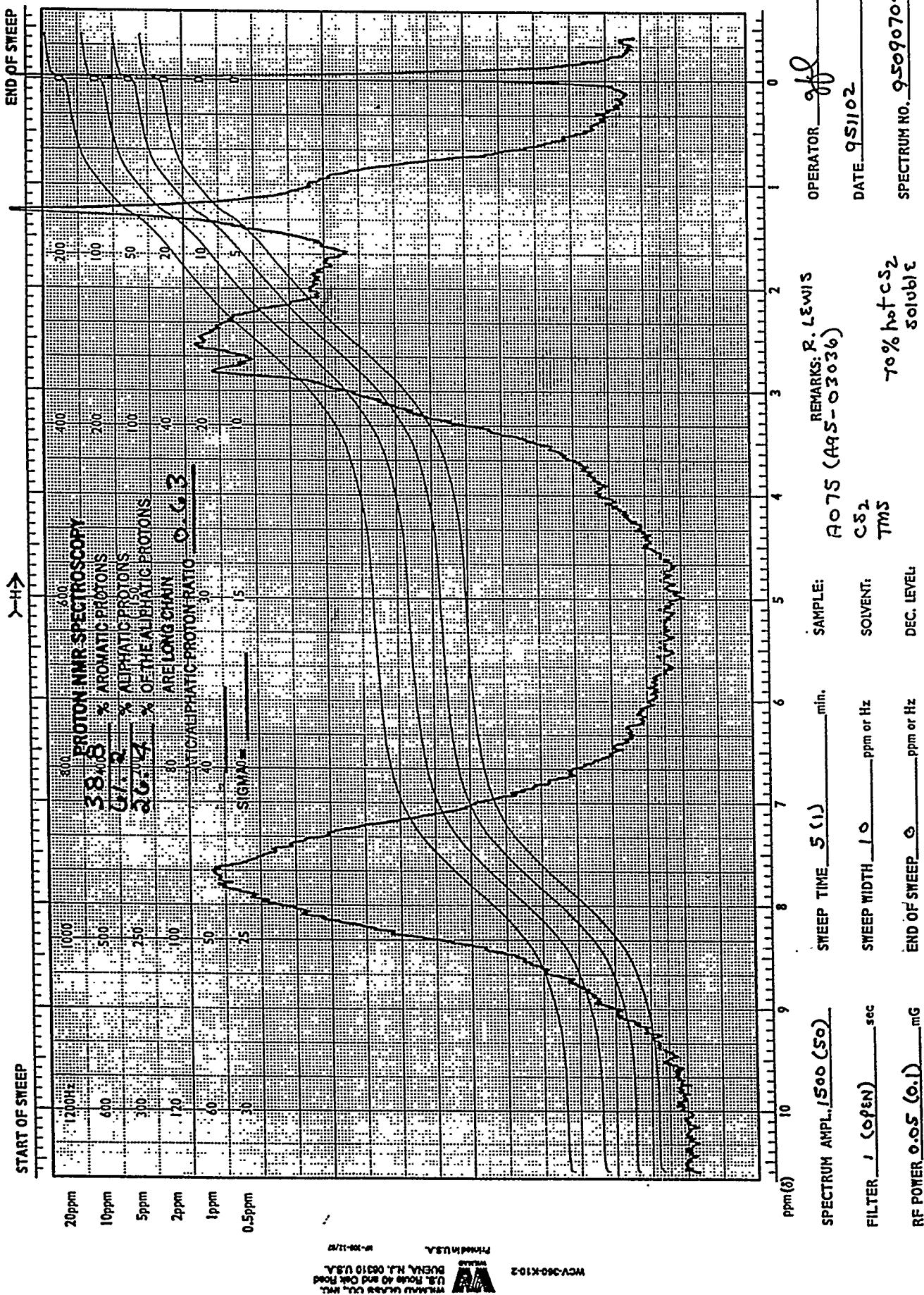


Figure 23: Proton NMR Spectrum for A075 from Hydrotreated Coal WVGS-13423 - 450°C, 1 Hour

Sample: A076 701-2-30-2
Size: 18.5080 mg
Method: 10 °C/MIN
Comment: ARGON 100CC/MIN Pt PAN

A95-03035 TGA

File: 95090704B.01
Operator: gf1
Run Date: 16-Oct-95 11:52

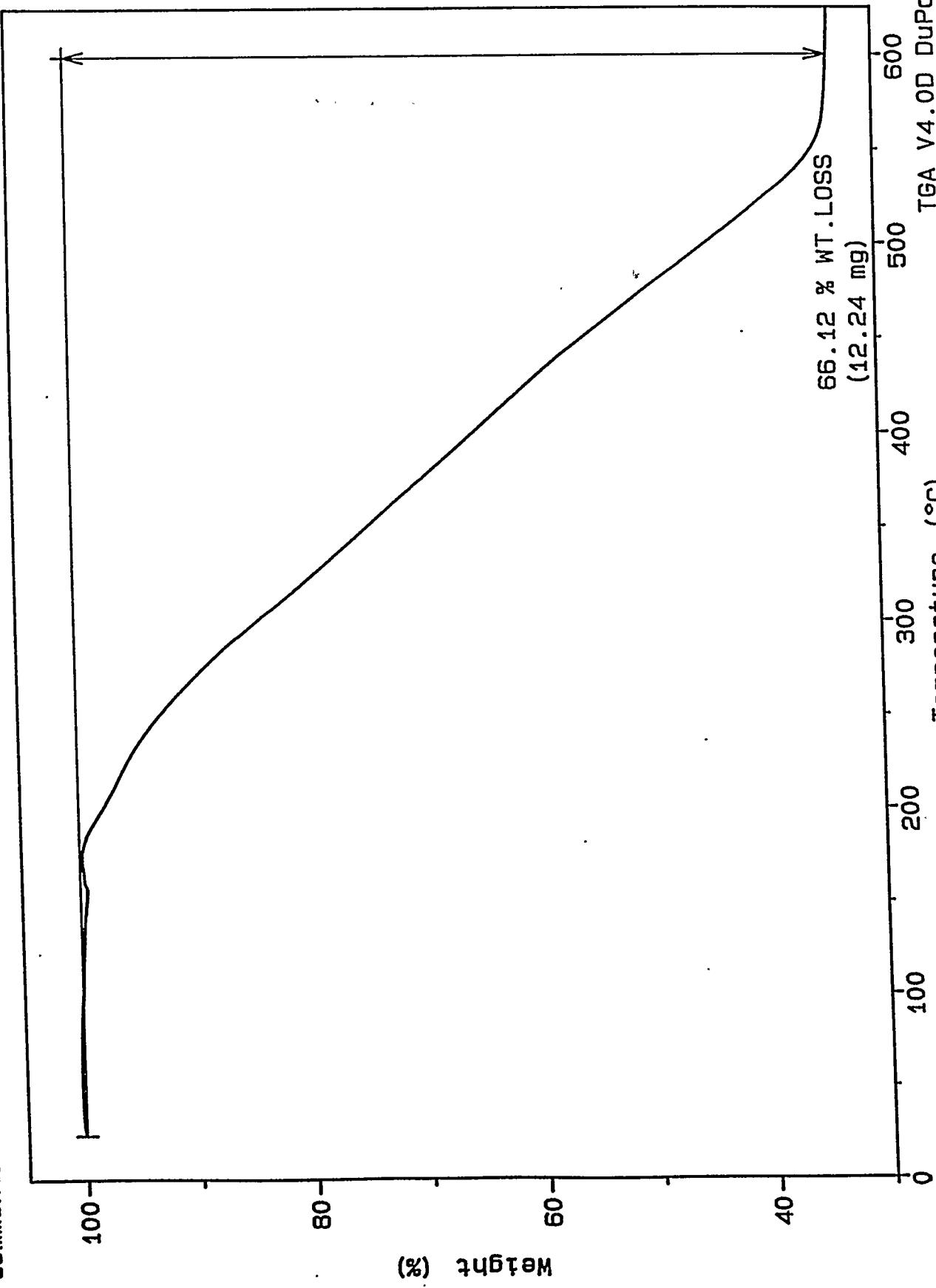


Figure 24: TGA Curve for A076 from Hydrotreated Coal
WVGGS-13421 - 450°C, 2 Hours

Sample: A066 701-2-30-1
Size: 24.6620 mg
Method: 10°C/MIN
Comment: ARGON 100CC/MIN Pt PAN

A95-03034 TGA

File: 95090704A.02
Operator: gf1
Run Date: 16-Oct-95 09:35

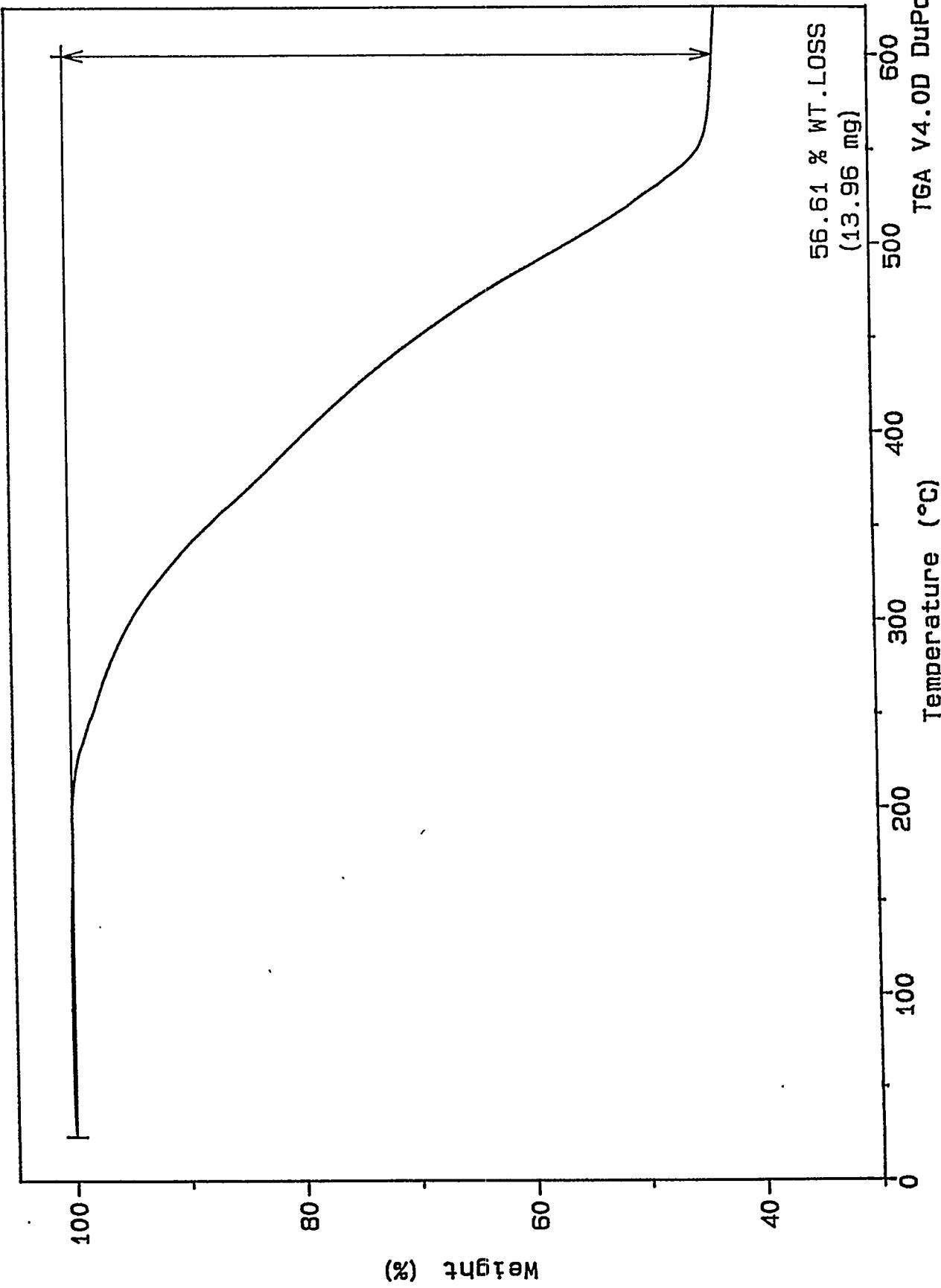


Figure 25: TGA Curve for A066 from Hydrotreated Coal
WVGS-13421 - 450°C, 1 Hour

Sample: A073 701-2-30-3
Size: 19.3970 mg
Method: 10°C/MIN
Comment: ARGON 100CC/MIN Pt PAN

File: 95090704D.02
Operator: gf1
Run Date: 18-Oct-95 08:49

A95-03037 TGA

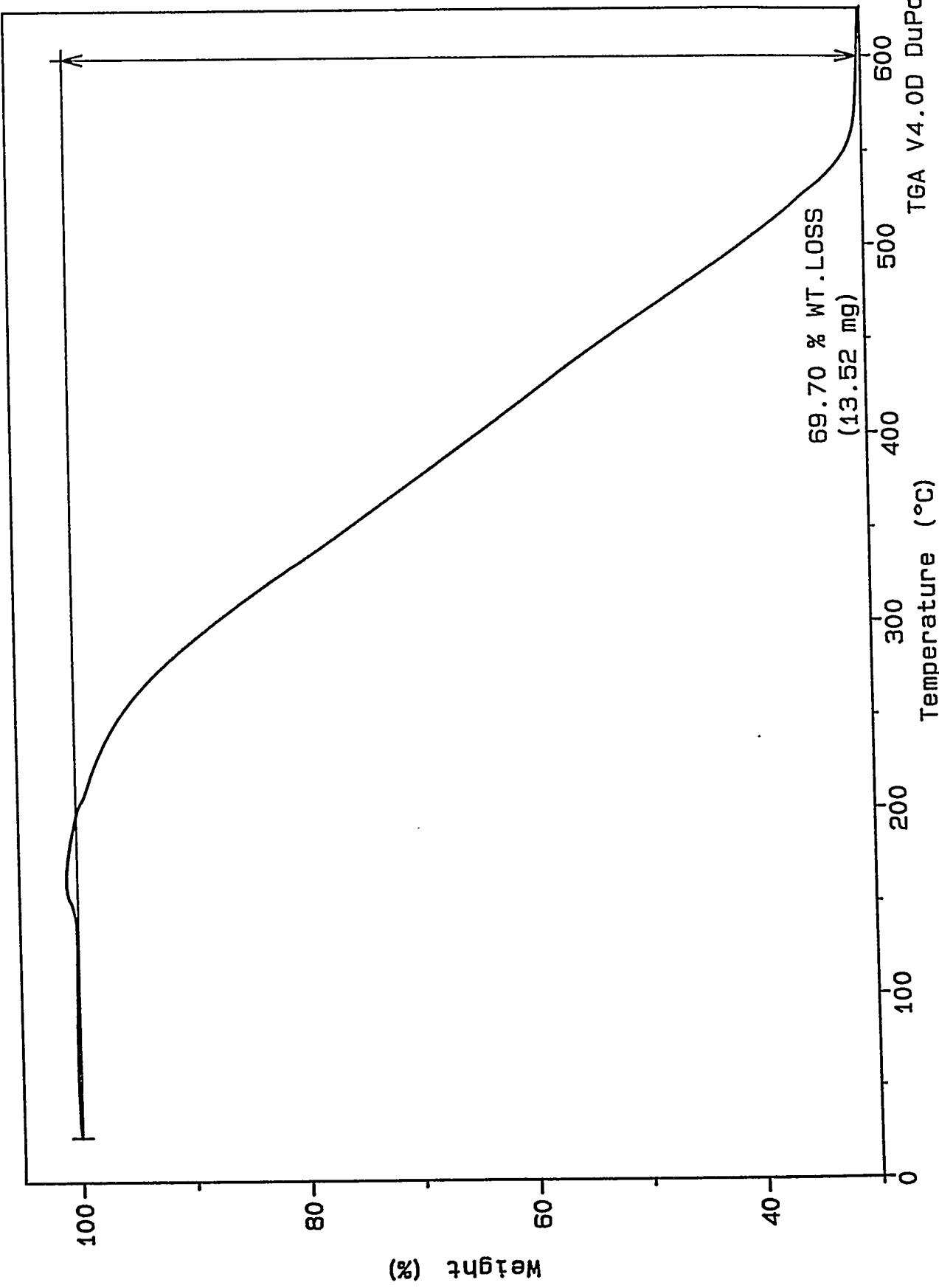


Figure 26: TGA Curve for A073 from Hydrotreated Coal
WVGS-13423 - 450°C, 2 Hours

Sample: A075 701-2-30-3
Size: 19.0000 mg
Method: 10°C/MIN
Comment: ARGON 100CC/MIN

A95-03036 TGA

File: 95090704C.02
Operator: gf1
Run Date: 17-Oct-95 16: 52

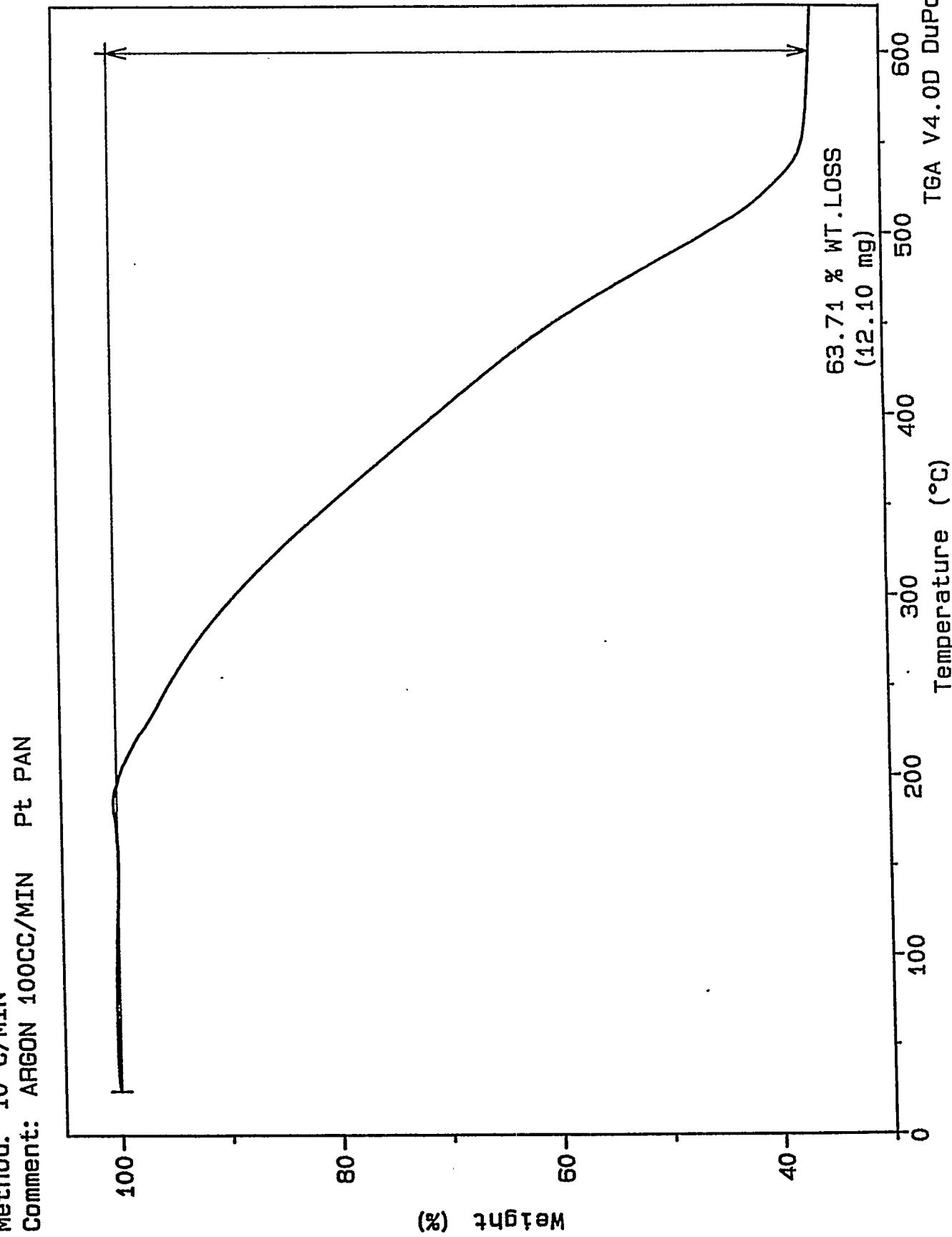
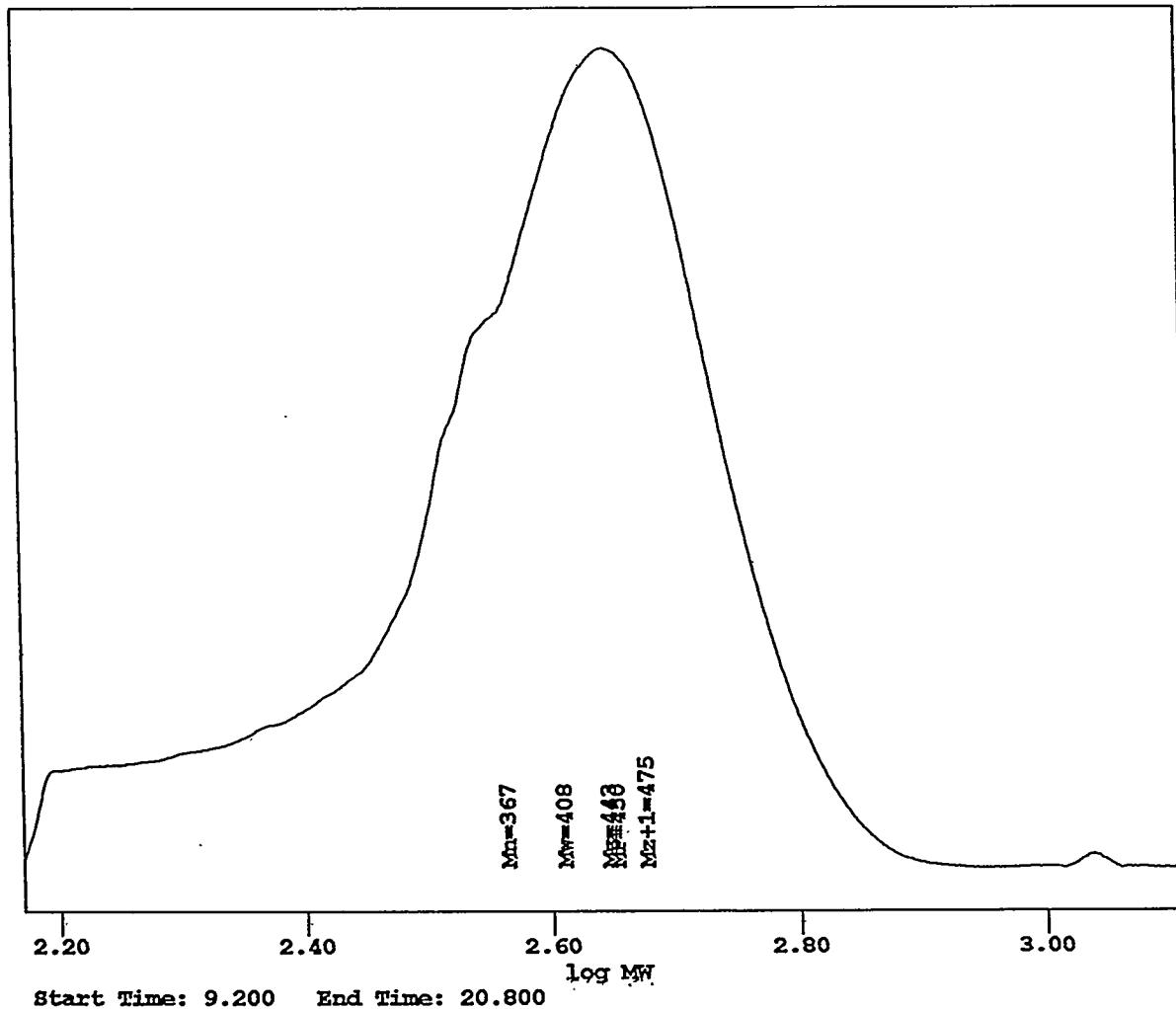


Figure 27: TGA Curve for A075 from Hydrotreated Coal
WVGGS-13423 - 450°C, 1 Hour

Project Name: GPC Sample Type: Broad Unknown
Sample Name: A076 Volume: 100.00
Vial: 4 Run Time: 30.0 min
Injection: 1 Date Processed: 09/25/95 03:49:51 PM
Date Acquired: 09/25/95 02:08:13 PM Pressure: 73
Processing Method: GPC Submitter: rtl
Comments: 701-2-30-2 (WVU) prepped 7/21/95

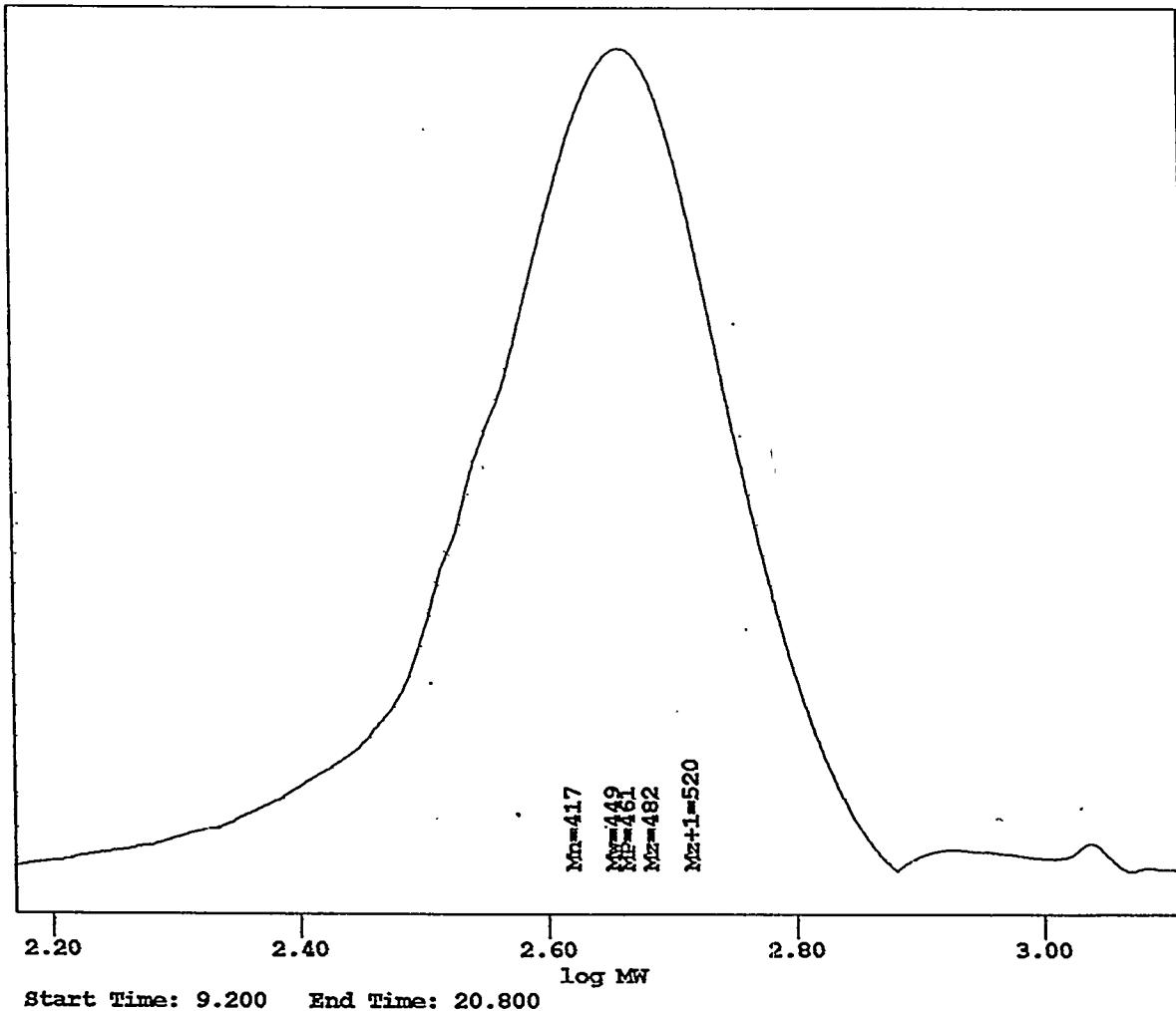


Peak Results

#	Ret Time (min)	Mn (Daltons)	MP (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.850	367	450	408	443	475	1.111614

Figure 28: Gel Permeation Chromatogram for A076 from Hydrotreated Coal WVGS-13421 - 450°C, 2 Hours

Project Name: GPC Sample Type: Broad Unknown
Sample Name: A066 Volume: 100.00
Vial: 3 Run Time: 30.0 min
Injection: 1 Date Processed: 09/25/95 03:48:09 PM
Date Acquired: 09/25/95 01:11:58 PM Pressure: 73
Processing Method: GPC Submitter: rtl
Comments: 701-2-30-1 (WVU) prepped 7/21/95



Peak Results

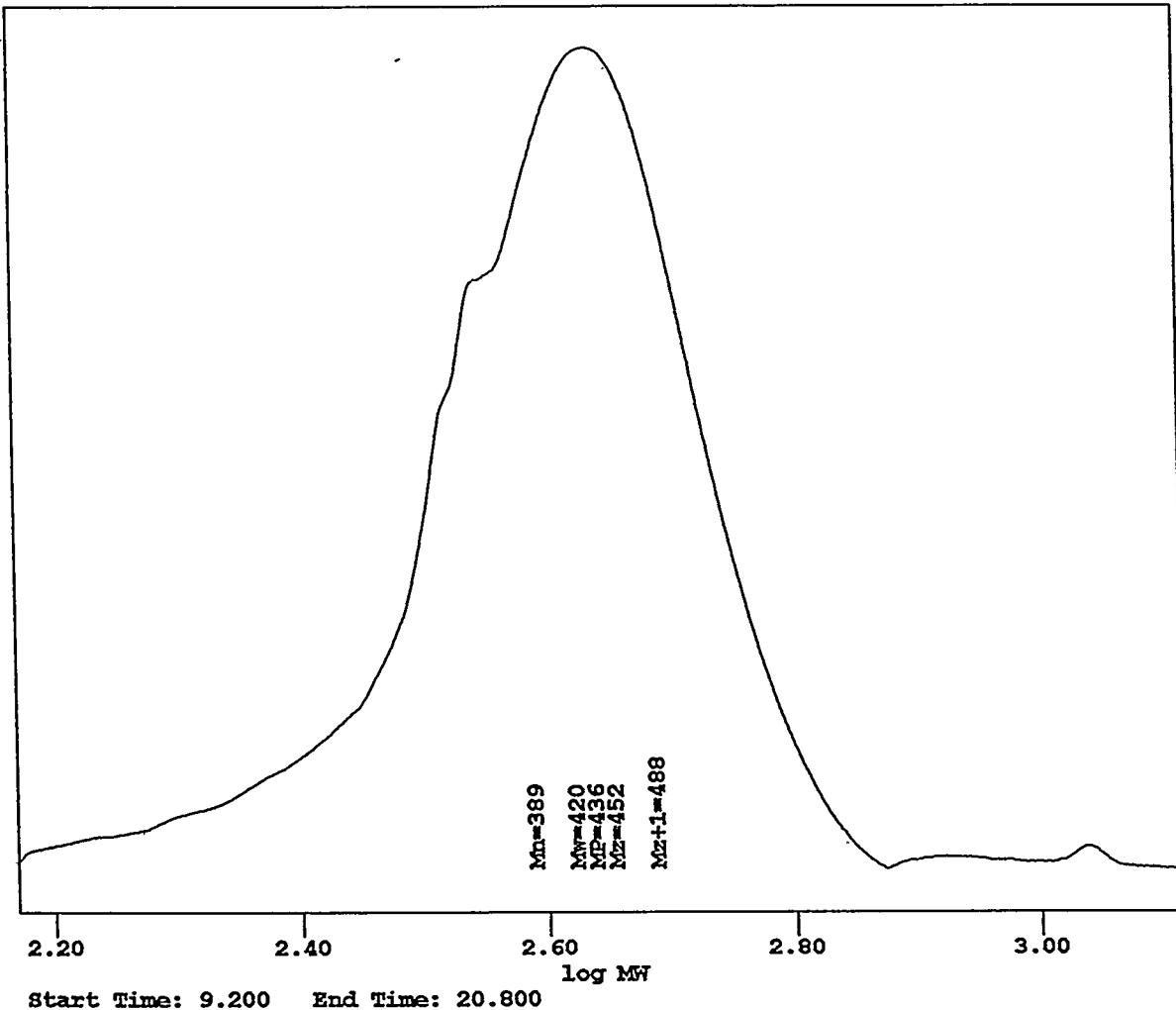
#	Ret Time (min)	Mn (Daltons)	MP (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.717	417	461	449	482	520	1.076375

Figure 29: Gel Permeation Chromatogram for A066 from Hydrotreated Coal WVGS-13421 - 450°C, 1 Hour

Project Name: GPC
Sample Name: A073
Vial: 6
Injection: 1
Date Acquired: 09/25/95 03:15:40 PM
Processing Method: GPC
Comments: 701-2-30-4 (WVU) prepped 7/21/95

Sample Type: Broad Unknown
Volume: 100.00
Run Time: 30.0 min
Date Processed: 09/25/95 03:48:35 PM
Pressure: 73
Submitter: rtl

dw/d(log MW)

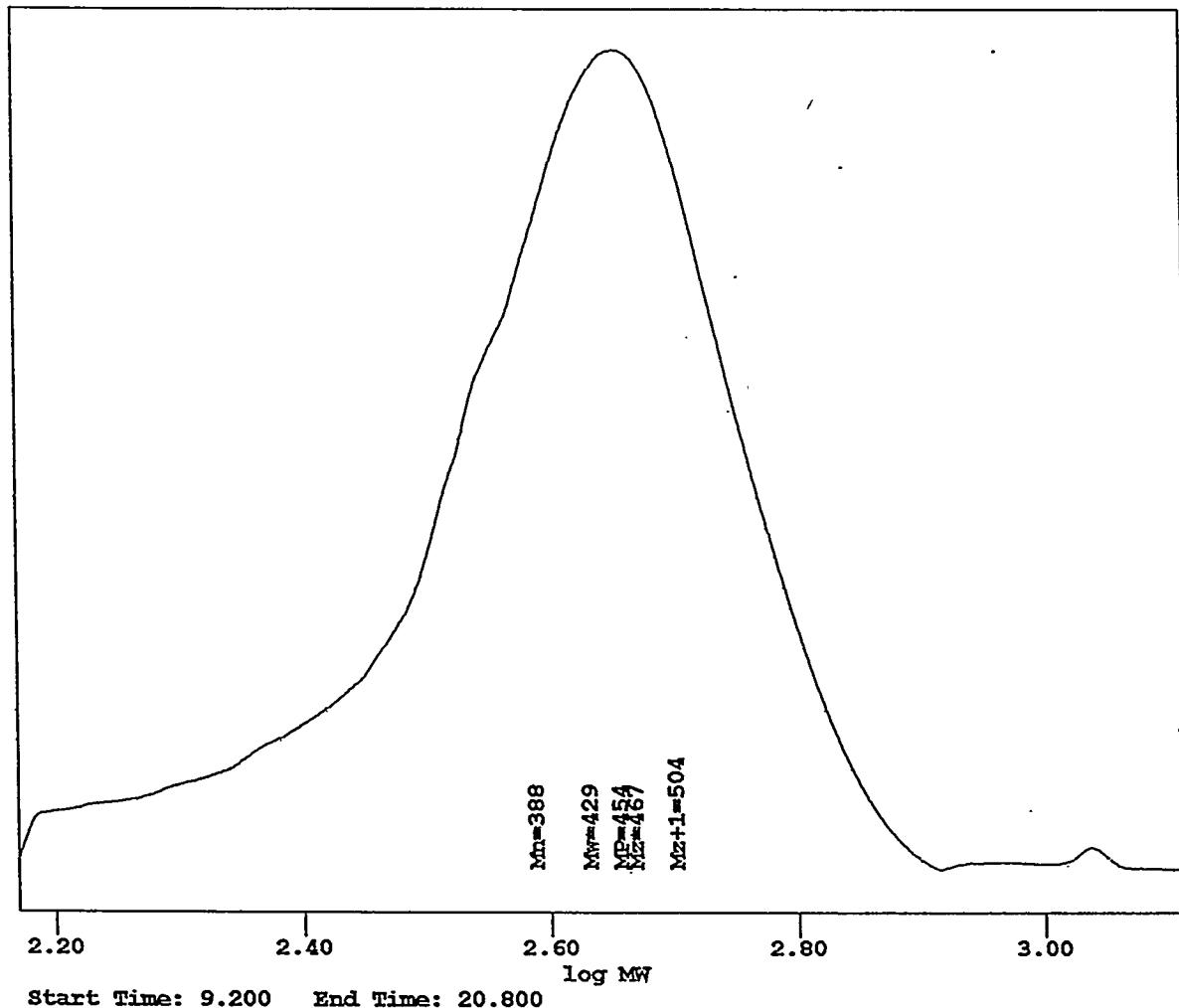


Peak Results

#	Ret Time (min)	Mn (Daltons)	Mp (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	15.017	389	436	420	452	488	1.079811

Figure 30: Gel Permeation Chromatogram for A073 from Hydrotreated Coal WVGS-13423 - 450°C, 2 Hours

Project Name:	GPC	Sample Type:	Broad Unknown
Sample Name:	A075	Volume:	100.00
Vial:	5	Run Time:	30.0 min
Injection:	1	Date Processed:	09/25/95 03:49:10 PM
Date Acquired:	09/25/95 02:44:30 PM	Pressure:	73
Processing Method:	GPC	Submitter:	rtl
Comments:	701-2-30-3 (WVU) prepped 7/21/95		



Peak Results

#	Ret Time (min)	Mn (Daltons)	MP (Daltons)	Mw (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	14.800	388	454	429	467	504	1.106079

Figure 31: Gel Permeation Chromatogram for A075 from Hydrotreated Coal WVGS-13423 - 450°C, 1 Hour

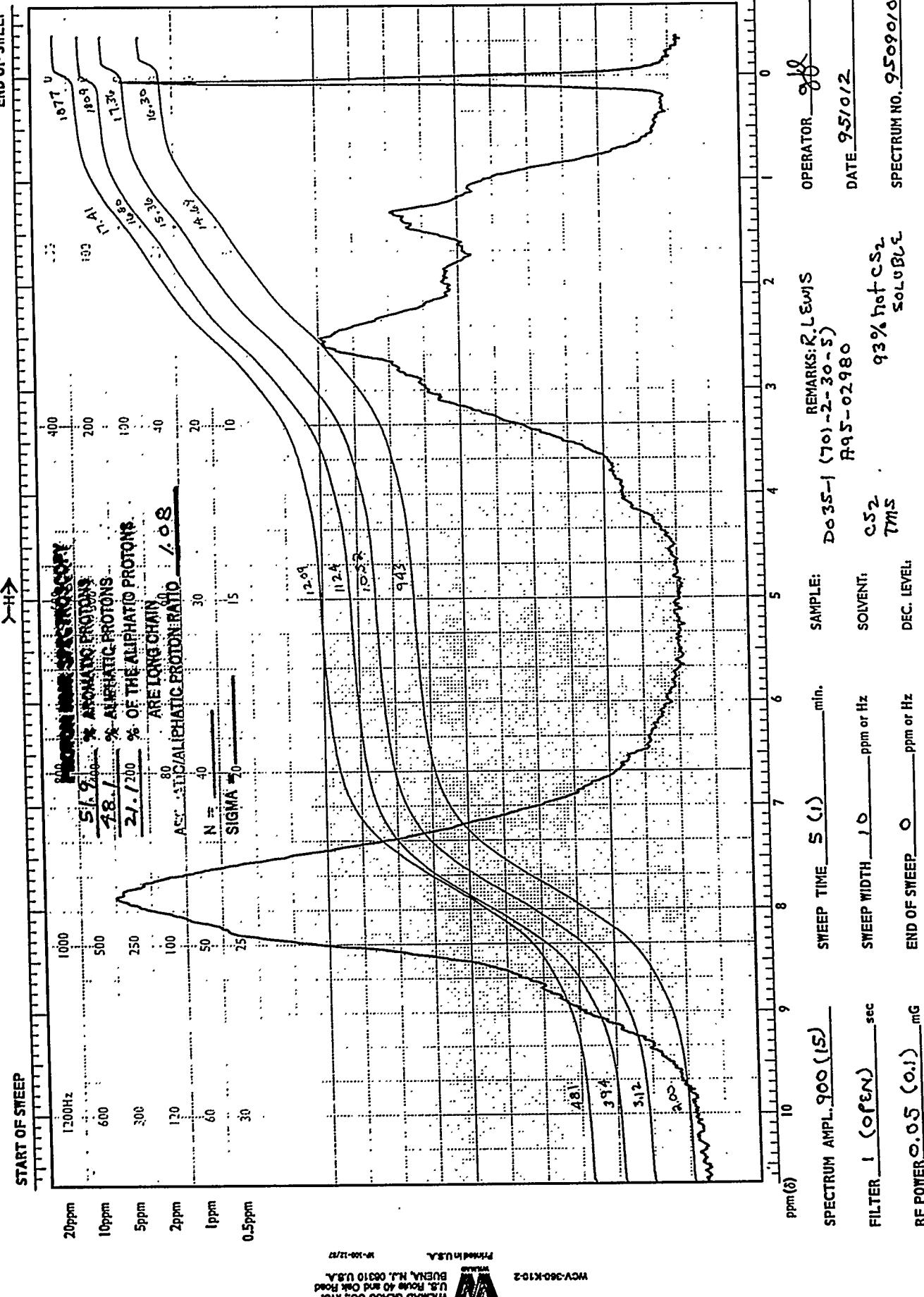


Figure 32: Proton NMR Spectrum for 250°C Distillation Residue D035-1

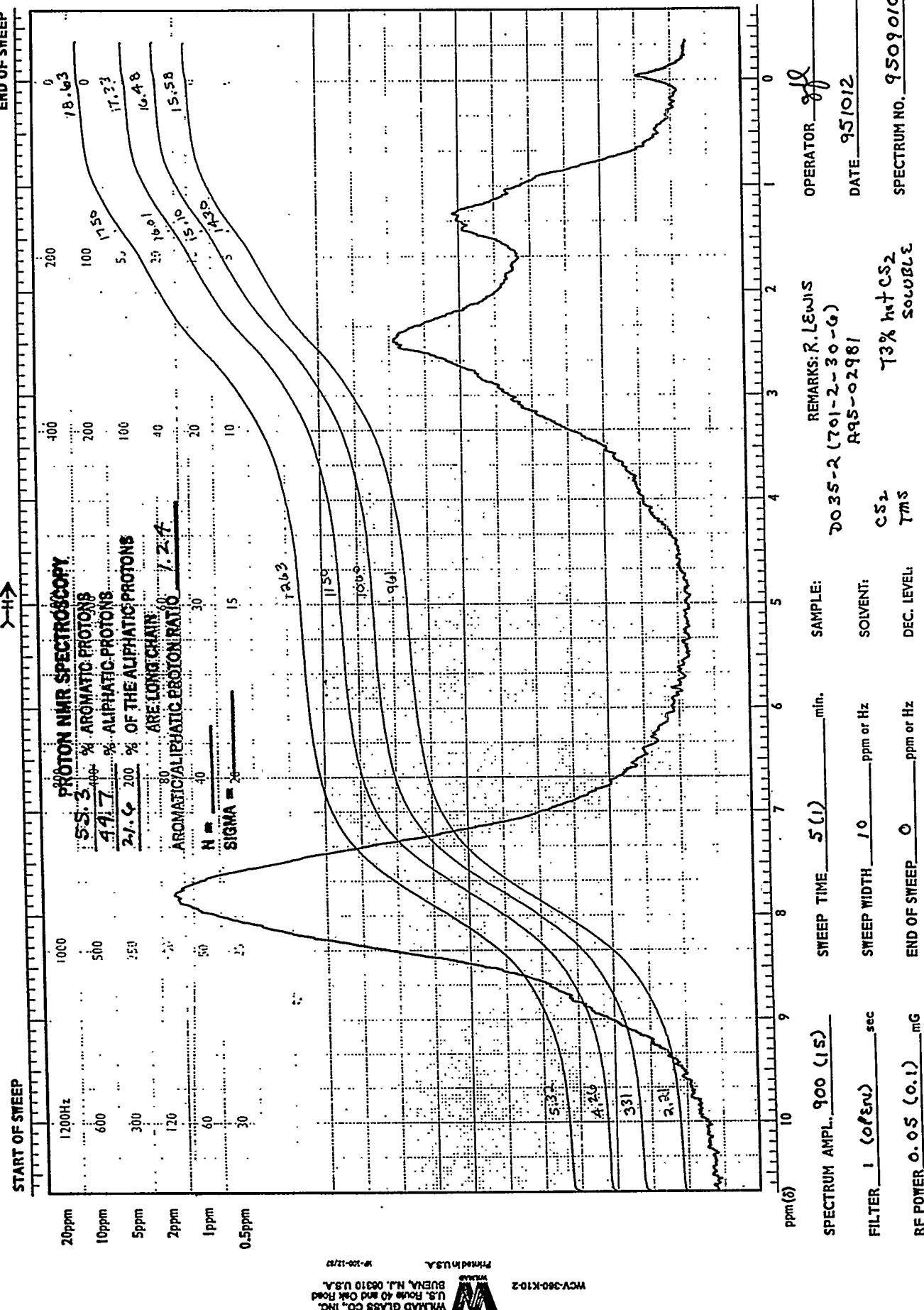
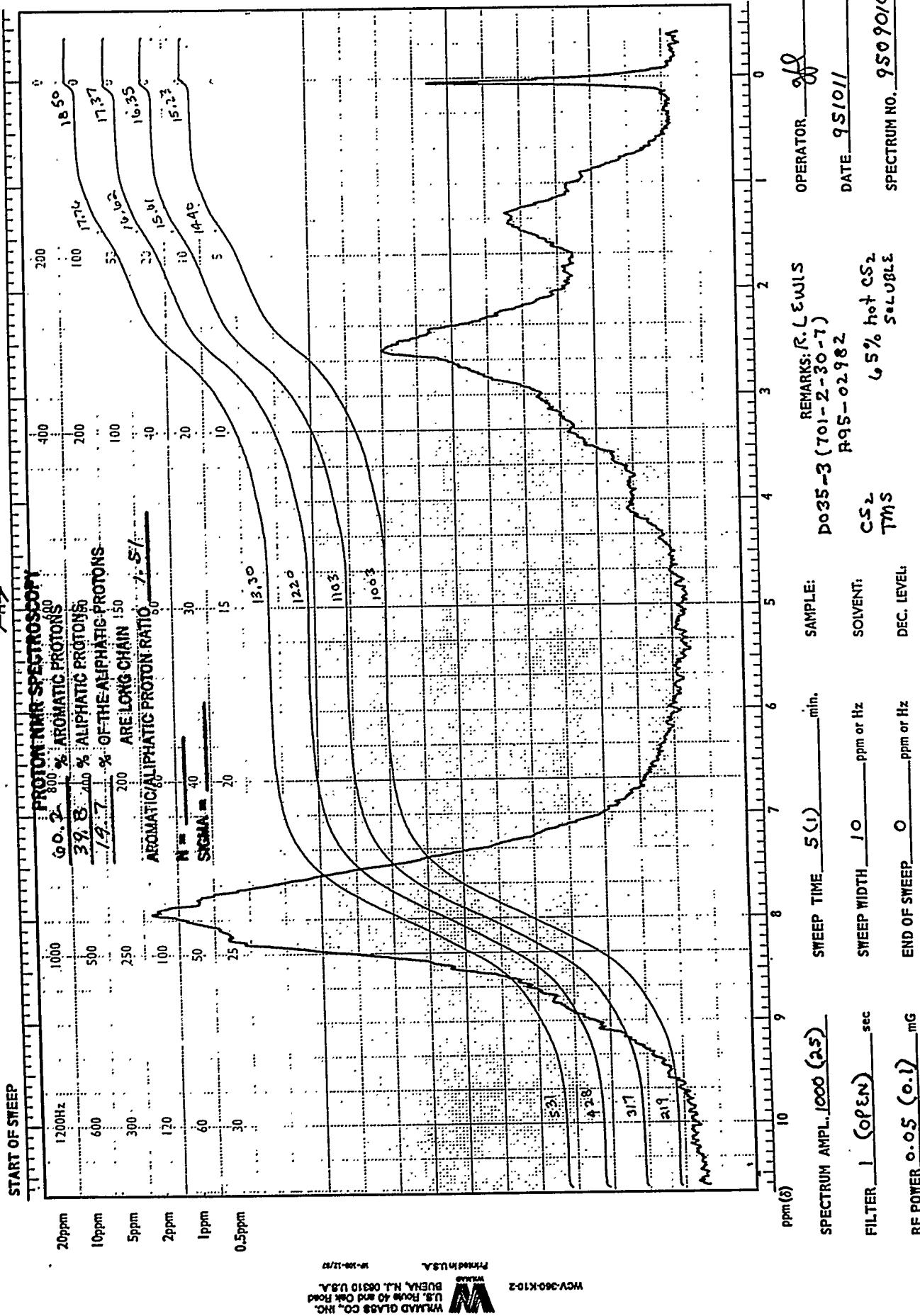


Figure 33: Proton NMR Spectrum for 350°C Distillation Residue D035-2



Sample: D035-1 (701-2-30-5)
Size: 26.1319 mg
Method: 10 °C/MIN
Comment: ARGON 100CC/MIN Pt PAN

A95-02980 TGA

File: A:95090401A.02
Operator: gf1
Run Date: 6-Sep-95 11:48

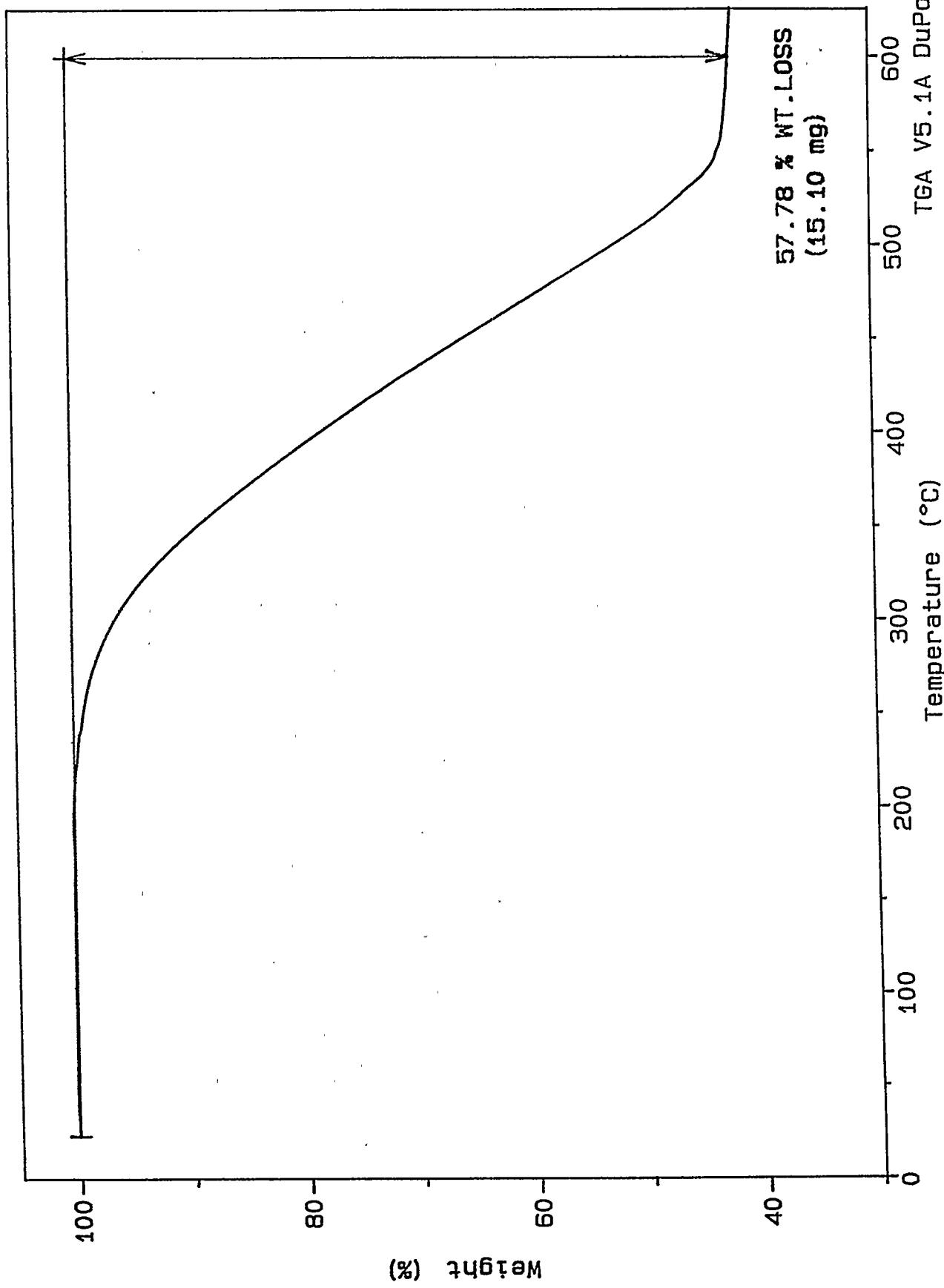


Figure 35: TGA Curve for 250°C Distillation Residue D035-1

Sample: D035-2 (701-2-30-6)
Size: 26.2477 mg
Method: 10°C/MIN
Comment: ARGON 100CC/MIN Pt PAN

A95-02981 TGA

File: A:95090101B.02
Operator: gf1
Run Date: 6-Sep-95 14:12

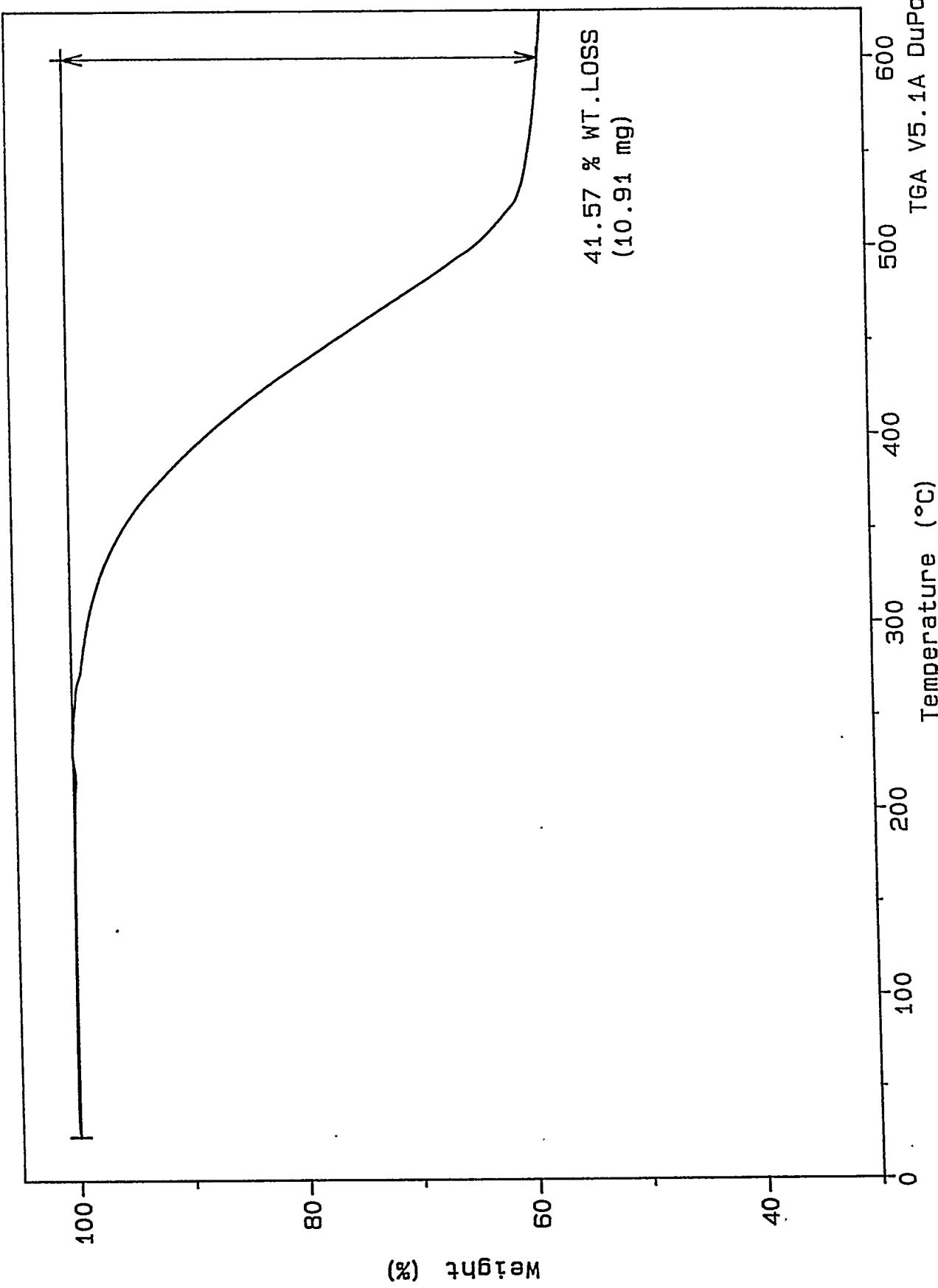


Figure 36: TGA Curve for 350°C Distillation Residue D035-2

Sample: D035-3 (701-2-30-7) A95-02982 TGA
Size: 25.0206 mg
Method: 10 °C/MIN
Comment: ARGON 100CC/MIN Pt PAN

File: A:95090101C.01
Operator: gf1
Run Date: 5-Sep-95 12:01

A95-02982 TGA

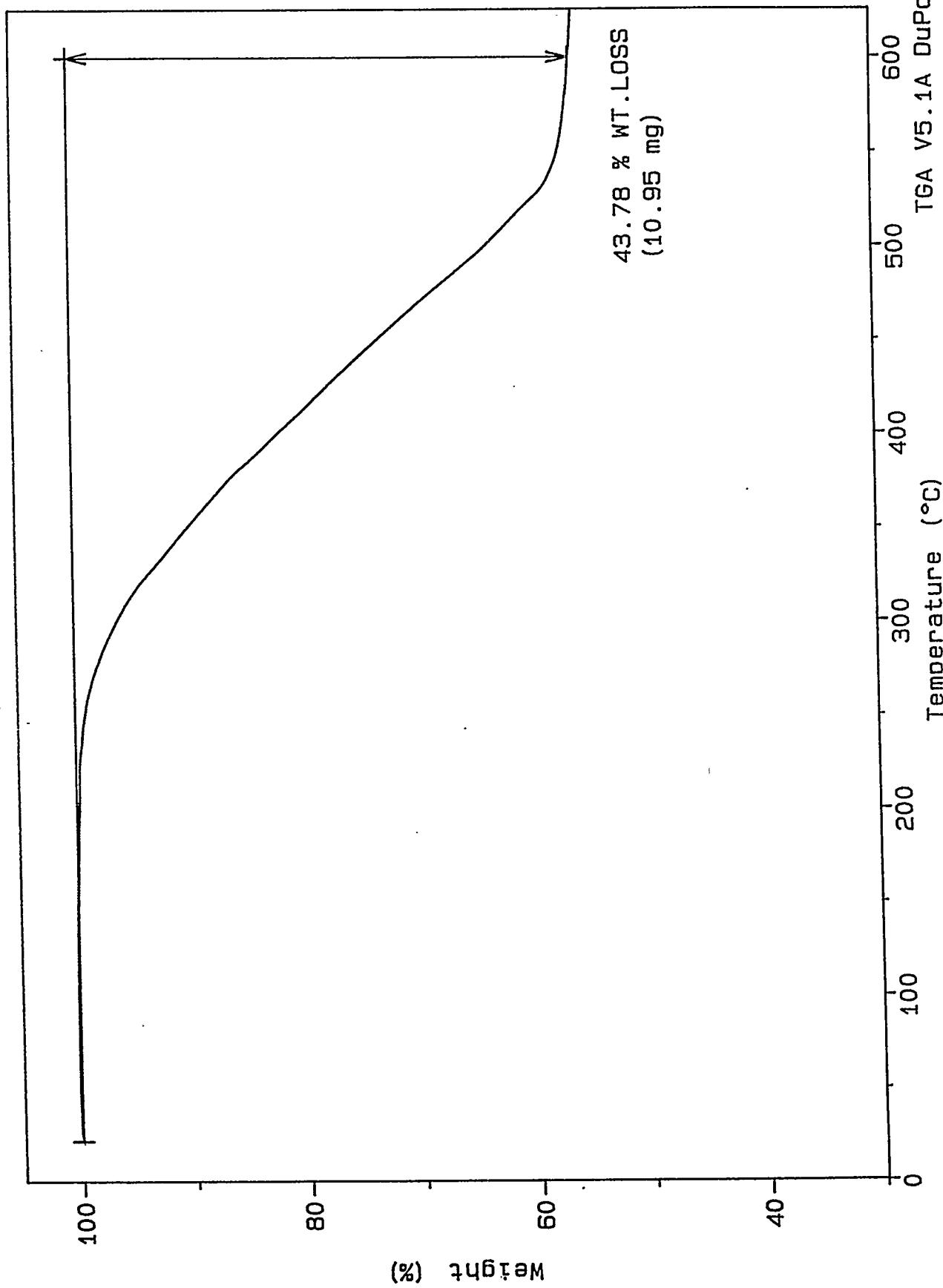


Figure 37: TGA Curve for 400°C Distillation Residue D035-3

Figure 38

Annealed Mesophase Pitch from Sample A076

450°C - 2 Hr., Coal WVGS 13421

A076 450 - 2 HR 13421



500 μ m

50X, POLARIZED LIGHT

A076



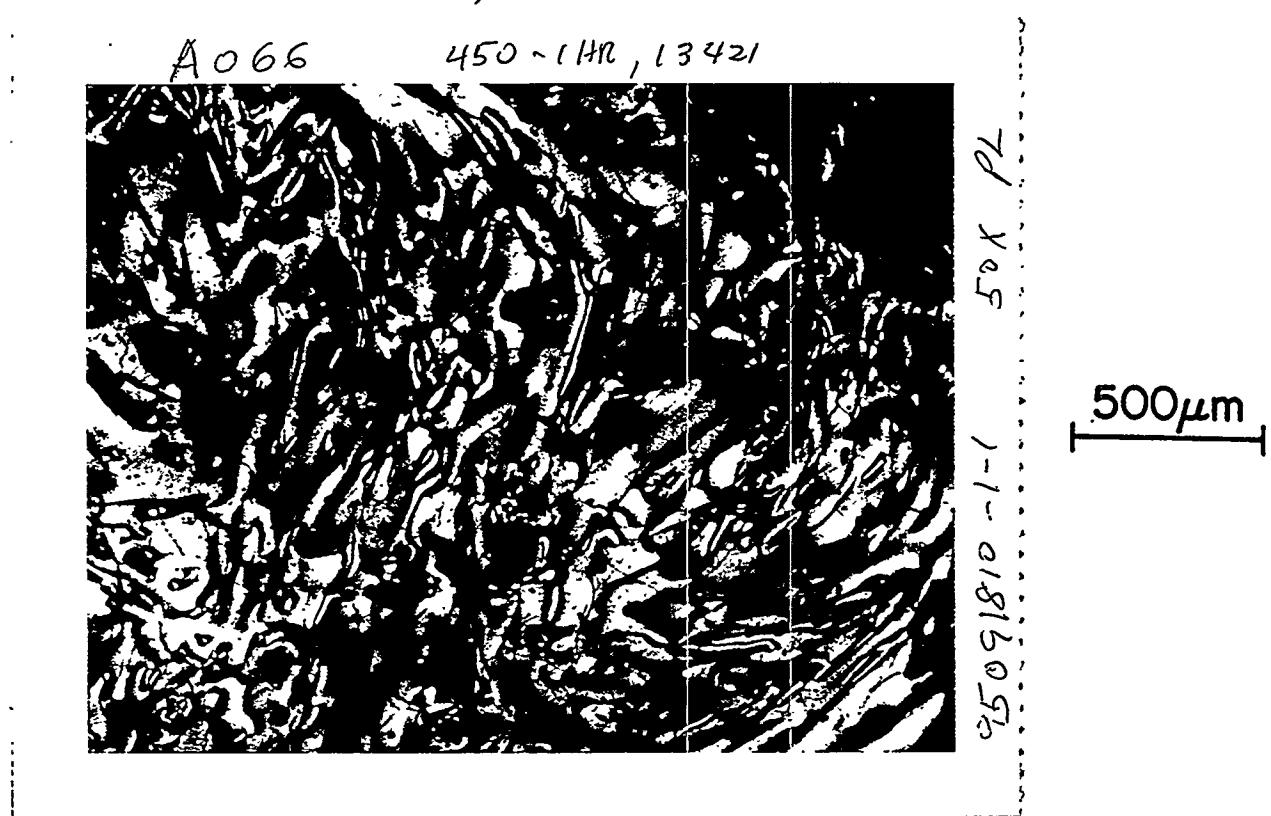
100 μ m

250X, POLARIZED LIGHT

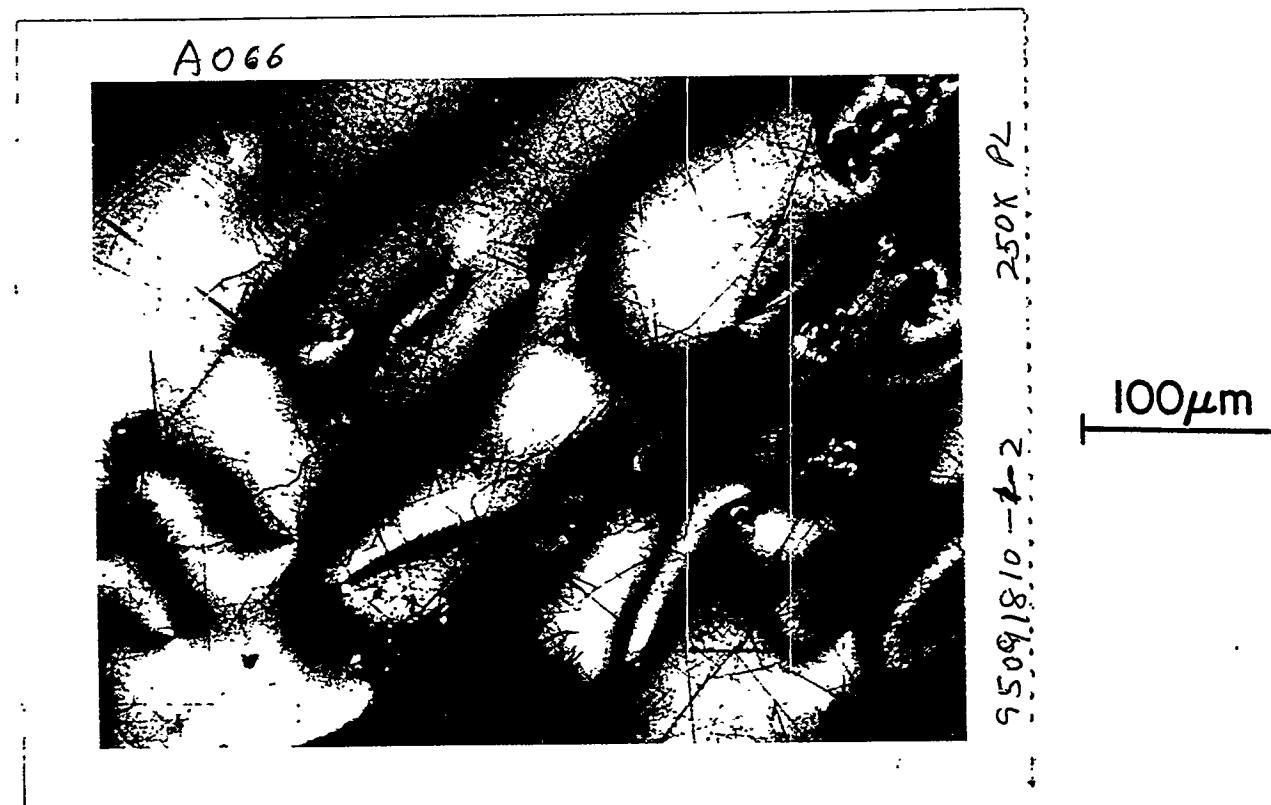
Figure 39

Annealed Mesophase Pitch from Sample A066

450°C - 1 Hr., Coal WVGS 13421



50X, POLARIZED LIGHT



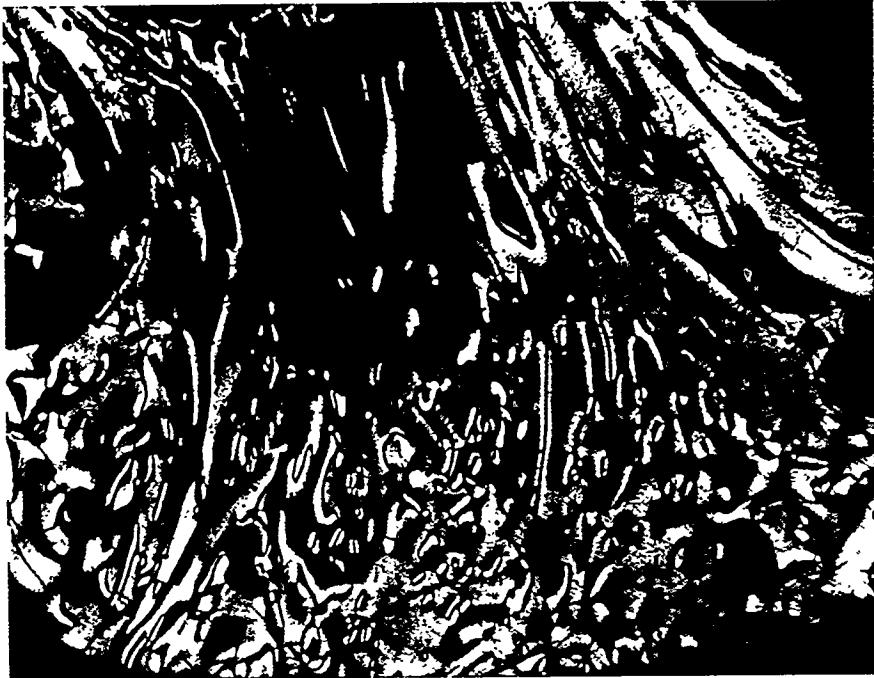
250X, POLARIZED LIGHT

Figure 40

Annealed Mesophase Pitch from Sample A073

450°C - 2 Hr., Coal WVGS 13423

A073 450 - 2 Hr 13423



50X, POLARIZED LIGHT

A073



250X, POLARIZED LIGHT

95091810-3-1
50X PL

95091810-3-2
250X PL

Figure 41

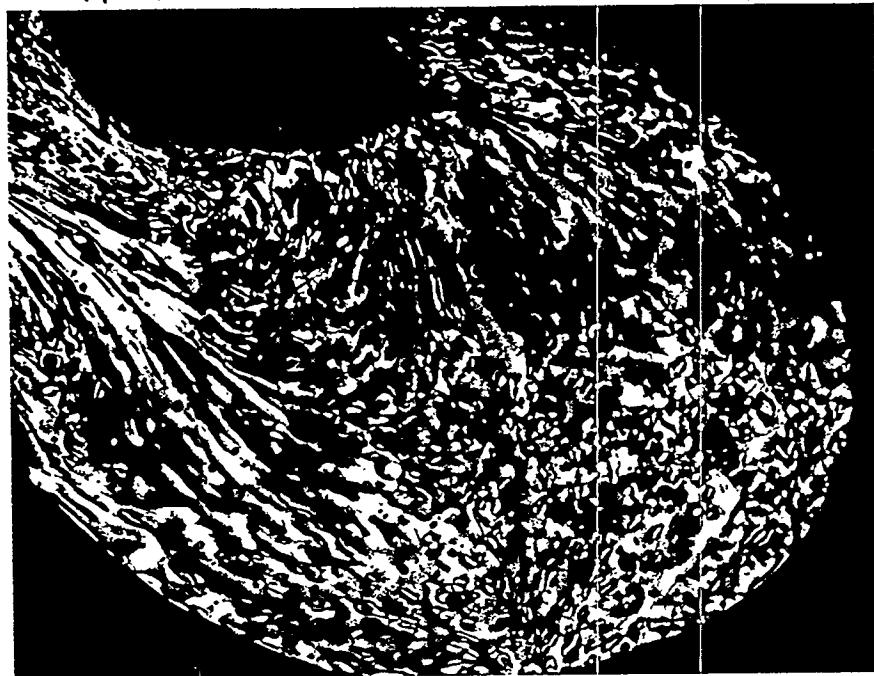
Annealed Mesophase Pitch from Sample A075

450°C - 1 Hr., Coal WVGS 13423

A075

450 - 1 HR

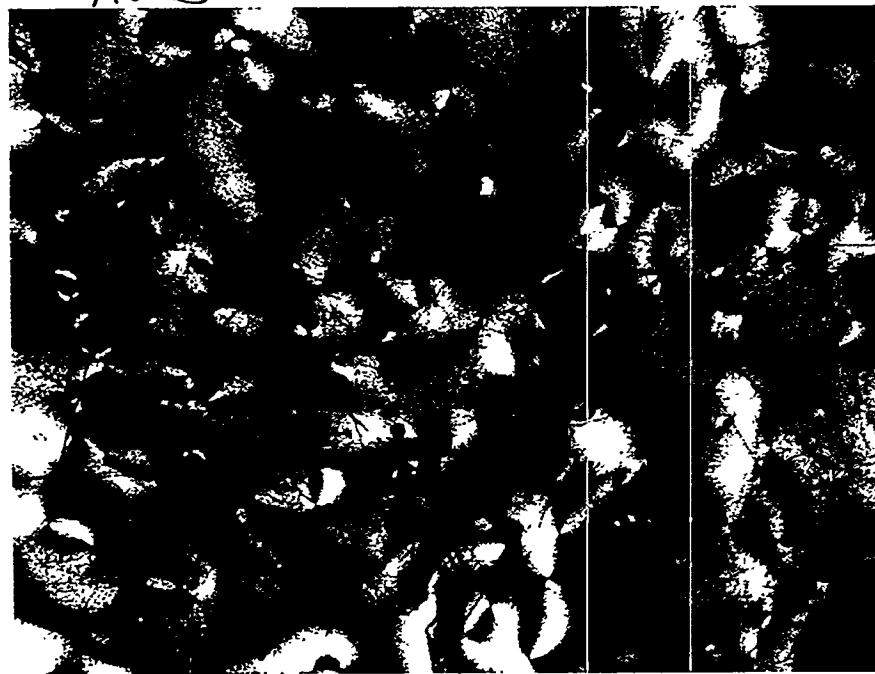
13423



500 μ m

50X, POLARIZED LIGHT

A075



100 μ m

250X, POLARIZED LIGHT

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