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PREDICTORS OF PLASTICITY IN BITUMINOUS COALS

Final Technical Report

February 1, 1984

Work Performed Under Contract No. FG22-81PC40793

Western Kentucky University
Bowling Green, Kentucky

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

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PREDICTORS OF PLASTICITY IN BITUMINOUS COALS

FINAL TECHNICAL REPORT

FEBRUARY 1, 1984

work performed under Grant DE-FG22-81PC40793

United States Department of Energy

William G. Lloyd¹

John W. Reasoner¹

James C. Hower²

Linda P. Yates²

Carol P. Clark¹

Eileen Davis²

Anita Fitzpatrick²

Adesoji Irefin¹

Alvaro Jiminez¹

Terri M. Jones²

Carol L. Reagles³

Lizbeth P. Sturgeon¹

Jana Mefford Whitt¹

Garry D. Wild²

¹Department of Chemistry, Western Kentucky University

²Institute for Mining and Minerals Research, University of Kentucky

³Department of Mathematics, Western Kentucky University

project manager: William McKinstry, PETC

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1. SUMMARY

A group of 40 hvb coals, mostly from western Kentucky fields, has been examined with regard to ASTM Gieseler plastometric properties. Twenty-nine of these coals have also been studied over a range of temperatures by isothermal Gieseler plastometry.

Raw Gieseler data provide melting and coking slopes and readily calculable fluidity spans. Maximum fluidity by slope intersection is a more consistent measure than observed maximum fluidity. Isothermal slopes and maximum fluidities follow Arrhenius temperature dependencies, with activation energies related systematically to fluid properties.

These freshly sampled coals are also characterized by chemical, physical and petrographic criteria, by quantitative solvent extractions, by pyrolysis gas chromatography, by Fourier Transform infrared analysis of coals and extraction residues, by the HPLC analysis of coal extracts, and by optical microscopy of coals and Gieseler semi-coke residues.

Multiple linear regression analysis yields three-term expressions which estimate maximum fluidities (both ASTM and isothermal) with R values of .90-.92. Slopes and critical temperatures are similarly predictable.

Plastometer experiments with selected coals under superatmospheric pressures show both melting slopes and maximum fluidities to be sharply increased, the latter by one to three orders of magnitude.

Some suggestions are offered to accomodate this new information into the general body of knowledge concerning the phenomenon of plasticity in mid-ranked coals.

2. ACKNOWLEDGMENTS

We are especially indebted to Gerald Thomas (IMMR) and John T. Riley (WKU) for their contributions in obtaining numerous physical and chemical analyses of the 46 fresh coal samples used in this study.

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W.G.L.

J.W.R.

J.C.H.

L.P.Y.

3. INTRODUCTION

When a mid-ranked coal is heated, typically to 380-400°C, a series of (first) physical and (then, concurrently) chemical changes takes place whereby the solid mass softens and becomes fluid. Contributing to this fluidity is an outgassing of gases and vapors. Coal in this fluid or 'plastic' state typically becomes more fluid with time, reaches a maximum fluidity, and then becomes progressively less fluid, eventually solidifying to a semicoke.

The phenomenon of plasticity in coals has been known for a long time but is still poorly understood. Plasticity is usually observed only in coals in the range hvb to mvb. Among such coals, even among coals of identical subrank and chemical composition, large differences in plastic behavior are commonly encountered. Furthermore the plastic state is transitory in nature, lasting for a period of minutes or (more rarely) hours. A sample of coal once taken through its plastic state is irreversibly altered; it will not become plastic a second time.

A plausible theory to account for this behavior is that of a fusible component or 'bitumen' which melts to provide a viscous slurry. The bitumen theory was first advanced nearly 70 years ago (1,2). One of the important modifications of this theory is that of Berkowitz (3), who suggests a micellar structure which undergoes surface melting only.

This view is supported by many studies involving solvent extraction of pulverized coal (4). Pierron and Rees studied three coals of identical rank and differing plasticity, and found a relationship between maximum fluidity and the amount of pyridine-extractable material (5). They also showed that plasticity fell rapidly as the pyridine-solubles were removed,

that the extraction residues were completely nonplastic, and that plasticity was restored when the extracted 'bitumen' was returned to the coal residues (6). Kirov and Stephens have shown that the addition of 5-10% pitch to coking coals results in a sharp transition from nonplastic (27% pitch) to "very high fluidity" (28% pitch), an observation which is consistent with the analysis of P. L. Waters (8,9) which accounts for coal plasticity in terms of the behavior of high-viscosity melts. Recently Karabon and Chodzinski have developed a centrifuge furnace which provides a repeatable method for the separation of the liquid portions of coals heated to their plastic regions (10,11). They obtain typically 3-18% nonvolatile liquids and 5-25% gases and condensable vapors. All of these observations are consistent with the view of coal as a mixture of fusible-and-extractables and infusible-and-insoluble components.

A second plausible theory to account for the plasticity phenomenon is based upon the formation of a mixture of liquid and gaseous products as a consequence of pyrolytic reactions taking place within the coal. This appears to have been first advanced by von Broche and Schmitz (12), who found that the material extracted from a plastic coal failed to confer plasticity upon a nonplastic coal. The view that pyrolytic bond cleavage is a necessary precursor to plasticity has been supported by a number of other workers (13-18). Dryden and Joy have shown that the amount of chloroform-solubles in a 'melting' coal increases as the coal approaches maximum fluidity, then decreases as the coal enters the coking phase (16). Attar explains the dependency of maximum fluidity upon particle size in terms of pyrolysis gas bubble nucleation (19). Neavel (20,21) provides a comprehensive mechanistic model of plastic behavior based upon the initial scission of the weakest covalent bonds in the coal structure. All of these

observations are consistent with the view that upon heating the coal (in van Krevelen's language) depolymerizes to produce a metastable plastic phase (metaplast), which when present in sufficient quantity will confer fluid properties upon the coal mass (4,17).

These views may seem more contradictory than they actually are. Our inclination here has been well expressed by R. Loison and his associates: "parallel to this fusion of meltable 'bitumen' and independently of it, pyrolysis develops and modifies the fusibility" (22). Evidence for the participation of both processes is substantial. But at this time an adequate, comprehensive and explicit theory -- i.e., a theory with useful predictive power -- still eludes us.

Yet there are compelling practical reasons to seek a better understanding of coal plasticity. The importance of plastic properties of coals in the coking process, and the relationship between these properties and the mechanical properties of the resulting cokes, can hardly be overstated (23). The optimum process temperatures for a number of hydro-liquefaction processes are closely grouped in the range 440-460°C (24), close to the maximum Gieseler fluidities of many bituminous coals and emphasizing the likelihood (20) that coal 'melting' is an important first step in hydroliquefaction. A new approach to the problem of charging coal to superatmospheric reactors entails the use of heated screw or gear pumps which can deliver the 'molten' coal against high head pressures and spray it into the reactor (25-28). Coal in the plastic state readily reacts with molecular hydrogen at moderate partial pressures (20, 22, 29), presenting the possibility of a relatively low-capital approach to liquefaction by 'solvent-free hydrogenolysis' (30,31). All of these present and potential

applications are acutely dependent upon the plastic properties of the coals used. All would be well served by a better understanding of coal plasticity.

4. OBJECTIVES

The objectives of this study are conveniently divided into four categories.

(1) A group of at least 36 coals is to be selected and fresh field samples sampled. At least 24 of these coal samples are to be eastern mid-continent coals, expected to be the major feedstock for the several synfuel plants planned for western Kentucky.

(2) The plastic properties of these coals are to be thoroughly characterized, using Gieseler plastometry under three sets of conditions:

- * ASTM plastometry (at 3.0 deg C / minute) is to be carried out in quadruplicate on all samples

- * Isothermal plastometry will be conducted in replicate at several selected temperatures

- * Isothermal plastometry at elevated pressures will be conducted with six selected coals, with at least 16 Gieseler runs per coal

(3) These coals are to be subjected to detailed characterization, including ASTM physical and chemical measurements, maceral analysis and petrographic characterization, pyrolysis gas chromatography, quantitative Soxhlet extraction with a polar solvent to be selected, Fourier Transform infrared analysis of raw coals, extraction residues and extracts,

chromatographic analysis of coal extracts, and optical microscopy using selected coals.

(4) The database, including plasticity data and the comprehensive characterizations described above, is to be analyzed to find and quantify a set of predictive relationships which will permit the inference of plastic properties from the general characterization data outlined in (3) above.

This work has now been completed, and is reported in the following sections.

5. EXPERIMENTAL WORK

5.1 Selection and Handling of Coals

The western Kentucky coals studies are from the Pennsylvania Tradewater, Carbondale and Sturgis formations. The principal seams and their counterparts in Illinois and Indiana are shown in Figure 1 (32). Although significant variations exist, most western Kentucky coals are believed to have been deposited under marine conditions, and consequently most have relatively high contents of pyrites and organic sulfur.

The Bancroft (Kentucky #5) and Elm Lick (Kentucky #5 to #6) coals are from the Tradewater Formation. Some Tradewater coals in Butler and Ohio counties are notably lower in ash (below 3%) and sulfur (below 1%) than most marine coals (33). Four coal samples of the Amos seam--representative of this low sulfur group--have been acquired for this study. The Elm Lick bench mined coal can also be low in sulfur; sulfur content is moderate in the sample used in this study. The Indiana Lower Block coal is also a low sulfur coal. In northern Indiana the Block coals are noted for low vitrinite and low total sulfur (34).

The Carbondale coals samples for this study include the Davis (KY#6), Springfield (KY #9), Briar Hill (KY #10) and Herrin (KY #11, IL #6) coals. In general the Carbondale coals are extensive coals with relatively uniform thickness and properties over wide areas. (In this regard the #10 coal is less uniform than most.) Both the #9 and #11 are high sulfur, high vitrinite coals. The petrography of these coals is relatively constant across the western Kentucky coal field, although the #9 seam has lower vitrinite content towards Daviess and Henderson counties (35,36).

The Sturgis coals include the Paradise (KY #12) in combination with #11 and the Coiltown (KY #14) coals. The Sturgis coals, while locally important, are not as widespread nor as consistent as the Carbondale coals. These are characteristically high sulfur and high vitrinite coals (37).

Coal rank in western Kentucky exhibits predictable trends (38). Coals in the Webster Syncline (Webster and southern Union counties - see Figure 2) have ranks as high as the lower part of the hvAb range, with vitrinite reflectances as high as $0.75\% R_{\max}$. Rank in the remainder of the field is mostly hvCb, with rank transition from the Webster Syncline to the Moorman Syncline resulting in hvBb coal along the Webster County / Hopkins County boundary (that is, in the area of the Central Faults). Rank in the middle of the hvAb range does occur in Butler County (Amos and Foster coals, roughly KY #2) and in grabens within the Rough Creek Fault Zone.

Most of the western Kentucky coals studied to date have been collected by the University of Kentucky's Institute for Mining and Minerals Research as part of a project funded by the U.S. Department of Energy through International Coal Refining Company. These are clean products from various coal preparation plants. As beneficiated coal these samples have a more uniform amount of mineral matter (and lower mineral matter) than channel or run-of-mine samples from the same sources. The organic chemistry and petrography of these coals, while modified by the preferential elimination of certain macerals during preparation, still exhibits the substantial variability of properties to be expected of a group of coals of different origin and different rank. The use of beneficiated coal in the present study has probably improved our correlations by diminishing the impact of adventitious inclusions of separable minerals.

DISTRIBUTION OF COAL PREPARATION PLANTS IN THE WESTERN KENTUCKY COAL FIELD

Figure 2

SITES OF WESTERN KENTUCKY COAL CLEANING PLANTS

Table 1 lists the sources of coal samples acquired for the main part of this study. The project reference number in the left-hand column is used for identification in following tables.

Coals coming in from the field to IMMR are rough crushed to minus 1 inch, and splits made (1) for reduction for in-laboratory ASTM analyses, (2) to provide five-pound samples for study at WKU, and (3) for reserve storage under nitrogen.

Coal samples are delivered to WKU in double-sealed plastic bags under nitrogen. At WKU each sample is reduced to -8 mesh, split, and stored under nitrogen in a storage freezer. Splits of this coal are reduced to -20 mesh, split again, and sub-splits reduced to -60 mesh; all samples are kept under nitrogen in the storage freezer until used.

5.2 Plastic Behavior

The fluid properties of each coal are determined by a method of dynamic fluidity measurement using a constant-torque Gieseler plastometer (38). The instruments used for this project are Research Model (Standard Instrumentation, Inc., Charleston, WV) units, providing fluidity measurements at the standard 60-sec. intervals and at 10-sec. intervals, and measuring fluidity to the nearest 0.1 dial division per minute (ddpm). The 60-sec. interval data conform to the standard procedure (38) and were used with most coals. For a few highly fluid coals, however, the softening curve is better characterized by using 10-sec. data, and for these coals the shorter interval was used.

Measurements of plasticity are well known to be difficult to reproduce, even difficult to repeat when the same operator uses the same instrument. As these measurements are of critical importance to this study, every effort has been made to uniformize and standardize the

Table 1

Sources of Western Kentucky Coals

<u>no.</u>	<u>KCER no.</u>	<u>Seam</u>	<u>Vertical location</u>	<u>Source key</u>	<u>County</u>	<u>Sample size</u>	<u>Nominal rank</u>
1	9021	KY #9	high	G1	Daviess	6 x 2"	hvcB/subA
2	9022	KY #9	high	G1	Daviess	2 x 1/2"	hvcB/subA
3	9029	Elm Lick	middle	S1	Ohio	CS	hvcB/hvBb
4	9036	Bancroft	high	B1	Muhlenberg	3 x 1/2"	hvBb
5	9037	Bancroft	high	B1	Muhlenberg	1/2 x 1/4"	hvBb
6	9045	Bancroft	high	O	Muhlenberg	3 x 1/2"	hvcB
7	9046	Bancroft	high	O	Muhlenberg	1/2 x 1/4"	hvcB
8	9052	KY #9	high	C1	Ohio	6 x 1-1/2"	hvcB
9	9055	KY #9	high	C1	Ohio	1-1/2 x 1/4"	hvcB
10	9064	KY #9	high	F1	Hopkins	1-1/4" x 28m	hvcB
11	9398	KY #14	middle	B1	Muhlenberg	3 x 1/2"	hvcB
12	9399	KY #14	middle	B1	Muhlenberg	1/2 x 1/4"	hvcB
13	9072	KY #9	high	H1	Union	6 x 1-1/4"	hvBb
14	9077	KY #9	high	H1	Union	1-1/4 x 28m	hvBb
15	9085	KY #9	high	H2	Union	6 x 1-1/4"	hvcB
16	9089	KY #9	high	H2	Union	1-1/4 x 28m	hvcB
17	9099	KY #9	high	C2	Muhlenberg	6 x 1-3/4"	hvcB
18	9100	KY #9	high	G2	Muhlenberg	1-3/4 x 1/4"	hvcB
19	9109	KY #11/#12	high	R1	Muhlenberg	4 x 1-1/2"	hvcB
20	9110	KY #11/#12	high	R1	Muhlenberg	1-1/2 x 1/4"	hvcB
21	9121	KY #9	high	D1	Webster	2 x 28m	hvBb/hvAb
22	9127	KY #6	middle	P1	Union	3 x 1/2"	hvAb
23	9129	KY #6	middle	P1	Union	- 1/2"	hvAb
24	9158	KY #11	high	C2	Union	5 x 1"	hvcB/subA
25	6083	Mason	---	---	Bell	run of mine	hvAb
26	7625	KY #10	---	---	Webster	run of mine	hvAb
27	7626	KY #9	---	---	Union	run of mine	hvAb
28	8055	Indiana Lower Block	---	---	Spencer (IN)	run of mine	hvcB

continued

Table 1, continued

<u>no.</u>	<u>KCER no.</u>	<u>Seam</u>	<u>Vertical location</u>	<u>Source key</u>	<u>County</u>	<u>Sample size</u>	<u>Nominal rank</u>
30	9146	KY #9/#11	high	K1	Ohio	3/4 x 1/4"	hvCb
31	9159	KY #11	high	C2	Union	1 x 3/16"	hvCb/subA
32	9335	KY #9	high	P2	Hopkins	1-1/4 x 28m	hvBb
33	9342	KY #11	high	P3	Union	3 x 1/2"	hvAb
34	9344	KY #11	high	P3	Union	- 1/2	hvAb
35	9418	KY #11/#12	high	C3	Hopkins	6 x 5/8"	hvCb
36	9419	KY #11/#12	high	C3	Hopkins	+ 6	hvCb
37	9556	IL #6	----	Y	Williamson	3 x 1/2"	hvBb
38	7701	Amos	channel	----	Butler	----	hvBb
39	7704	Amos	channel	----	Butler	----	hvBb
40	7707	Amos	channel	----	Butler	----	hvBb
41	7708	Amos	channel	----	Butler	----	hvBb

analyses themselves and the pre-analysis handling of the coal samples.

Three areas of importance to the validity of Gieseler data are noted below:

(1) Plasticity is extremely sensitive to prior oxidation or 'weathering' of the coal. Samples received from the field are split immediately, and the 'plasticity split' is reduced to -40 mesh and placed under argon in a storage freezer until ready to analyze.

(2) The torque clutch setting is specified to be 40 "g.-in." (100.6 g.-cm.). The actual torque is measured with a torque gauge on a daily basis, more frequently when there is any indication of drift.

(3) The packing (tamping) of the coal sample has proven in our experience to be a critical step. The standard tamping assembly is used exactly as specified in ASTM Procedure D-2639, with 12 tamping strokes of the 10-kg weight.

The careful observance of these and other details of the procedure, and the emphasis upon uniformity of treatment (even extending to the sandblast crucible cleaning procedure between runs) has resulted in plastometry data of reasonably good reproducibility.

5.2.1 ASTM Gieseler Plastometry

In the ASTM procedure (38) the crucible assembly is lowered into the solder-pot furnace preset at 300°C, is maintained at that temperature for 10 min., and the furnace is then warmed at a constant rate of 3.0°C/min. The parameters which are directly measured are as follows:

Softening Temperature, at which an initial fluidity of 1.0 ddpm is attained. This corresponds to a nominal viscosity of approximately 10 megapoise.

Maximum Fluid Temperature, at which the highest fluidity reading is attained.

Solidification Temperature, at which the fluidity drops to a value of 1.0 ddpm. This is a slight departure from the ASTM procedure (38), which defines solidification temperature as that point "at which the dial movement stops". With a good instrument it is easier and in our judgment more accurate to identify the temperature at which a specified fluidity is attained.

Maximum Observed Fluidity, the highest observed fluidity reading. The Gieseler plastometer cannot measure fluidity greater than 30,000 ddpm (see below).

The ASTM recommends that the plastometry runs be carried out in duplicate, and indicates an expected repeatability of 5°C for each temperature point and 10% (up to a 20% spread) in values of maximum fluidity.

In this study we have carried out all ASTM Gieseler plastometry runs in quadruplicate. Temperatures are averaged arithmetically. Maximum fluidities are averaged as their natural logarithms (i.e., averaged geometrically). The expression of fluidity as its logarithm was first shown to be a useful representation by Fitzgerald (39,40) and since then has been used by most others in the field.

Quadruplicate averages are tested for outliers as follows. The most remote of the four values is removed, and the average and standard deviation calculated for the 'close three' data. If the fourth datum falls more than three standard deviations from the average of the 'close three' it is rejected and the reported average value is the average of the best three. This corresponds approximately to a 95% probability of valid rejection.

The results of the ASTM Gieseler plastometric analysis of the 40 coals are given in Table 2. The critical temperatures of these coals fall in relatively narrow ranges: for the softening temperature $374-402^{\circ}\text{C}$, for maximum fluidity $418-438^{\circ}\text{C}$, and for the solidification temperature $437-471^{\circ}\text{C}$. Maximum observed fluidities, however, range from less than 10 ddpm to greater than 30,000 ddpm, a range of several orders of magnitude.

The Gieseler plastometer cannot read fluidities of extremely fluid coals. The constant-speed motor drives at 300 rpm and the instrument is calibrated to 100 ddpm per stirring shaft rotation, so a very fluid coal mass -- one with an effective viscosity of about 3 kilopoise or less -- will 'peg' the instrument at 30,000 ddpm. Seven coals in this group have maximum fluidities greater than 30,000 ddpm.

The average standard deviations of determinations of softening temperature, maximum fluidity temperature, and solidification temperature are 1.7°C , 1.7°C , and 1.2°C . The average s.d. of $\ln(\text{maximum fluidity})$, after excluding the seven coals which 'pegged' at 30,000 ddpm, is 0.1315, or 14% of the average fluidity (DDPM).

A typical ASTM Gieseler run is shown in Figure 3, with $\ln(\text{fluidity})$ plotted against run time in minutes. The use of the slopes in this figure is discussed in Part 6.1.

5.2.2 Isothermal Gieseler Plastometry

The standard $3^{\circ}\text{C}/\text{min}$. ASTM Gieseler analysis provides a fixed-angle slice across the fluidity-temperature surface. There are several advantages, however, in conducting Gieseler analyses under isothermal conditions. The melting and coking regions of the isothermal curves are even more strikingly linear. The linearity of the isothermal coking slope was noted some time ago by Fitzgerald (39,40). We have confirmed this

Table 2

ASTM Gieseler Plasticity Data*

coal	T(softening)	T(max fluidity)	T(solidificn)	ln(max fluidity)	Max fluidity
01	386.0 ± 2.6	418.3 ± 2.6	437.4 ± 2.1	2.565 ± .454	13.0
02	384.6 0.4	422.7 0.6	437.8 0.4	2.259 .033	9.6
03	390.4 3.7	432.0 0.0	450.3 1.4	3.343 .046	28.3
04	382.8 0.6	428.3 1.0	451.5 0.5	6.300 .099	544.
05	390.9 1.8	430.8 1.5	452.8 0.6	4.456 .023	86.1
06	381.7 1.0	421.0 1.0	457.3 0.6	9.888 .254	19,690
07	383.0 0.1	425.5 2.9	453.2 0.7	6.653 .029	775.
08	387.0 4.2	427.5 4.4	448.1 1.2	3.927 .135	50.7
09	389.3 2.8	426.3 0.6	446.9 0.2	3.744 .101	42.3
10	389.8 2.2	426.3 0.6	450.0 1.2	4.502 .070	90.2
11	390.8 0.6	424.5 2.3	448.5 0.2	4.594 .044	98.9
12	387.8 0.6	423.0 0.0	450.5 0.3	5.431 .011	228.
13	376.4 0.3	422.3 0.6	451.8 0.6	6.292 .185	540.
14	385.7 3.9	425.0 4.7	452.7 3.8	5.214 .036	184.
15	378.9 0.9	424.0 0.0	449.9 1.1	5.992 .116	400.
16	384.1 4.1	423.5 1.3	445.7 1.8	4.164 .122	64.3
17	392.8 3.8	430.0 5.4	448.7 3.1	3.812 .320	45.3
18	388.3 2.5	428.0 0.8	446.5 0.4	3.287 .106	26.8
19	383.3 1.2	428.0 1.0	450.4 2.6	4.756 .046	116.
20	383.2 1.6	423.3 1.5	448.8 0.2	4.513 .117	91.2
21	374.8 0.3	(419-428°)	463.4 0.6	10.315 .019	>30,000.
22	375.7 0.5	(422-435°)	467.0 0.4	10.318 .015	>30,000.
23	383.5 1.5	(422-434°)	467.1 1.7	10.326 .006	>30,000.
24	384.8 1.7	423.7 0.6	444.6 1.0	3.551 .056	34.9
25	391.2 0.4	428.3 2.8	471.4 1.4	10.323 .010	>30,000.
26	402.1 1.5	437.7 0.6	461.4 0.6	4.768 .047	118.
27	378.8 1.5	422.6 4.2	464.1 1.2	10.113 .185	25,150.
28	396.6 0.8	437.3 1.0	451.2 1.9	2.924 .332	18.6

continued

Table 2, continued

<u>coal</u>	<u>T(softening)</u>		<u>T(max fluidity)</u>		<u>T(solidificn)</u>		<u>ln(max fluidity)</u>		<u>Max fluidity</u>
30	389.2	2.7	426.3	1.5	442.9	1.1	2.786	.052	16.2
31	387.0	1.4	424.3	0.6	445.3	0.8	2.889	.003	18.0
32	376.7	2.7	418.0	3.4	461.3	1.4	10.298	.018	>30,000.
33	377.3	2.1	(415-431 ⁰)		464.8	2.3	10.3	---	>30,000.
34	380.6	1.2	419.8	3.2	465.4	0.3	10.3	---	>30,000.
35	375.0	0.8	421.6	0.5	457.6	2.0	9.262	.022	10,530.
36	385.1	0.1	427.0	3.6	456.0	1.0	5.220	.174	185.
37	382.0	3.0	431.0	0.0	457.3	0.3	6.046	.089	423.
38	396.0	0.5	433.5	2.4	458.6	1.5	5.230	.064	187.
39	395.5	2.2	433.0	0.0	456.9	1.2	5.414	.052	224.
40	401.0	3.0	435.8	1.5	454.0	3.0	3.096	.517	22.1
41	397.7	0.9	436.0	1.6	459.0	1.2	5.379	.137	217.

* Data are averages of quadruplicate runs by constant-torque Gieseler plastometer, using ASTM Standard D2639.

Figure 3

A Typical ASTM Gieseler Plastometry Run with a Fluid Coal

linearity in our laboratories, and have found that for most mid-ranked Americal coals the isothermal melting curve is also substantially linear (41-43).

Figure 4 illustrates a typical isothermal run. The experimental curve provides the standard information which is sought with a plastometer -- softening point, time to maximum fluidity, solidification point, maximum observed fluidity, and a measure of the fluidity span (the time interval during which the coal mass is in a measurably fluid state). In addition this run provides well-defined melting and coking slopes, and an additional measure, intersection maximum fluidity (obtained by extrapolation of the two slopes to their point of intersection). Finally, this same experiment with this same coal can be repeated at various other temperatures, and in this way one can determine the temperature dependencies of any or all of these parameters of fluidity.

Fitzgerald studied the coking slopes of several English coals, and found them to exhibit a systematic Arrhenius dependency:

$$m = a * \exp(-E_a/RT) \quad (1)$$

where R is the gas constant, T is temperature in $^{\circ}\text{K}$, a is a pre-exponential constant and E_a is the activation energy associated with the slope.

We have conducted a detailed examination of 29 of the 40 coals described above, making between 20 and 25 isothermal Gieseler plastometry runs with each coal. Table 3 summarizes the data obtained for one of these coals. Both melting and coking slopes, and both $\ln(\text{maximum observed fluidity})$ and $\ln(\text{maximum intersection fluidity})$, follow the Arrhenius dependency, as is illustrated for Coal #41 in Figure 5. This is generally true of all of these coals, and consequently is of considerable interest, both theoretically and practically:

Figure 4

A Typical Isothermal Gieseler Plastometry Run

Table 3

Summary of Isothermal Gieseler Plastometry Runs - Coal #41*

run	minimum ddpm	temp & s.d.	melt slope & sd	coke slope & sd	max fluidity observed	max fluidity intersection	notes
01	10.	435.4 $\pm$ 1.3	1.273 $\pm$.145	0.930 $\pm$.016	1,044	2,014	good curve
02	5.	436.6 1.4	1.279 .124	1.015 .009	899.3	1,742	" "
03	5.	437.8 1.1	1.328 .039	1.069 .011	1,412	2,290	" "
04	10.	438.1 1.5	1.293 .048	1.065 .017	1,728	2,409	" "
05	10.	429.9 2.5	1.034 .039	0.845 .020	648.0	1,274	" "
06	10.	430.8 1.4	1.017 .004	0.728 .026	618.0	1,222	" "
07	10.	431.5 1.2	1.069 .067	0.809 .010	1,136	1,552	" "
08	10.	431.0 1.4	1.011 .081	0.690 .038	833.0	1,393	" "
09	10.	430.7 1.9	0.933 .097	0.842 .036	808.6	1,311	" "
09r	5.	"" ""	0.914 .045	0.834 .024	""	1,258	better fit
10	5.	424.0 1.3	0.781 .109	0.570 .053	315.5	504.8	good curve
11	5.	423.5 1.5	0.788 .092	0.674 .054	413.1	849.6	" "
12	5.	423.3 0.9	0.841 .039	0.523 .013	230.8	470.0	" "
13	5.	424.2 0.8	0.754 .050	0.452 .007	237.8	380.1	" "
14	5.	424.3 1.9	0.594 .093	0.428 .022	247.5	376.0	fair curve
14r	2.5	"" ""	0.621 .056	0.443 .018	""	414.1	better fit
15	1.	416.8 1.1	0.486 .023	0.347 .006	108.8	164.8	good curve
16	1.	416.7 0.9	0.531 .017	0.338 .004	106.1	159.0	" "
17	1.	417.0 1.4	0.604 .019	0.395 .008	158.2	250.4	" "
18	1.	416.7 1.8	0.487 .028	0.354 .013	88.2	191.0	" "
19	1.	415.9 1.9	0.437 .017	0.309 .009	74.2	137.8	" "
20	1.	413.2 1.1	0.306 .032	0.278 .010	50.6	86.5	" "
21	1.	412.5 1.7	0.399 .035	0.312 .012	74.9	134.5	" "
22	1.	412.5 1.0	0.452 .030	0.250 .017	81.1	103.6	" "
23	1.	411.9 1.9	0.526 .028	0.324 .008	76.3	143.6	" "

* All runs are plotted; minimum ddpm is set to exclude 'tailing' in early melting curves (Figure 16).

Figure 5

Arrhenius Dependencies of Isothermal Fluidity. A: $\ln$ (maximum intersection fluidity). B: melting slope. C: coking slope.

* It provides an estimate of the activation energies associated with the melting and coking processes, and an indication of how these activation energies vary among different coals.

* It permits interpolation or (within prudent limits) extrapolation to another temperature of particular process interest.

For each coal studied, a battery of isothermal Gieseler runs was conducted, over a temperature range (typically 20-30 deg. C) providing a convenient range of fluidities. The best Arrhenius slopes were calculated, typically using 90% (in no case less than 80%) of the raw data, and from these were calculated the melting and coking slopes at the arbitrarily selected temperatures 380, 400, and 420°C. Table 4 presents the melting and coking slope data (in units of reciprocal minutes) and the activation energy associated with each slope (in units of kcal/mole).

From the same runs the temperature dependencies were determined for $\ln(\text{maximum observed fluidity})$ and for $\ln(\text{maximum intersection fluidity})$, and the same temperature interpolations/extrapolations made, to provide estimates of maximum fluidity at 380, 400, and 420°C. Table 5 presents these data, and the associated 'activation energies of fluidity'.

The average of the standard deviations of activation energy of slope is 2.9 kcal (melting) and 2.6 kcal (coking). The average of the standard deviations of activation energy of $\ln(\text{maximum fluidity})$ is 1.8 kcal (observed fluidity) and 2.1 kcal (intersection fluidity).

The significance and uses of slope and intersection fluidity data are discussed in Part 6.

Table 4

Isothermal Melting and Coking Slopes of some Bituminous Coals*

coal	runs	T range	Melting Slope					Coking Slope				
			<u>E(a), kcal</u>	<u>s.d.</u>	<u>@ 380</u>	<u>@ 400</u>	<u>@ 420</u>	<u>E(a), kcal</u>	<u>s.d.</u>	<u>@ 380</u>	<u>@ 400</u>	<u>@ 420</u>
02	16	406-423	25.4	± 4.8	0.176	0.316	0.546	56.1	± 4.7	0.0611	0.221	0.739
03	18	408-433	41.0	3.8	0.0920	0.235	0.569	57.1	3.7	0.0368	0.136	0.467
04	16	406-431	55.9	2.7	0.0702	0.252	0.842	55.2	1.3	0.0475	0.168	0.554
06	17	393-418	52.5	2.0	0.156	0.518	1.606	52.3	1.6	0.0620	0.205	0.634
07	17	404-426	36.5	3.9	0.219	0.505	1.109	52.9	2.6	0.0614	0.206	0.645
09	20	403-427	30.7	2.7	0.1741	0.352	0.683	54.6	3.7	0.0592	0.207	0.671
10	18	405-429	30.1	2.1	0.222	0.442	0.846	56.4	2.1	0.0588	0.214	0.723
11	17	412-432	23.8	2.4	0.286	0.493	0.824	56.9	3.5	0.0486	0.179	0.611
14	20	398-422	33.8	1.7	0.215	0.466	0.966	46.5	1.9	0.0942	0.273	0.745
15	18	400-427	40.8	3.1	0.137	0.350	0.844	43.5	1.9	0.102	0.276	0.706
18	20	398-424	31.0	2.5	0.195	0.396	0.773	48.5	3.2	0.0889	0.270	0.767
20	22	401-428	28.1	2.4	0.221	0.420	0.769	44.1	2.2	0.0993	0.272	0.704
21	22	387-410	48.1	2.9	0.340	1.023	2.885	50.1	2.5	0.0567	0.179	0.526
22	20	389-413	56.5	1.8	0.193	0.702	2.375	48.7	2.0	0.0429	0.131	0.374
24	20	405-431	18.8	2.2	0.282	0.435	0.653	41.9	3.8	0.109	0.284	0.701
25	16	404-420	41.2	5.0	0.246	0.631	1.535	44.6	2.0	0.0379	0.105	0.276

-- continued --

Table 4, continued

coal	runs	T range	Melting Slope					Coking Slope				
			<u>E(a), kcal</u>	<u>s.d.</u>	<u>@ 380</u>	<u>@ 400</u>	<u>@ 420</u>	<u>E(a), kcal</u>	<u>s.d.</u>	<u>@ 380</u>	<u>@ 400</u>	<u>@ 420</u>
26	17	412-436	39.7	± 3.8	0.113	0.280	0.661	47.8	± 1.6	0.0363	0.109	0.304
27	18	379-404	65.1	2.5	0.197	0.875	3.564	43.5	1.6	0.0565	0.153	0.391
28	19	413-437	29.4	4.3	0.201	0.394	0.743	73.8	4.5	0.0123	0.0670	0.329
30	18	399-426	32.2	4.0	0.191	0.400	0.803	44.4	4.6	0.0965	0.267	0.694
32	21	389-411	48.4	2.9	0.392	1.187	3.373	41.5	1.7	0.0797	0.206	0.506
34	20	390-409	52.5	3.1	0.371	1.232	3.823	42.7	2.7	0.0653	0.1736	0.436
35	17	400-419	39.9	2.7	0.263	0.656	1.551	43.2	2.4	0.0912	0.245	0.624
36	16	404-425	43.8	2.6	0.140	0.382	0.982	46.5	2.7	0.0829	0.240	0.656
37	22	406-432	38.4	2.9	0.179	0.431	0.986	48.0	2.5	0.0648	0.195	0.549
38	16	411-436	54.7	1.7	0.0443	0.155	0.505	54.5	1.5	0.0341	0.119	0.385
39	19	410-435	42.5	2.9	0.101	0.267	0.667	47.1	2.0	0.0565	0.167	0.460
40	20	417-443	18.4	2.6	0.278	0.424	0.631	44.1	2.4	0.0587	0.161	0.418
41	18	412-438	43.8	1.8	0.0880	0.240	0.616	51.4	2.0	0.0435	0.141	0.429

* Slopes are $d(\ln \text{fluidity})/dt$ in units of min.^{-1}

Table 5

Maximum Isothermal Fluidities of some Bituminous Coals

coal	runs	T range	ln(maximum observed fluidity, ddpm)					ln(maximum calculated fluidity, ddpm)				
			<u>E(a), kcal</u>	<u>s.d.</u>	<u>@ 380</u>	<u>@ 400</u>	<u>@ 420</u>	<u>E(a), kcal</u>	<u>s.d.</u>	<u>@ 380</u>	<u>@ 400</u>	<u>@ 420</u>
02	16	406-423	35.2	± 3.7	0.380	0.852	1.822	40.8	± 5.1	0.408	1.038	2.504
03	18	408-433	41.3	3.4	0.273	0.704	1.715	41.0	6.7	0.445	1.138	2.758
04	16	406-431	33.2*	1.8	1.327	2.837	5.803	25.5	1.1	2.041	3.656	6.334
06	17	393-418	28.4	1.3	2.956	5.668	10.470	23.3	1.1	3.587	6.109	10.089
07	17	404-426	23.6	1.3	2.581	4.428	7.363	18.6	1.5	3.361	5.147	7.692
09	20	403-427	51.1	3.6	0.252	0.813	2.447	44.4	4.3	0.484	1.336	3.483
10	18	405-429	38.5	2.3	0.651	1.572	3.608	30.7	3.2	1.178	2.382	4.623
11	17	412-432	30.8	2.5	0.631	1.277	2.478	31.2	2.5	0.856	1.748	3.424
14	20	398-422	27.5	1.3	1.613	3.027	5.478	20.5	1.1	2.424	3.877	6.035
15	18	400-427	21.9	1.1	2.100	3.467	5.561	22.4	1.2	2.264	3.781	6.132
18	20	398-424	47.1	2.4	0.428	1.258	3.474	35.9	2.5	0.907	2.062	4.472
20	22	401-428	41.9	1.3	0.616	1.607	3.965	27.7	1.6	1.415	2.669	4.854
21	22	387-410	22.6	1.4	4.836	8.107	13.191	16.8	1.7	5.912	8.679	12.462
22	20	389-413	22.0	1.1	4.052	6.707	10.784	20.0	1.5	4.958	7.840	12.074
24	20	405-431	36.9	2.8	0.394	0.916	2.030	23.7	3.4	1.024	1.762	2.939
25	16	404-420	1.9	0.7	9.520	9.934	10.340	-0.2	1.3	11.096	11.040	10.988

-- continued --

Table 5, continued

coal	runs	T range	ln(maximum observed fluidity, ddpm)						ln(maximum calculated fluidity, ddpm)					
			<u>E(a), kcal</u>	<u>s.d.</u>	<u>@ 380</u>	<u>@ 400</u>	<u>@ 420</u>		<u>E(a), kcal</u>	<u>s.d.</u>	<u>@ 380</u>	<u>@ 400</u>	<u>@ 420</u>	
26	17	412-436	27.9	± 2.2	1.178	2.229	4.066		21.0	± 1.3	1.924	3.110	4.890	
27	19	379-404	28.7	1.3	4.371	8.428	15.647		19.5	1.1	5.643	8.810	13.404	
28	19	413-437	32.8	2.0	0.160	0.339	0.687		27.2	3.0	0.314	0.585	1.053	
30	18	399-426	53.0	3.9	0.287	0.967	3.033		32.3	4.1	1.014	2.123	4.257	
32	21	389-411	18.0	1.1	5.564	8.403	12.394		12.6	1.2	6.918	9.230	12.111	
34	20	390-409	7.3	1.2	8.240	9.738	11.398		12.4	1.7	7.602	10.096	13.189	
35	17	400-419	20.9	1.3	3.531	5.865	9.214		17.4	1.3	4.356	6.493	9.459	
36	16	404-425	23.9	1.0	1.993	3.456	5.789		21.2	1.1	2.526	4.107	6.491	
37	22	406-432	23.8	1.4	1.975	3.404	5.615		19.3	1.1	2.717	4.229	6.415	
38	16	411-436	25.2	0.7	1.485	2.702	4.750		25.0	1.1	1.730	3.066	5.257	
39	19	410-435	24.3	1.8	1.739	3.029	5.110		22.6	1.4	2.041	3.426	5.581	
40	20	417-443	35.1	2.1	0.476	1.088	2.372		16.3	1.5	1.993	2.892	4.107	
41	20	412-438	21.6	1.0	1.952	3.199	5.096		19.7	0.8	2.347	3.681	5.625	

5.2.3 Plastometry at Elevated Pressures

Six freshly sampled coals from active western Kentucky mines have been examined using a special pressurized Gieseler plastometer, built by Standard Instrumentation with the crucible, shaft and torque clutch placed inside a steel bomb. Experiments were carried out at selected isothermal conditions, using helium as the pressurant.

These coals (designated as #42 through #47) are hvAb and hvBb in rank, and are characterized in Table 10. Their ASTM Gieseler maximum fluidities range from 8.5 ddpm (Coal #43) to 352 ddpm (Coal #46).

For each coal a series of runs has been made, starting with atmospheric pressure isothermal runs and proceeding to 400 psig (415 psia). Table 6 presents a summary of the Gieseler runs for the series with Coal #44. The column headings 'min' and 'max' refer to the minimum fluidity (in ddpm) and the fraction of the maximum observed fluidity used for melting slope and coking slope calculations. The analytical program used for these data (Part 9.4) makes a final plot of experimental data and calculated slopes. Occasionally the limits are changed and a Gieseler run recalculated, as in run 21 of Table 6.

The general expectations which we bring to this pressure study are indicated schematically in Figure 6a.

If the fluid component(s) of the plastic coal mass are substantially nonvolatile liquids or nonvolatile liquid envelopes containing encapsulated solids, then to a first approximation pressure in this moderate range below 3 MPa (450 psia) will be expected to have no effect (Case A in Figure 6a).

If the fluid components are substantially liquids and include a significant fraction of liquids volatile at 400-440°C, then increasing pressure will at first lead to significant increases in maximum fluidity

Table 6

Gieseler Plastometer Runs at Elevated Pressures - Coal #44

<u>run</u>	<u>temp & s.d.</u>	<u>pressure</u>	<u>min</u>	<u>max</u>	<u>melt slope & sd</u>	<u>coke slope & sd</u>	<u>max obs flu</u>	<u>max calc flu</u>	<u>notes</u>
01	420.8 + 0.4	atm	1	.5	0.8960 + .0295	0.3435 + .0060	628.0	1236	ok
02	420.0 0.0	atm	1	.5	0.9607 .0437	0.4134 .0050	416.0	1070	good
03	419.9 0.3	atm	1	.5	0.9441 .0162	0.3557 .0060	738.5	1485	good
04	420.9 0.3	25	1	.5	1.0083 .1186	0.3583 .0030	531.5	1239	good
05	420.9 0.4	25	1	.5	1.0929 .0303	0.3648 .0028	1030	2301	good
06	420.0 0.0	25	1	.5	1.1465 .0513	0.3923 .0059	679.9	1908	good
07	419.1 0.3	50	1	.5	1.1800 .0290	0.3373 .0027	977.3	3999	good
08	421.0 0.0	50	1	.5	1.2640 .0804	0.3705 .0046	2572	5727	good
09	420.0 0.0	50	1	.5	1.3391 .0535	0.3928 .0079	1197	5228	good
10	418.9 0.4	75	1	.5	1.2770 .0480	0.3574 .0043	1548	5091	good
11	420.9 0.3	75	1	.5	1.3768 .0535	0.4244 .0139	18,109	13,171	v good
12	419.9 0.3	75	1	.5	1.3527 .0702	0.4278 .0060	1,992	6,971	v good
13	418.7 0.5	100	1	.5	1.4367 .0763	0.3895 .0031	3,499	12,786	v good
14	418.7 0.5	100	1	.5	1.3499 .1153	0.3359 .0046	4,390	10,151	f good
15	419.1 0.6	100	1	.5	1.4547 .0741	0.4044 .0037	4,781	14,112	f good
16	418.5 0.6	100	1	.5	1.4271 .0559	0.3346 .0049	16,249	10,611	f good
17	419.6 0.5	125	1	.5	1.6327 .1590	0.3971 .0023	12,706	20,179	v good
18	419.9 0.4	125	1	.5	1.4063 .0200	0.4218 .0161	28,627	46,531	rough
19	419.5 0.5	125	1	.5	1.5905 .0585	0.3809 .0027	11,095	17,105	good
20	419.3 0.7	150	1	.5	1.4510 .0462	0.3100 .0049	20,132	14,397	good
21	419.9 0.4	150	1	.5	1.3264 .1565	0.3947 .0056	5.647	12,743	f good
21r			1	.25	1.3264 .1565	0.3973 .0067		13,218	no improvement
22	419.9 0.3	150	1	.25	1.2512 .1547	0.3922 .0048	6,124	13,230	fair to good
23	419.5 0.6	175	1	.25	1.4466 .0702	0.3474 .0030	11,344	20,741	good
24	419.6 0.5	175	1	.25	1.4627 .0866	0.3539 .0038	8,589	13,810	ok

c o n t i n u e d

Table 6 (Cont.)

run	temp & s.d.	pressure	min	max	melt slope & sd	coke slope & sd	max obs flu	max calc flu	notes
25	419.8 $\pm$ 0.4	175	5	.5	1.7843 $\pm$.0485	0.4087 $\pm$.0048	6,450	24,770	v good
26	419.3 $\pm$ 0.7	200	5	.5	1.5906 $\pm$.0599	0.3974 $\pm$.0273	6,466	46,381	ok
27	418.9 $\pm$ 0.5	200	5	.5	1.7180 $\pm$.0377	0.3594 $\pm$.0045	5,388	22,508	good
23	420.0 $\pm$ 0.0	200	5	.5	1.8688 $\pm$.1299	0.3929 $\pm$.0048	5,445	19,868	good
29	419.6 $\pm$ 0.6	225	5	.25	1.6327 $\pm$.1622	0.4475 $\pm$.0099	6,693	25,875	f good
29r			5	.5	1.8305 $\pm$.1352	0.4383 $\pm$.0083		27,133	about same
30	418.6 $\pm$ 0.5	225	5	.5	1.8039 $\pm$.2210	0.4001 $\pm$.0030	7,173	28,864	v good
31	419.1 $\pm$ 0.7	225	5	.5	1.7478 $\pm$.1154	0.3713 $\pm$.0030	6,090	28,087	good
32	418.7 $\pm$ 0.5	250	5	.5	1.9485 $\pm$.0707	0.4146 $\pm$.0386	14,005	59,593	v good
33	418.9 $\pm$ 0.3	250	5	.5	2.1989 $\pm$.1495	0.4518 $\pm$.0087	9,295	44,878	good
34	418.5 $\pm$ 0.5	250	5	.5	1.5691 $\pm$.0468	0.2945 $\pm$.0046	8,739	15,530	good
35	418.4 $\pm$ 0.5	275	5	.5	2.1111 $\pm$.2936	0.4350 $\pm$.0036	11,559	41,890	f good
36	418.4 $\pm$ 0.6	275	5	.25	1.8969 $\pm$.1545	0.4737 $\pm$.0083	28,616	72,426	f good
37	419.9 $\pm$ 0.4	275	5	.5	1.9188 $\pm$.0929	0.4919 $\pm$.0061	11,415	43,408	good
38	418.9 $\pm$ 0.7	275	5	.5	1.9371 $\pm$.0912	0.3641 $\pm$.0022	6,867	28,482	v good
39	419.1 $\pm$ 0.8	300	5	.5	1.4349 $\pm$.1721	0.3107 $\pm$.0042	27,153	25,103	good
40	419.3 $\pm$ 0.6	300	5	.5	2.2243 $\pm$.1785	0.4968 $\pm$.0050	13,396	81,353	good
41	418.7 $\pm$ 0.8	300	5	.5	1.8062 $\pm$.0723	0.4006 $\pm$.0031	27,962	36,249	v good
42	418.5 $\pm$ 0.5	300	5	.5	2.1227 $\pm$.1396	0.4836 $\pm$.0043	18,387	81,738	v good
43	419.6 $\pm$ 0.7	325	5	.5	1.8138 $\pm$.1108	0.5237 $\pm$.0117	26,751	106,345	good
44	419.1 $\pm$ 0.7	325	5	.5	2.3773 $\pm$.4788	0.4831 $\pm$.0062	17,437	116,930	f good
45	418.2 $\pm$ 0.7	325	5	.5	1.9004 $\pm$.2486	0.4234 $\pm$.0084	27,478	69,714	ok
46	418.3 $\pm$ 0.6	325	5	.5	2.0009 $\pm$.3022	0.5155 $\pm$.0077	18,309	78,854	v good
47	418.1 $\pm$ 0.7	350	5	.5	2.0485 $\pm$.1185	0.4542 $\pm$.0080	19,706	86,404	good
48	420.5 $\pm$ 0.5	350	5	.5	1.9817 $\pm$.1634	0.3347 $\pm$.0098	29,165	38,864	fair
49	420.0 $\pm$ 0.0	350	5	.5	2.1070 $\pm$.1820	0.4463 $\pm$.0029	15,626	62,193	good
50	417.9 $\pm$ 0.9	375	5	.5	2.1818 $\pm$.1767	0.4478 $\pm$.0082	20,017	79,158	f good
51	419.1 $\pm$ 0.8	375	5	.5	2.0909 $\pm$.1675	0.4158 $\pm$.0065	30,276	69,537	good

c o n t i n u e d

Table 6 (Cont.)

<u>run</u>	<u>temp & s.d.</u>		<u>pressure</u>	<u>min</u>	<u>max</u>	<u>melt slope & sd</u>		<u>coke slope & sd</u>		<u>max obs flu</u>	<u>max calc flu</u>	<u>notes</u>
52	418.8	1.0	375	5	.5	1.7421	.1621	0.3861	.0050	11,832	57,811	v good
53	420.0	0.0	400	5	.25	2.1190	.2437	0.4488	.0396	28,256	220,451	poor coke slope
53r	""	""	""	5	.25	2.1190	.2437	0.3960	.0073	""	82,538	f good
54	417.5	0.6	400	5	.25	1.7623	.1080	0.4078	.0251	16,986	70,495	bad run
54r	""	""	""	5	.25	1.7623	.1080	0.4078	.0024	""	63,883	good
55	418.3	0.6	400	5	.25	2.0075	.1229	0.3994	.0044	14,438	69,121	v good

Figure 6

The Effect of Pressure upon Maximum Fluidity. (a) (top) Theoretical. (b) (middle) Coal #42. (c) (bottom) Coal #46.

owing to retardation of the volatilization of the fluid fraction, but at successively higher pressures the effect will diminish and the system will become rather insensitive to further increases of pressure (Case B in Figure 6a).

If the fluid components include a significant amount of materials which are gases at 400-440°C, then we expect the same initial increase in fluidity as in Case B, but as pressure increases this will be counteracted by a reduction of the total fluid phase by PV compression of the entrained gases, and the fluidity will pass through a maximum and thereafter decrease with increasing pressure (Case C in Figure 6a).

From what we think we know about actual coals, we may expect to see mixtures of these three limiting cases.

Among these six coals one (Coal #42) appears to be clearly different from the others. Figure 6b shows the effect of helium pressure upon the value of $\ln(\text{intersection maximum fluidity})$. The maximum fluidity is essentially unresponsive to pressure (Case A).

Another coal (Coal #46) affords a well-defined curve (Figure 6c) which appears to have a very flat maximum region at 250-300 psia and a slight decrease in fluidity with further increases of pressure. This suggests a somewhat gassy coal (a blend of Cases B and C).

The remaining four coals afford curves very much like Case B. These are illustrated by the plot of $\ln(\text{intersection maximum fluidity})$ vs. pressure for Coal #44 (Figure 7c). The first 125 psi of superatmospheric pressure brings about a marked increase in maximum fluidity, from 1200 ddpm to more than 20,000 ddpm. The magnitude of $d(\ln \text{ fluidity})/dP$ decreases with further increases in pressure, however, and the final fluidity at 415 psia is only about treble that at 140 psia. The other three coals (#43,

Figure 7

The Effect of Pressure upon Fluid Behavior of Coal #44. (a) (top) Melting-slope. (b) (middle) Coking slope. (c) (bottom) Intersection maximum fluidity.

#45 and #47) show fluidity-pressure curves very similar to that of Coal #44. These are all essentially Case B coals.

Table 7 provides summary data on the melting and coking slopes and $\ln(\text{maximum fluidity})$ values for all six coals. Except for Coal #42, the melting slopes show significant increases with increasing pressure, with the extent of increase for the first 100-150 psi noticeably greater than that found from the last 100-200 psi applied. A typical dependency pattern, for Coal #44, is shown in Figure 7a.

The effect of helium pressure upon coking slope is much less than upon melting slope, and indeed is scarcely perceptible by examination (Figure 7b). For Coals #44 and #45 the calculated changes in coking slopes with pressure are of the order of magnitude of their standard deviations. For coals #43 and #47 the calculated $d(\text{coke slope})/dP$ is positive although small. Coal #42 shows a small negative value of $d(\text{coke slope})/dP$, and Coal #46 shows a probably significant negative value.

In summary, five of the six coals tested show substantial increases in maximum fluidity when examined under elevated pressure. The increases range from slightly more than an order of magnitude to as much as three orders of magnitude. The difference is greater when referring back to ASTM Gieseler maximum fluidities. For Coal #43, for example, the ASTM maximum fluidity averages 8.5 ddpm at 425°C; the isothermal maximum fluidity at 420°C averages 94 ddpm, and the maximum fluidity at the same temperature and under 415 psia averages 18,480 ddpm.

Table 7

Effects of Pressure upon Fluidity Characteristics*

coal	temp., °C	MF(observed) at 1 atm	<u>d(melt slope)/dP</u>		<u>d(coke slope)/dP</u>		<u>d(observed MF)/dP</u>		<u>d(intersection MF)/dP</u>	
# 42	391 + 1.2	823 ddpm								
	P 15-150 psia:		4.02E-4	(4)	-8.40E-5	(4)	5.04E-3	(4)	1.15E-2	(2)
	P 15-415 psia:		-1.02E-5	(4)	-6.98E-5	(1)	3.00E-3	(2)	2.24E-3	(2)
# 43	420 + 1.6	6.0 ddpm								
	P 15-150 psia:		4.11E-3	(2)	5.80E-4	(3)	2.04E-2	(1)	1.96E-2	(1)
	P 15-415 psia:		3.72E-3	(1)	6.82E-4	(1)	1.00E-2	(1)	1.11E-2	(1)
# 44	420 + 0.7	578 ddpm								
	P 15-150 psia:		4.45E-3	(1)	-7.05E-5	(4)	2.53E-2	(1)	2.05E-2	(1)
	P 15-415 psia:		2.69E-3	(1)	1.83E-4	(2)	8.02E-3	(1)	9.47E-3	(1)
# 45	424 + 0.9	248 ddpm								
	P 15-150 psia:		1.07E-2	(1)	4.57E-4	(4)	3.16E-2	(1)	3.19E-2	(1)
	P 15-415 psia:		6.05E-3	(1)	3.58E-4	(2)	7.51E-3	(1)	1.49E-2	(1)
# 46	418 + 0.8	680 ddpm								
	P 15-150 psia:		8.01E-3	(1)	1.04E-3	(2)	3.82E-2	(1)	3.46E-2	(1)
	P 15-415 psia:		1.66E-3	(2)	-3.48E-4	(2)	5.65E-3	(2)	7.67E-3	(1)
# 47	438 + 1.1	158 ddpm								
	P 15-150 psia:		7.84E-3	(1)	1.30E-4	(4)	3.35E-2	(1)	3.15E-2	(1)
	P 15-415 psia:		3.40E-3	(1)	6.86E-4	(1)	1.09E-2	(1)	1.25E-2	(1)

* Slope units are $\text{min}^{-1} \text{psia}^{-1}$; $\ln(\text{maximum fluidity})$ units are psia^{-1} . Numbers in parentheses indicate a significance of calculated slopes: (1) indicates definite significance; slope exceeds standard deviation by more than fourfold. (2) indicates probable significance; slope exceeds standard deviation by more than twofold. (3) indicates possible significance; slope is greater than its standard deviation but is less than two standard deviations. (4) indicates that the calculated slope is not significantly different from zero; slope is less than its standard deviation.

5.3 Coal Characterization

5.3.1 Physical, Chemical and Petrographic Data

Each of these coals after reduction has been characterized by proximate analysis (moisture content, ash content, volatile matter and fixed carbon, in accordance with ASTM Methods D3172-3175). Samples were also subjected to ultimate analysis (C, H and N by instrumental combustion analysis, and S by a dedicated commercial combustion sulfur analyzer). Both instrumental procedures have been thoroughly evaluated against the classical gravimetric methods, and have been shown to meet or exceed the accuracy and repeatability of ASTM methods D3177-3179. Sulfur trioxide in ash, a measure of mineral alkalinity, was also determined instrumentally.

Heating value (Btu) data were obtained by the adiabatic bomb method (ASTM D2015), using a recording Parr calorimeter. Free swelling index (FSI) values were obtained in accordance with ASTM D720, using an automated crucible heating device to improve repeatability. Analysis for forms of sulfur was conducted in accordance with ASTM D2492.

Tables 8 and 9 present the proximate and ultimate analyses, forms of sulfur, sulfate in ash, heating value and free swelling index, and the ASTM-defined rank. Since the objective of this study is the prediction of properties developing at 380-480°C, all measurements (except that of moisture) are reported on a dry ash-included basis.

Ash contents range from 2.8% to 17.8%, mean value 8.9%. Volatile matter is in the range 32.2 - 46.8%, mean 41.1%. The H/C atomic ratio (dry basis) is in the range 0.68 - 0.90, mean value 0.84. Total sulfur is in the range 0.80 - 4.10%, mean value 2.98%. Pyritic sulfur content is 0.2 - 2.2%, mean value 1.31%. Organic sulfur content is 0.6 - 3.0%, mean value 1.76%. The ash sulfate (% sulfate as SO_3 in ash) is 0.4 to 12.4%, mean

Table 8Proximate and Ultimate Analyses*

<u>Coal</u>	<u>Mois- ture</u>	<u>Ash</u>	<u>Volatile Matter</u>	<u>Fixed Carbon</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%S</u>	<u>%O**</u>
01	10.03	8.69	42.9	48.4	73.86	5.41	1.73	4.10	6.19
02	7.86	10.77	42.6	46.5	71.67	5.05	1.62	3.41	7.44
03	6.75	5.40	41.6	52.9	77.60	5.38	1.60	2.02	7.96
04	5.33	6.44	46.8	46.6	76.48	5.37	1.60	3.29	6.79
05	4.08	6.50	45.0	48.4	74.55	5.33	1.40	2.79	9.40
06	5.02	7.86	44.5	47.5	72.19	5.09	1.11	3.68	10.04
07	5.21	6.48	44.8	48.6	76.46	4.78	1.04	3.20	8.00
08	7.76	8.79	41.4	49.7	73.16	5.43	1.52	3.13	7.94
09	7.08	9.05	41.5	49.4	75.00	5.58	1.54	3.37	5.43
10	6.32	8.49	41.7	49.7	75.08	4.30	1.13	3.14	7.83
11	5.94	17.71	38.4	43.8	63.32	4.61	1.25	3.40	9.69
12	4.72	17.75	38.7	43.5	66.27	4.82	1.28	3.45	6.40
13	6.92	8.44	41.8	49.6	74.15	5.24	1.23	3.21	7.71
14	6.70	7.60	41.1	51.2	74.12	5.21	1.35	2.75	8.93
15	6.31	10.38	41.3	48.3	73.18	5.47	1.54	3.77	5.62
16	6.20	8.42	41.0	50.5	75.03	5.61	1.46	3.03	6.42
17	7.97	8.42	41.2	50.2	74.94	5.04	1.39	3.60	6.59
18	7.09	8.36	40.6	50.9	74.08	5.11	1.50	3.59	7.34
19	7.55	10.16	41.2	48.6	73.28	5.20	1.31	3.18	6.84
20	7.77	9.70	43.5	46.7	74.06	5.28	1.22	2.92	6.79
21	2.57	8.68	40.3	50.9	75.41	5.27	1.07	3.35	6.18
22	2.45	9.60	39.4	50.9	75.98	5.42	1.44	2.91	4.63

continued

Table 8, continued*

Coal	Mois- ture	Ash	Volatile Matter	Fixed Carbon	%C	%H	%N	%S	%O**
23	2.61	8.25	40.1	51.5	77.04	5.44	1.47	2.66	5.11
24	7.87	7.15	42.8	49.9	75.68	5.55	1.51	3.56	6.52
25	1.68	6.79	40.2	52.9	77.79	5.33	2.04	1.38	6.64
26	2.12	14.20	32.2	53.5	69.87	4.43	1.50	2.76	7.22
27	2.86	8.12	40.0	51.8	76.18	5.17	1.54	3.53	5.43
28	10.96	8.26	42.2	49.5	76.65	5.78	1.58	1.42	6.28
30	6.44	8.95	42.3	48.7	74.67	5.41	1.54	4.01	5.37
31	7.42	7.85	43.6	48.5	75.43	5.26	1.39	3.48	6.56
32	2.94	7.23	42.8	49.9	76.05	5.37	1.65	3.00	6.66
33	2.24	10.76	40.7	48.5	72.90	5.22	1.43	3.14	6.53
34	2.28	8.03	41.0	50.9	74.36	5.25	1.45	2.77	8.11
35	6.59	10.61	39.3	49.9	73.77	5.10	1.25	4.06	5.18
36	7.00	12.58	38.2	49.1	70.38	4.91	1.29	4.06	6.76
37	3.30	12.48	37.2	50.2	72.88	4.91	1.53	2.90	5.28
38	9.89	3.41	40.5	56.0	81.75	5.64	1.65	0.83	6.69
39	7.63	13.41	38.5	48.0	70.57	5.12	1.56	1.91	7.40
40	9.29	3.75	39.6	56.5	81.33	5.68	1.73	0.80	6.68
41	7.78	2.77	42.1	55.0	80.73	5.74	1.61	1.06	8.06

*Moisture as determined, other values on a dry ash-included basis.

*By difference.

Table 9Forms of Sulfur, Ash Sulfate, Heating Value, FSI and ASTM Rank*

Coal	Forms of Sulfur			% SO ₃ in ash	Heating Value Btu/lb	F S I	ASTM Rank
	Pyritic	Sulfate	Organic				
01	2.04	0.06	1.98	5.58	12,948	2 1/2	hvCb
02	1.43	0.02	1.96	5.96	12,622	4 1/2	hvBb
03	0.98	0.01	1.02	0.42	13,715	4	hvBb
04	2.22	0.13	0.92	0.74	13,647	3 1/2	hvBb
05	1.70	0.25	0.83	0.77	13,479	3 1/2	hvBb
06	1.38	0.02	2.27	0.37	13,297	6	hvBb
07	1.08	0.03	2.08	0.72	13,587	3 1/2	hvBb
08	1.16	0.05	1.91	4.30	13,096	5	hvBb
09	1.25	0.12	1.99	2.89	13,054	4 1/2	hvBb
10	1.18	0.10	1.85	2.83	13,332	4	hvBb
11	1.61	0.14	1.63	1.14	11,769	2 1/2	hvBb
12	1.78	0.09	1.57	0.72	11,754	2 1/2	hvBb
13	1.34	0.04	1.82	3.97	13,332	4 1/2	hvBb
14	0.93	0.05	1.76	9.02	13,408	4	hvBb
15	1.62	0.05	2.10	6.63	12,850	4 1/2	hvBb
16	1.17	0.05	1.81	4.18	13,336	4 1/2	hvBb
17	1.57	0.13	1.90	0.48	13,158	5	hvBb
18	1.47	0.25	1.86	1.13	13,023	4 1/2	hvBb
19	1.43	0.15	1.59	2.88	12,882	4	hvBb
20	0.92	0.29	1.71	2.30	12,913	5	hvBb
21	1.33	0.08	1.93	2.16	13,537	8 1/2	hvAb
22	1.45	0.10	1.35	2.04	13,490	8	hvAb

continued

Table 9, continued

Coal	Forms of Sulfur			% SO ₃ in ash	Heating Value Btu/lb	F S I	ASTM Rank
	Pyritic	Sulfate	Organic				
23	1.22	0.05	1.39	3.14	13,718	8 1/2	hvAb
24	1.22	0.05	2.27	1.23	13,296	4	hvBb
25	0.19	0.01	1.17	0.87	14,249	7	hvAb
26	0.48	0.08	2.20	0.70	12,607	7	hvAb
27	0.48	0.07	2.97	0.46	13,650	7	hvAb
28	0.80	0.02	0.59	6.13	13,241	2 1/2	hvCb
30	1.46	0.32	2.23	1.44	13,007	4 1/2	hvBb
31	1.26	0.07	2.14	1.35	13,220	4	hvBb
32	0.92	0.03	2.05	1.92	13,733	5	hvAb
33	1.16	0.02	1.95	0.62	13,277	5 1/2	hvAb
34	1.08	0.01	1.67	1.92	13,671	6 1/2	hvAb
35	2.05	0.09	1.91	12.41	12,775	6	hvBb
36	2.22	0.11	1.72	10.21	12,468	4 1/2	hvBb
37	1.70	0.03	1.16	3.92	12,740	4 1/2	hvAb
38	0.16	0.01	0.65	---	14,171	3	hvBb
39	1.20	0.05	0.64	---	12,525	3	hvBb
40	0.15	0.02	0.62	---	14,154	2 1/2	hvBb
41	0.24	0.01	0.80	---	14,281	3	hvBb

*Forms of sulfur and heating value on a dry, ash-included basis.

value 2.94%. The heating value is in the range 11,750 to 14,280 Btu/lb (ash-included), mean value 13,230. The free swelling index (FSI) value is from 2.5 to 8.5, average 4.5. All of these coals are high volatile bituminous, ranging from hvAb through hvCb.

Late in the project, six additional freshly mined coal samples were obtained, for additional plastometer studies at elevated pressures. These coals are characterized in Table 10. As these were obtained from six of the sites sampled for the main study, these closely resemble six of the main group of coals:

Coal #42 is similar to coal #25.

Coal #43 is similar to coal #39.

Coal #44 is similar to coal #22.

Coal #45 is similar to coal #24.

Coal #46 is similar to coal #9.

Coal #47 is similar to coal #40.

The 40 coals have been analyzed for maceral composition (Table 11) and for total reactive macerals, mineral matter (Parr procedure) and vitrinite maximum reflectance (Table 12). Again, assays are reported on a dry basis, not corrected for mineral matter content. Vitrinite contents are in the range 62.2 - 84.4%, mean value 72.3%. Total reactive macerals estimated as the sum of vitrinite, pseudovitrinite, exinite, resinite and one-third of the semifusinite) range from 73.5% to 93.1%, mean value 81.5%. Parr mineral matter is in the range 3.3% to 21.1%, mean value 11.3%, systematically higher than furnace ash, as expected.

Table 10

Coals Used for High Pressure Plastometry Runs*

Coal	#42	#43	#44	#45	#46	#47
KCER no.	6102	7953	7799	7912	7913	7957
Seam	Mason	Amos	KY#6	KY#11	KY#9	Amos**
County (KY)	Bell	Butler	Union/ Webster	Union	Ohio	Butler
Moisture	3.21	4.48	3.58	4.34	2.98	6.36
Ash	15.69	12.32	8.69	8.32	10.22	1.74
Volatile matter	33.6	37.0	37.8	40.1	39.5	37.1
Btu/lb	12,774	12,999	13,775	13,200	13,101	14,673
Carbon %	71.2	71.5	76.1	73.6	72.3	82.2
Hydrogen %	4.66	5.04	5.06	4.94	4.92	5.42
Nitrogen %	1.83	1.62	1.62	1.46	1.60	1.81
Sulfur, total %	1.84	2.61	2.88	3.52	3.61	0.82
pyritic	0.94	1.89	1.17	1.24	1.35	0.11
organic	0.87	0.71	1.64	2.25	2.23	0.69
Vitrinite %	79.3	86.7	79.9	82.1	85.6	84.4
Pseudovitrinite %	5.7	2.7	8.5	6.7	0.	3.7
Exinite %	3.6	1.9	3.4	4.2	2.8	6.2
Resinite %	0.7	0.3	1.0	0.6	0.2	1.2
Fusinite %	2.4	4.5	2.7	2.1	2.8	1.1
Semifusinite %	3.7	2.2	2.7	2.1	5.9	0.8
Micrinite %	4.6	1.1	1.4	2.0	2.6	2.5
Macrinite %	0.0	0.6	0.4	0.2	0.1	0.1
Vitrinite maximum reflectance, %	0.87	0.60	0.69	0.56	0.57	0.61
std. dev.	0.039	0.019	0.036	0.033	0.033	0.033
ASTM rank	hVAb	hVAb	hVAb	hVBb	hVAb	hVAb

* Moisture is as determined; all other measurements on a dry ash-included basis.

** Locally identified as Crabshooter #3 seam.

Table 11
Maceral Composition of Coals¹

<u>Coal</u>	<u>Vitrin</u> ²	<u>PseudoV</u> ²	<u>Exinite</u>	<u>Resin</u> ²	<u>Fusin</u> ²	<u>SemiF</u> ²	<u>Micrin</u> ²	<u>Macrin</u> ²
1	75.9	0.8	2.9	0.4	4.3	3.2	0.8	0.4
2	66.3	0.1	6.0	1.2	4.1	3.3	5.5	0.0
3	84.4	0.8	4.7	0.3	1.5	0.6	0.7	0.0
4	70.3	4.1	7.1	0.5	2.7	3.2	3.0	0.3
5	73.6	4.1	6.0	0.3	3.2	2.2	1.8	0.2
6	72.0	6.4	3.2	1.0	2.1	1.9	3.0	0.0
7	78.1	3.8	1.9	0.8	2.6	2.2	1.8	0.0
8	67.6	3.6	3.3	1.0	4.3	5.3	3.2	0.4
9	73.3	2.1	3.9	0.3	5.1	2.7	0.8	0.3
10	73.1	2.4	2.5	0.3	5.9	3.2	1.5	0.1
11	67.5	2.2	2.1	1.1	1.9	3.0	0.9	0.2
12	66.0	3.5	2.7	0.4	2.0	2.8	1.5	0.1
13	69.9	0.9	7.2	1.6	2.6	3.6	3.4	0.0
14	73.4	5.7	2.6	0.5	3.2	3.3	1.3	0.4
15	69.4	2.3	3.5	0.2	5.6	3.9	1.6	0.3
16	72.7	2.4	3.2	0.4	3.7	4.0	3.5	0.2
17	74.6	2.2	2.8	0.4	3.9	2.9	1.7	0.1
18	76.1	1.2	3.5	0.4	3.3	3.6	1.7	0.2
19	76.1	3.2	2.3	1.0	2.1	1.8	0.9	0.3
20	77.2	2.7	1.9	1.0	2.2	2.3	0.9	0.1
21	68.0	7.5	2.5	1.8	3.4	3.0	2.4	0.1
22	70.7	5.3	3.2	0.5	3.5	2.8	1.9	0.1

continued

Table 11, continued

<u>Coal</u>	<u>Vitrin</u> ²	<u>PseudoV</u> ²	<u>Exinite</u>	<u>Resin</u> ²	<u>Fusin</u> ²	<u>Semif</u> ²	<u>Micrin</u> ²	<u>Macrin</u> ²
23	73.3	3.9	3.5	0.9	5.0	1.8	1.3	0.0
24	76.8	3.4	2.5	0.7	2.3	2.5	0.9	0.1
25	69.2	6.5	4.0	1.7	2.4	5.0	2.8	0.4
26*	62.2	10.0	1.5	1.2	1.9	5.0	0.5	0.2
27	64.1	7.0	2.7	0.9	4.1	8.6	1.2	0.8
28	67.5	1.5	6.9	0.9	3.1	1.4	9.0	0.1
30	66.3	2.1	7.4	2.2	4.2	2.5	3.3	0.0
31	80.6	0.5	2.7	0.9	1.8	2.2	0.9	0.1
32	75.6	2.9	1.8	1.3	2.6	3.0	2.9	0.5
33	72.6	5.7	1.7	1.7	1.2	1.9	1.6	0.2
34	74.2	6.3	2.1	1.8	2.7	1.4	2.1	0.2
35	74.8	2.7	1.9	0.8	2.7	2.2	1.2	0.1
36	74.2	2.0	2.3	0.2	3.1	1.6	0.8	0.1
37	69.4	5.9	2.0	0.4	3.2	2.3	1.4	0.3
38	71.2	5.5	7.6	0.8	4.5	3.0	3.5	0.0
39	68.9	3.3	6.8	0.8	1.0	1.4	2.3	0.0
40	74.0	6.1	6.4	1.5	2.4	1.5	3.5	0.0
41	79.0	6.7	6.3	0.9	0.4	0.7	2.7	0.0

* Sample is visibly weathered.

¹ dry basis, not corrected for mineral matter content

² abbreviations: Vitrin = vitrinite, PseudoV = pseudovitrinite, Resin = resinite, Fusin = fusinite, Micrin = micrinite, and Macrin = macrinite

Table 12

Maceral and Mineral Composition and Vitrinite Reflectance of Coals*

<u>Coal</u>	<u>Reactive macerals</u>	<u>Inert macerals</u>	<u>Mineral matter</u>	<u>Vitrinite maximum reflectance</u>	<u>Standard devn of max reflect</u>
1	81.7%	6.8%	11.6%	0.61	$\pm$ 0.047
2	80.2	6.3	13.5	0.42	0.038
3	91.1	1.9	7.0	0.70	0.042
4	86.1	5.1	8.8	0.59	0.032
5	86.5	4.9	8.6	0.56	0.031
6	86.2	3.4	10.5	0.57	0.038
7	87.1	4.1	8.8	0.60	0.032
8	80.5	8.2	11.3	0.53	0.033
9	81.2	7.2	11.6	0.58	0.038
10	80.9	8.3	10.9	0.57	0.036
11	74.8	4.1	21.0	0.56	0.042
12	75.0	4.0	21.1	0.55	0.039
13	84.2	5.0	10.9	0.61	0.030
14	84.6	5.8	9.7	0.58	0.043
15	78.3	8.5	13.3	0.61	0.037
16	83.5	6.6	10.8	0.54	0.047
17	82.6	5.9	11.1	0.54	0.042
18	84.1	5.9	11.0	0.54	0.041
19	84.1	3.6	12.4	0.57	0.042
20	84.5	3.8	11.8	0.53	0.035
21	83.2	5.5	11.2	0.71	0.026
22	82.5	5.5	12.0	0.73	0.032
23	83.5	6.2	10.4	0.74	0.035
24	85.1	4.1	9.7	0.60	0.049
25	85.8	6.1	8.1	0.87	0.041
26	77.0	5.7	17.3	0.87	0.041
27	78.7	10.6	10.7	0.76	0.032
28	86.3	4.0	9.7	0.64	0.034
30	82.1	6.0	11.9	0.58	0.037

continued

Table 12, continued

<u>Coal</u>	<u>Reactive macerals</u>	<u>Inert macerals</u>	<u>Mineral matter</u>	<u>Vitrinite maximum reflectance</u>	<u>Standard devn of max reflect</u>
31	86.3	3.3	10.4	0.59	0.041
32	85.5	5.0	9.5	0.65	0.037
33	83.8	2.9	13.3	0.72	0.030
34	87.0	2.8	10.2	0.69	0.047
35	82.1	4.2	13.7	0.58	0.030
36	80.0	4.2	15.8	0.58	0.032
37	79.9	5.0	15.1	0.66	0.042
38	89.6	6.5	3.9	0.67	0.031
39	82.5	1.9	15.6	0.65	0.026
40	92.0	3.4	4.6	0.70	0.036
41	95.8	0.9	3.3	0.67	0.031

* Maceral compositions on dry basis, not corrected for mineral matter content; mineral matter content by Parr procedure; vitrinite reflectance in oil at 546 nm. Reactive macerals are calculated as the sum of vitrinite, pseudovitrinite, exinite, resinite, micrinite, and one third of the semifusinite; other maceral components (Table 11) are counted as inert.

5.3.2 Quantitative Extractions

Solvent extraction of coal has been established and utilized extensively as a convenient method in the study of coal structure and the chemical characterization of coal. Upon contact with a solvent or its hot vapors, most coals will absorb solvent, swell, and release to the solvent a significant amount of more or less soluble material, resulting in a separation of the coal into a solvent extractable fraction and a cross-linked network residue. Dryden has designated 'specific' solvents as those which are able to selectively dissolve a substantial amount of coal at temperatures near or below the normal boiling point of the solvent. Typically, these solvents consist of a molecule with an unshared pair of electrons on a nitrogen or oxygen atom (44,45). Two common examples are N,N-dimethylformamide (DMF) and tetrahydrofuran (THF), the two solvents used in this study. All 40 coals have been subjected to quantitative separations with both DMF and THF at atmospheric reflux.

The following procedure was used for the drying, extracting, rinsing, and redrying of each coal, using standard Soxhlet extraction assemblies at the atmospheric reflux temperatures of the two solvents employed, DMF and THF. Each coal sample was run in triplicate with each solvent.

- 1) Oven dry 100 ml beakers, cool in a desiccator, and weigh to nearest mg. (All subsequent weighings are to the nearest mg.)
- 2) Add to each beaker approximately 10 g. of powdered coal (-60 mesh), without predrying. Weigh, then place samples in a vacuum oven at $60 \pm 4^{\circ}\text{C}$ for a period of six hours. Allow temperature to drop to less than 50°C to prevent rapid air oxidation, remove samples to desiccator, cool to room temperature and reweigh to obtain moisture loss.
- 3) Concurrently with step 2, mark cellulose Soxhlet thimbles, vacuum dry with the coal, cool in desiccator, and weigh. Transfer the dry coal samples to the thimbles and weigh again.

- 4) Set up the Soxhlet extraction apparatus units, load the coal-containing thimbles, charge the 250 ml flasks with 150 ml of DMF or THF. Insulate the glass assembly below the condenser so that most of the heat loss occurs in the condenser. Carry out reflux extraction 20 to 24 hours.
- 5) Collect DMF or THF extract from flasks. Add 150 ml of methanol to flasks, reassemble, and carry out reflux rinsing of the coal residue for 5 to 6 hours.
- 6) Remove Soxhlet thimbles, allow free solvent to drain away and air dry samples (to prevent blowouts of coal powder under vacuum drying). Place in vacuum desiccator, evacuate for about 30 minutes, and allow to stand overnight.
- 7) Transfer to vacuum oven and dry at 150°C for a period of six hours. Allow temperature to drop to 50°C, remove samples to cool in desiccator, and weigh to obtain extraction loss.
- 8) Replace samples in vacuum oven and dry at 150°C for two hours. Allow temperature to drop to less than 50°C, remove samples to cool in desiccator and weigh. Repeat this step until constant weight is obtained. The third weighing usually provides a good verification of the second weighing.
- 9) Store coal residues in airtight vials at freezer temperature. Calculate percent weight loss due to moisture (step 2) and percent weight loss by solvent extraction of the moisture-free coal.

A few procedural steps are critical, the most significant being the final vacuum drying temperature of 150°C. This temperature was chosen in order to more fully remove the residual DMF from the extracted coal matrix. In FT-IR analysis of DMF-extracted residues which were vacuum dried at 60°C, bands were evident at 1680 and 1095 cm^{-1} , assignable to DMF. This supports an observation by Fort that a significant amount of nitrogen-base extractant can be retained, owing to the great affinity of extracted coal residue for nitrogen compounds (46). The 150°C final vacuum drying temperature overcomes this problem. This temperature was also employed in the final drying of the THF-extracted residues and proved to result in improved reproducibility, suggesting that THF is also retained in the coal residues at the 60°C drying temperature.

Table 13 lists the average percent extraction weight losses for the forty coals run in triplicate with DMF and THF. The table also lists the average percentages calculated after applying a six-sigma test to reject outlier values. These percentages appear in parentheses if they differ from the average of all three runs. Due to its greater polarity, DMF consistently extracts a larger percentage of material than THF. However, the proportional increase with DMF is quite variable, exhibiting a range from less than 25% (Coal #07) to greater than 160% (Coal #25). This variation could reflect differences in the solubility parameters of the several coals (47). Both the THF and the DMF extraction data exhibit a systematic relationship to ASTM maximum fluidity.

The averages of the THF- and DMF-extractables for coals with maximum ASTM fluidities below 100 ddpm, between 100 and 1,000 ddpm, and above 1,000 ddpm are:

Below 100 ddpm:	THF $13.5 \pm 1.4\%$	DMF $23.0 \pm 1.7\%$
100-1,000 ddpm:	THF $14.2 \pm 2.3\%$	DMF $24.5 \pm 2.3\%$
Above 1,000 ddpm:	THF $15.9 \pm 2.3\%$	DMF $30.0 \pm 4.0\%$

These groupings show some trends, especially in the case of DMF-extractables, but do not appear to be highly sensitive predictors of maximum fluidity. It will be seen later, however, the THF-extractables is a particularly useful co-predictor in multiple linear regression analysis.

The completeness of extraction with DMF using the above procedure was checked by conducting sequent extractions with Coals #42 and 43. Fresh samples of each coal were extracted using the above procedure, dried to constant weight, and the extraction residues then treated as new coals and subjected to another complete extraction cycle. All extractions were performed in triplicate. For Coal #42 the initial weight loss was

Table 13

Coal Fractions Extractable by THF and DMF*

<u>Coal</u>	<u>% Loss of Dry Coal with hot THF</u>		<u>% Loss of Dry Coal with hot DMF</u>	
	<u>Average Loss**</u>	<u>Standard Devn.</u>	<u>Average Loss**</u>	<u>Standard Devn.</u>
01	12.75%	+ 0.18%	23.78% (24.18)	+ 0.03%
02	11.99	0.46	22.46	1.76
03	13.37	0.29	19.28 (18.84)	0.19
04	14.59	0.71	22.75	1.88
05	12.58	0.27	22.92	1.71
06	17.35 (17.82)	0.03	23.03	0.41
07	19.28 (19.64)	0.11	24.20	0.31
08	12.44	0.96	22.78	1.47
09	12.89 (13.02)	0.02	23.30 (23.77)	0.03
10	13.37 (13.62)	0.05	22.30	0.30
11	13.27 (13.45)	0.02	24.41	0.74
12	12.74	0.58	24.24	0.43
13	15.26 (14.65)	0.08	29.02	2.17
14	17.21	1.15	29.00	2.94
15	13.25 (13.49)	0.08	25.11	1.55
16	14.88 (15.07)	0.02	26.13	0.98
17	13.86 (13.99)	0.06	24.78	1.48
18	13.27 (12.75)	0.14	21.75 (21.12)	0.20
19	15.69	0.17	23.45	2.86
20	15.60 (15.34)	0.09	23.12	1.72
21	16.25	0.38	32.71 (32.01)	0.12
22	14.27 (14.16)	0.03	33.64	0.62
23	14.21	0.11	32.14	0.84
24	15.07 (14.85)	0.03	23.03	0.33
25	10.99	0.19	28.22 (28.70)	0.02
26	10.73 (10.79)	0.02	22.12	0.55
27	16.34	0.58	35.12	0.94
28	10.74 (11.10)	0.13	18.40 (18.79)	0.18

- continued -

Table 13 (Cont.)

Coal Fractions Extractable by THF and DMF*

<u>Coal</u>	<u>% Loss of Dry Coal with hot THF</u>		<u>% Loss of Dry Coal with hot DMF</u>	
	<u>Average Loss**</u>	<u>Standard Devn.</u>	<u>Average Loss**</u>	<u>Standard Devn.</u>
30	14.54%	$\pm$ 1.06%	23.49%	$\pm$ 0.67%
31	14.24	0.90	23.48 (23.97)	0.16
32	18.69 (18.86)	0.05	27.55 (26.23)	0.26
33	17.65 (17.98)	0.06	29.44 (27.41)	0.14
34	17.07	0.35	34.87 (34.47)	0.18
35	16.13 (15.72)	0.13	27.50 (27.43)	0.02
36	14.67	0.37	26.17 (25.73)	0.14
37	13.48 (13.63)	0.06	24.50	1.82
38	12.21	0.32	22.39 (22.65)	0.03
39	12.48	0.26	22.89	0.81
40	11.36 (11.03)	0.09	19.71	1.06
41	13.33	1.02	22.98	1.87
averages:	14.27%	$\pm$ 0.29%	25.12%	$\pm$ 0.85%

* Replicate (mostly triplicate) Soxhlet extractions at atmospheric pressure reflux with tetrahydrofuran (THF) and with N,N-dimethylformamide (DMF), upon predried coal samples. Data not corrected for mineral matter content.

** Percentages appearing in parenthesis are the average of the best two of three determinations after applying a six sigma test. Outlier data was rejected if more than six standard deviations from the average of other replicates.

25.27 $\pm$ 0.73%, and the cumulative weight loss after two extractions was 26.19 $\pm$ 0.72%. For Coal #43 the initial weight loss was 35.23 $\pm$ 0.84% and the cumulative weight loss after two extractions was 35.07 $\pm$ 1.11% (a slight negative weight loss). These differences are not statistically significant. We conclude that the extraction procedure outlined above is substantially quantitative.

Several additional exploratory extractions were undertaken, using these same coals, to investigate the effects of basicity and steric hindrance. Results are summarized in Table 14.

Pyridine derivatives are well known to be excellent extraction solvents for coals. 2-Methylpyridine (2-picoline) removes more extractables than DMF for both coals tested.

2,6-Dimethylpyridine (2,6-lutidine) is an interesting case, since there are two factors which might be expected to make it superior to 2-methylpyridine: it is a slightly stronger base, and its reflux boiling point is higher. Yet although it is a good solvent, it is not as good as 2-methylpyridine, and not as good as the much weaker base DMF. This loss in efficacy in going from 2-methylpyridine to 2,6-dimethylpyridine appears to be a consequence of the greater steric hindrance of the nitrogen base atom in the dimethyl compound.

To test this notion, additional triplicate extractions were carried out with triethylamine, a very strong Lewis base and an excellent hydrogen-bond former, and also a compound with well known steric hindrance around its base atom. Notwithstanding its basicity, triethylamine is less efficient even than the neutral and lower-boiling dichloromethane. This observation leads us to conclude that when coal reacts with small molecules in acid-base reactions, the role of steric hindrance -- just as in the case

Table 14Effects of Solvents in Exploratory Extractions

<u>Solvent</u>	<u>b.p.</u>	<u>Average Weight Loss on Extraction</u>			
		<u>Coal #42</u>		<u>Coal #43</u>	
2-Methylpyridine	129°C	28.63 $\pm$ 2.75%		36.32 $\pm$ 0.36%	
2,6-Dimethylpyridine	146	22.06	0.89	29.72	0.91
N,N-Dimethylformamide	153	25.27	0.73	35.23	0.84
Triethylamine	89	0.81	0.18	0.48	0.28
Dichloromethane	40	2.38	0.18	3.09	1.48
Carbon disulfide : pyridine (1:1)	24*	19.26	0.50	22.46	0.52

* Slurried at ambient temperature.

of reactions of synthetic high polymers with small molecules (48) -- is much more important than is usually thought to be the case in ordinary chemical reactions.

One other exploratory experiment is reported in Table 14. Iino and Matsuda (49) have recently reported that mixtures of carbon disulfide and pyridine are fast and effective extractants at room temperature. The results of a 24-hour room temperature slurry extraction with a 1:1 solvent mixture are not quite as good as the Soxhlet extractions with the pyridines or with DMF, but nevertheless are surprisingly good. Carbon disulfide alone is not a strong swelling solvent for hvb coals, but in combination with a good base its very small minimum cross-section area may facilitate penetration of the fine pore structure.

5.3.3 Pyrolysis/Gas Chromatography

A pyrolysis/GC system has been used for this portion of the study. The system consists of a Chemical Data Systems Model 100 Pyroprobe (coil probe) interfaced with a Varian Model 3700 gas chromatograph (flame ionization detection) and a Laboratory Data Control Model 308 computing integrator. For low-ramp and extended pyrolyses the Pyroprobe is connected to a CDS Model 310 concentrator. At the conclusion of the pyrolysis the trap loop of the concentrator is pulse-heated to 250°C and backflushed into the chromatograph. Most of our work has been conducted using a relatively high heating ramp, under which conditions the Pyroprobe is directly connected to the chromatograph inlet.

In using the platinum coil probe a small quartz tube (2.4 o.d. x 25 mm) is charged with approximately 4 mg of coal and is placed inside the platinum coil. The sample is then heated linearly to a preset ceiling temperature, and is then held at this ceiling temperature for a specified

interval. Except as noted otherwise we have used a 500 deg C/sec heating ramp, a ceiling temperature of 450 or 650°C, and a ceiling temperature heating period of 20 sec.

In order to verify that the temperature of the sample inside the quartz tube was at least close to the instrument setpoint temperature, calibration was undertaken using the "molecular thermometer" technique of Levy (50) and Walker (51). When Kraton 1107 copolymer (Shell Chemical Co., Houston, TX) is pyrolyzed, the ratio of the isoprene and dipentene peaks is sensitive to ceiling temperature. Using the literature calibration for the pyrolysis products of this copolymer and a 4 ft x 1/4 in Porapak Q column for the peak ratio measurements, at a nominal ceiling temperature of 650°C the polymer products (5 of 6 runs) yielded a calculated temperature of 645°C, s.d. 19 deg. The temperature calibration of the instrument is therefore considered adequate.

After the coal sample is charged to the Pyroprobe unit, the tube and contents are dried at 200°C, and the unit is then brought rapidly (at 500 deg/sec) to the ceiling temperature and held at that temperature for 20 sec. During this period the nitrogen sweep through the pyrolysis stage carries volatilized matter to the gas chromatograph inlet stage (held at 270°C) and thence to the analytical column. Most of this work has made use of an inert silicone stationary phase (OV-101 5%) charged to a 50 cm x 1/8 in. stainless steel column with a nitrogen flow rate of 30 ml/min. The column oven is maintained at 60°C for 10 min, during which time the pyrolysis gases pass through the column and are analyzed by the FID (held at 270°C). At the end of this interval the detector signal has returned to the baseline. The column is then heated at a rate of 20 deg/min to 250°C, and is held at this temperature for 30 min. Under these conditions a

substantial amount of condensible material passes through the detector.

The product envelope has substantially passed through the system by the end of the first 15 min at 250°C.

Exploratory runs with Coal #01 were made using ceiling temperatures from 450 to 950°C. Over this range of ceiling temperature the weight loss of the coal increases smoothly from 11% at 450°C to 41% at 950°C. The total integrator counts per microgram of coal charge increases from 38 at 40°C to 181 at 650°C, and thereafter only slowly to 230 at 850-950°C. The proportion of gaseous products (products readily passing through the OV-101 column at 60°C) increases from 3% of the total at 450°C to 31% at 650°C, and thereafter only slightly, reaching 34% at 950°C.

Exploratory runs were also made using a much slower heating ramp, 5 deg C/sec, and holding the ceiling temperature for 60 min. The comparison with the 500 deg/sec ramp and 20-sec ceiling period is shown below for two coals:

coal no.	slow ramp		fast ramp	
	cts/microgm	% gas	cts/microgm	% gas
12	98.	18.5	21.	7.3
22	101.	31.1	35.	14.7

On the basis of these runs it was determined to use the high heating ramp and short pulse. The information above 650°C appears to be less selective and less likely to be of correlative value. We have therefore selected two temperatures, 450 and 650°C, and have subjected the set of 40 coals to replicate pyrolysis/GC analyses at each of these ceiling temperatures.

Table 15 summarizes the results of (mostly quadruplicate) runs using the high-ramp procedure and a ceiling temperature of 650°C. Although these data have been examined in detail, there is little useful distinction evident among their pyrograms. For example, the high volatile fractions of Coals #31 and 32 are 32% and 34%, and on the basis of weight loss or total counts per microgram Coal #31 appears marginally more reactive; but the maximum fluidity of Coal #32 is in fact more than a thousandfold greater than that of Coal #31.

At 450°C the pyrolysis/GC data are more promising. Differences are illustrated using a higher-resolution GC column, 3% DEXIL 300, 200 cm x 1/8 in, with a nitrogen flow rate of 15 ml/min. Figure 8 shows a typical pyrolysis/gas chromatogram for a sparingly plastic coal (Coal #03, maximum ASTM fluidity 28 ddpm). The pyrolysis gas signal at 2-5 min consists of a single peak at 2+ min. The pyrolysis liquids signal at 15-22 min shows mainly a 'marker peak' common to all of these hvb coals and appearing on this column at 19+ min.

Figure 9 provides a direct comparison for a highly fluid coal (Coal #34, maximum ASTM fluidity greater than 30,000 ddpm). The pyrolysis gas signal at 2-5 min consists of a group of peaks. The liquids signal at 15-22 min is considerably stronger than that of Figure 8. This signal in Figure 9 shows the 'marker peak' at 19+ min, and in addition it shows two strong compound peaks at (approximately) 17 and 18 min. These peaks are absent in Figure 8. The 17- and 18- peaks are in fact found only in the pyrolysates of moderately fluid to highly fluid coals, and -- within the range of this set of hvb coals -- have been found in every fluid coal.

Table 16 summarizes the results of pyrolysis/GC analysis on the OV-101 column using a ceiling temperature of 450°C. The proportion of high

Table 15

650°C Pyrolysis/Gas Chromatographic Analysis of hvb Coals*

coal	runs	% wt loss		counts/microgram		% high volatile	
01	5	25.9	4.7	142.6	20.4	32.6	1.4
02	7	43.2	8.5	175.2	23.4	30.7	2.2
03	4	---		177.1	6.6	34.1	0.9
04	4	19.8	1.3	164.9	24.4	29.8	1.8
05	4	37.2	9.7	158.3	41.5	30.0	1.7
06	3	25.1	4.5	206.1	17.6	32.5	0.3
07	4	33.8	6.9	228.7	8.3	31.5	0.9
08	4	32.0	7.5	184.3	21.5	31.7	0.8
09	5	24.0	2.5	141.9	16.4	30.2	1.9
10	5	32.5	5.4	199.1	12.8	33.9	1.8
11	4	19.7	1.5	191.0	11.4	31.8	2.4
12	3	22.5	4.3	185.3	9.9	33.0	1.9
13	4	23.3	0.8	168.7	12.0	32.6	0.7
14	4	29.8	4.5	163.7	14.6	33.6	0.4
15	4	24.9	1.8	189.5	10.5	34.0	0.7
16	4	24.2	1.4	214.1	4.8	32.5	1.1
17	4	23.0	0.8	188.3	8.1	33.6	0.6
18	4	24.5	3.3	193.6	6.3	33.1	1.5
19	4	22.3	2.5	202.2	7.4	32.8	0.3
20	4	26.8	1.0	174.1	6.2	31.2	0.5
21	4	14.9	2.9	175.4	7.8	35.3	0.5
22	6	37.3	7.3	203.0	16.1	37.2	2.3
23	4	18.2	2.0	173.3	6.4	35.0	0.8
24	4	---		203.9	12.5	33.3	0.2
25	4	17.3	1.3	199.2	8.3	36.1	1.8
26	4	18.5	1.8	158.3	9.9	39.7	0.6
27	4	18.0	1.5	197.1	17.1	34.2	1.4
28	3	22.7	1.3	175.0	9.9	32.1	1.7
30	4	25.3	3.8	207.6	26.8	32.3	1.7
31	4	24.7	1.6	248.6	17.1	31.8	1.1
32	4	19.9	2.1	188.7	5.7	33.8	1.0
33	4	16.0	1.2	205.0	14.7	31.5	2.6
34	4	18.9	2.7	191.8	24.1	34.7	1.0
35	3	23.7	0.1	197.8	11.5	30.4	1.2
36	3	23.2	1.2	167.6	3.2	31.4	0.9
37	4	18.2	1.2	140.7	15.5	31.7	0.6

- continued -

Table 15 (Cont.)650°C Pyrolysis/Gas Chromatographic Analysis of hvb Coals*

coal	runs	% wt loss		counts/microgram		% high volatile	
38	4	23.4	1.0	165.9	3.0	33.3	1.1
39	4	22.2	1.6	169.5	2.9	35.1	1.6
40	4	20.1	1.2	156.8	9.5	34.5	0.2
41	3	24.3	1.4	201.7	1.3	35.5	1.1

* Run at 500 deg/sec heating ramp and 20-sec pulse at 650°C; analyzed on OV-101 column as described in text.

Figure 8

450°C Pyrolysis/GC of Coal #03 on 3% DEXIL 300.
Note the sharp marker peak at 19+ min.

Figure 9

450°C Pyrolysis/GC of Coal #34 on 3% DEXIL 300.
Note strong fluidity peaks at 17-18 min.

Table 16

450°C Pyrolysis/Gas Chromatographic Analysis of hvb Coals*

coal	runs	% wt loss		counts/microgram		% high volatile	
01	3	17.5	4.0	20.2	4.6	8.1	0.6
02	4	18.0	2.3	18.2	1.5	8.3	1.2
03	4	---		18.7	4.6	5.9	1.1
04	5	5.3	2.9	23.7	7.0	5.4	1.3
05	5	6.2	4.5	29.3	5.3	7.5	1.5
06	4	7.8	0.5	26.9	1.8	5.4	0.3
07	4	17.4	2.1	26.6	4.8	5.8	1.4
08	4	10.3	1.0	21.1	1.6	5.8	0.6
09	4	11.9	2.4	21.4	5.0	6.6	1.6
10	5	10.7	4.8	31.3	6.5	3.6	0.7
11	4	14.5	4.8	23.0	2.1	7.2	1.5
12	4	10.4	3.7	20.8	5.7	7.3	0.9
13	5	9.6	2.2	18.2	4.6	9.9	1.4
14	4	12.7	2.3	19.8	1.7	7.3	0.9
15	3	10.3	3.2	27.6	1.1	8.9	0.7
16	4	7.1	1.3	20.1	1.2	9.0	0.5
17	4	9.0	1.9	18.7	1.4	5.1	0.5
18	4	9.6	3.4	21.3	1.6	5.3	0.8
19	3	8.0	1.2	24.9	0.9	5.6	0.8
20	4	11.1	3.5	18.4	2.3	6.8	0.5
21	4	7.0	4.3	37.0	1.1	14.4	1.1
22	5	10.0	7.4	34.7	3.2	14.7	1.2
23	4	12.2	3.6	27.6	1.5	15.9	0.8
24	4	11.7	0.7	21.6	1.5	7.5	0.1
25	4	7.4	2.0	44.7	2.8	12.1	0.3
26	4	6.9	0.5	23.7	2.3	6.3	0.9
27	4	---		32.2	1.7	12.4	1.6
28	4	12.1	2.7	20.8	2.0	2.6	0.4
30	3	6.4	1.3	25.4	1.8	6.4	0.8
31	4	10.2	2.7	17.3	0.4	4.9	0.9
32	4	3.5	1.1	37.0	3.4	12.0	1.1
33	4	7.7	2.5	38.2	3.2	12.9	0.2
34	4	3.9	0.9	35.2	1.3	14.0	0.5
35	4	11.4	3.4	24.4	1.3	9.1	1.0
36	4	11.3	2.5	22.6	1.7	7.8	0.7
37	3	8.6	1.1	21.2	1.1	7.9	1.2

- continued -

Table 16 (Cont.)450°C Pyrolysis/Gas Chromatographic Analysis of hvb Coals*

coal	runs	% wt loss		counts/microgram		% high volatile	
38	4	11.8	1.3	17.8	0.9	3.4	1.8
39	4	11.1	1.2	14.4	1.5	1.7	0.6
40	3	8.2	0.9	13.4	0.7	1.5	0.1
41	4	9.5	1.0	21.1	2.3	3.5	0.8

* Run at 500 deg/sec heating ramp and 20-sec pulse at 450°C; analyzed on OV-101 column as described in text.

volatiles and the total counts per microgram for Coal #34 are seen to be roughly double those for Coal #03.

These differences can be crudely digitized by recording the distribution of the pyrolysis signal in various one-minute windows of the chromatogram. Table 17 shows the average distributions in the 2-, 3-, 4-, 5- and 6-minute windows (pyrolysis gases) and in the 13- through 18-minute windows (major areas for pyrolysis liquids). This information is brought forward to Part 6 for further analysis.

Solvent Extracts and Extraction Residues. A comparison of Figure 8 and Figure 9 suggests that a group of prominent peaks in the 16-20 minute part of the low-volatiles envelope are associated with high plasticity coals. It has been known for some time that solvent extraction with a polar aprotic solvent effectively destroys plasticity (5). It seems of interest, therefore, to examine the effect of solvent extraction upon these prominent 'plasticity peaks' in the 16-20 minute region of the low-volatile envelope.

The residue from hot DMF extraction of the highly plastic coal #34 was subjected to pyrolysis/GC analysis at 450°C. The liquids region of the chromatogram (15-22 min) is shown (Figure 10, bottom tracing) to have lost all of the prominent peaks present in Figure 9, and to have collapsed the liquid product envelope. When the DMF extract from this coal is isolated and subjected to this same pyrolysis/GC treatment, the liquids portion of the chromatogram (Figure 11) not only shows a strong envelope but also displays the strong 17- and 18-min peaks associated with plastic coals as well as the marker peak at 19+ min.

Effect of Temperature upon Residue Pyrolysis. It is evident that the 650°C pyrograms have much less predictive power than the 450°C pyrograms.

Table 17

Distribution of Pyrolyzate Signal: Pyroprobe/GC Analysis at 450°C*

<u>Coal</u>	<u>total cts per mmg</u>	<u>2-min window</u>	<u>3-min window</u>	<u>4-min window</u>	<u>5-min window</u>	<u>6-min window</u>	<u>13-min window</u>	<u>14-min window</u>	<u>15-min window</u>	<u>16-min window</u>	<u>17-min window</u>	<u>18-min window</u>
01	20.2	4.86%	1.37%	0.41%	0.29%	0.19%	0.91%	2.11%	4.18%	6.98%	7.77%	10.38%
02	18.2	4.25	1.32	0.55	0.45	0.35	1.05	2.49	5.01	8.29	8.72	10.11
03	18.7	2.66	0.66	0.28	0.36	0.41	0.63	1.44	2.60	4.60	5.62	10.55
04	23.7	2.08	0.99	0.74	0.45	0.33	0.92	2.27	4.36	7.10	8.-9	11.37
05	29.3	2.88	1.21	0.68	0.61	0.52	1.12	2.43	4.04	6.67	7.88	11.07
06	26.9	1.86	1.04	0.62	0.46	0.35	0.62	1.75	3.75	6.56	7.96	9.97
07	26.6	2.16	0.79	0.49	0.39	0.36	0.76	1.85	3.36	5.96	7.64	10.02
08	21.1	2.54	1.25	0.60	0.40	0.29	0.71	1.92	3.96	6.99	8.48	9.90
09	21.4	3.37	1.26	0.49	0.40	0.29	0.72	1.93	3.28	5.77	6.88	8.84
10	31.3	2.20	0.87	0.29	0.03	0.01	0.69	1.92	3.26	5.74	7.07	8.35
11	23.0	2.98	1.07	0.73	0.55	0.41	0.93	2.53	4.67	7.21	8.59	10.54
12	20.8	2.68	1.24	0.81	0.65	0.48	1.02	2.62	4.96	8.22	9.34	13.45
13	18.2	4.79	2.73	0.90	0.69	0.39	1.20	3.28	6.88	10.14	9.21	10.80
14	19.8	3.78	2.18	0.78	0.61	0.36	0.79	2.53	4.78	7.33	7.08	7.43
15	27.6	4.13	1.91	0.79	0.60	0.45	0.93	2.56	4.72	7.05	7.15	7.83
16	20.1	4.21	2.05	0.97	0.55	0.48	0.74	2.70	6.43	9.08	9.33	9.43
17	18.7	2.20	0.73	0.42	0.41	0.23	0.65	1.82	3.64	5.94	7.69	9.58
18	21.3	2.10	0.64	0.41	0.44	0.38	0.47	1.42	3.07	5.04	6.46	8.24
19	24.9	2.25	1.18	0.70	0.33	0.29	0.51	1.86	4.36	6.57	6.94	6.90
20	18.4	2.29	1.39	0.69	0.40	0.20	0.85	1.98	4.48	7.70	8.52	8.54
21	37.0	7.32	3.65	1.36	0.96	0.51	1.36	2.68	5.38	8.28	7.95	9.19
22	34.7	6.27	3.42	1.44	1.16	0.79	1.24	2.68	5.24	8.28	8.08	8.74
23	27.6	6.46	3.70	2.19	0.98	0.89	1.01	3.12	6.74	9.62	9.84	10.18
24	21.6	2.58	0.98	0.59	0.59	0.51	0.78	1.76	3.09	6.56	7.45	8.31

- continued -

Table 17, continued

<u>Coal</u>	<u>total cts per mmg</u>	<u>2-min window</u>	<u>3-min window</u>	<u>4-min window</u>	<u>5-min window</u>	<u>6-min window</u>	<u>13-min window</u>	<u>14-min window</u>	<u>15-min window</u>	<u>16-min window</u>	<u>17-min window</u>	<u>18-min window</u>
25	44.7	4.32%	2.78%	1.70%	0.85%	0.69%	0.73%	2.46%	5.48%	7.91%	8.35%	9.47%
26	23.7	1.73	1.34	0.63	0.66	0.37	0.72	1.41	2.55	5.30	5.81	7.05
27	32.2	4.13	2.89	1.78	0.89	0.77	0.76	2.48	5.60	8.17	8.50	8.53
28	20.8	1.51	0.42	0.15	0.11	0.07	0.24	0.77	1.92	4.53	5.31	6.87
30	25.4	2.76	0.81	0.46	0.41	0.27	0.43	1.47	3.29	5.53	7.03	9.34
31	17.3	1.90	0.78	0.49	0.40	0.27	0.57	1.45	3.00	6.18	7.37	8.13
32	37.0	5.23	2.97	1.60	0.74	0.62	0.63	2.23	4.90	6.60	6.83	7.37
33	38.2	5.18	3.05	1.70	0.86	0.73	0.70	2.53	5.75	7.69	7.64	7.64
34	35.2	5.48	3.30	1.99	0.97	0.83	0.73	2.72	6.12	8.35	8.31	8.32
35	24.4	3.48	2.12	1.16	0.58	0.44	0.70	2.02	4.84	7.82	7.76	7.68
36	22.6	2.80	1.76	0.83	0.69	0.38	0.88	1.98	4.62	7.98	8.07	7.98
37	21.2	2.90	1.20	0.72	0.73	0.55	0.76	1.81	3.56	6.62	7.89	9.59
38	17.8	0.90	0.36	0.24	0.30	0.25	0.29	0.80	1.98	3.77	4.61	7.87
39	14.4	0.79	0.11	0.00	0.00	0.00	0.33	0.80	2.14	4.22	5.56	9.57
40	13.4	0.79	0.23	0.09	0.11	0.06	0.27	0.71	1.66	3.15	3.82	6.52
41	21.1	1.56	0.23	0.06	0.19	0.23	0.58	1.19	2.55	5.08	6.94	10.71

* Window data are percentages of total pyrogram integrator count.

Figure 10

Pyrolysis/GC Analyses of the DMF Extraction Residue of Coal #34

Figure 11

Pyrolysis/GC Analysis of the DMF-Extracted Material from Coal #34

We attribute this to a more complete fragmentation of the coal matrix at the higher temperature: covalent bonds which are fairly stable at 450°C and which are likely to survive a Gieseler plastometry run in the vicinity of this temperature may still be subject to thermal cleavage at higher temperatures.

This view is conveniently tested using the DMF extraction residue of Coal #34, a residue which gives a very weak signal in the 15-22 min (liquid products) region (Figure 10, bottom tracing). Additional portions of this extraction residue have been pyrolyzed using the identical pyrolysis/GC program except for higher pyrolysis ceiling temperatures. The middle and top tracings in Figure 10 show the liquid products regions of the pyrograms with ceiling temperatures of 500 and 550°C. A substantial product signal is evident by 550°C. Runs with this extraction residue at 650°C (not illustrated) show a striking similarity to the 650°C pyrolysis/GC signals of the original coal.

These results are consistent with the view that pyrolytic cleavage of bridging bonds in coal structures occurs on many levels. Bonds which are cleaved at 450°C and below, and which are involved in the plasticity phenomenon and in the initial reactions of coals under hydroliquefaction conditions, can be viewed as one group of thermally reactive sites. At 550°C another group of bonds are ruptured, bonds which are substantially stable at 450°C. The total integrator signal at 550°C is more than treble that at 450°C. Again, by 650°C yet another group of bonds, which are stable at 550°C, are cleaved, generating an additional signal of about 300 counts/microgram.

5.3.4 Infrared Spectrometry

A number of investigators have noted the importance of the aliphatic hydrogen content of a coal with regard to its thermal behavior.

Liquefaction reactivity, plasticity and coking behavior are reported to correlate with aliphatic hydrogen content. Neavel (52) has proposed that aliphatic hydrogen is transferred to thermally generated carbon free radicals during coal pyrolysis. Sentfle and his coworkers (53) have shown a correlation between total aliphatic hydrogen and plasticity for a number of vitrinite concentrates. Furimsky and coworkers (54) stress the importance of aliphatic hydrogen in the ultimate yield of volatile products from coal pyrolysis.

All 40 coals in this study have been examined by Fourier Transform infrared spectrometry, using a Nicolet Model MX-1 spectrometer. In addition, the THF and DMF extraction residues of all coals have been examined, as have several extracts and low-temperature ash residues.

The sample preparation procedure which in our hands has been most effective is that of Painter and his co-workers (55). This entails the reduction of -60 mesh coal or residue to -200 mesh, then thorough mixing with 200 parts of finely powdered KBr for preparation of the pellet. In order to prepare pellets of reproducible thickness we have standardized upon 1.3 mg of coal with 300 mg KBr.

The great sensitivity of FTIR puts special requirements upon the sample preparation procedure. The original blender (a Perkin-Elmer 'Wig-L-Bug') with a hard plastic mortar and pestle resulted in plastic contamination of the pellets. Consistently good pellets were obtained only after installation of an air drying system and a stainless steel and agate mortar and pestle unit for the mixer.

The standard data collection procedure entails a 16-minute acquisition (collection of 512 scans at the rate of 32 scans/min).

A number of band assignments are common to all of these hvb coals. A broad strong band at 3040 cm^{-1} is assignable to O-H stretching. A weak band at 3040 cm^{-1} is due to aliphatic C-H stretch. The strong band at 1610 cm^{-1} looks like carbonyl but in these fresh unweathered coals is more likely to be due to aromatic ring stretching (55). The strong band at 1450 cm^{-1} is due to methylene and methyl bending. The bands between 1000 and 1100 cm^{-1} are often assigned to the C-O single bond stretch of aliphatic ethers and alcohols. Our low-ash coals have weak bands here; our high-ash coals have strong bands, and the mineral residues from low-temperature (oxygen plasma) ashing have extremely strong bands here. We believe these to be primarily inorganic in origin. Finally, the bands between 700 and 900 cm^{-1} may be assigned to the aromatic C-H out-of-plane bending modes.

It has been noted previously (Part 5.3.2) that we have been obliged to heat DMF extraction residues to 150°C under 1 torr in order to desorb completely the solvent from its more secure hydrogen-bonded sites on the coal residue. This problem was discovered in examining DMF residues by FTIR. After thorough vacuum-drying at 60°C these residues show clear peaks at 1680 and 1095 cm^{-1} , both major peaks for DMF. The early extraction runs were then repeated, using the more rigorous solvent removal procedure.

In terms of quantitative measurements we have been primarily interested in the aromatic/aliphatic hydrogen atom ratio. J. K. Brown, one of the first to use infrared analysis to measure hydrogen distribution in coals, determined the ratio of the C-H stretching band intensities at 3030 and 2920 cm^{-1} (56). Durie and co-workers have also examined this problem (57). The procedure we have used is that proposed by Solomon (58): aliphatic hydrogen is estimated by the intensity of the 2920 cm^{-1} and

aromatic hydrogen by the average intensities of three bands near 800 cm^{-1} . We have used the extinction coefficient ratio suggested by Solomon to calculate the H(aromatic)/H(aliphatic) ratios for the 40 coals and the 80 extraction residues. These data are presented in Table 18.

We have not found the H(aromatic) / H(aliphatic) ratio to be a useful measure of fluid behavior of hvb coals. The averages for several groupings of low, moderate and high plasticity coals are all in the range 0.50 - 0.55, with no detectable trend. On the other hand, there are trends among the THF extraction residues. The average H(aromatic)/H(aliphatic) ratio for of THF extraction residues of the eleven least plastic coals is 1.02; that for the thirteen most plastic coals is 0.82.

The differences among raw coals, their THF extraction residues, and their DMF extractions residues are quite evident. The THF residues have substantially higher H(aromatic) / H(aliphatic) ratios than their parent coals, and the DMF extraction residues show still higher ratios -- ratios approximately double those of the parent coals. The evident inference is that the extractable or 'sol' fraction in coal is relatively rich in aliphatic CH, while the insoluble macromolecular residue is relatively rich in aromatic CH. It is noteworthy that DMF, a polar solvent and unlikely to be more selective than THF for aliphatics, nevertheless removes more aliphatic-rich material, and leaves a more aliphatic-depleted residue, than does THF.

One possible view of the differences between sparingly plastic and highly plastic hvb coals is that the extractable interstitial small molecules may differ significantly in the abundance and distribution of functional groups. To test this notion, the THF extracts of two sparingly plastic coals (#03 and #24) and of two moderate to highly plastic coals

Table 18

Hydrogen Distribution in Coals and Coal Residues

<u>Coal</u>	<u>ln(max ASTM fluidity</u>	<u>H(aromatic)/H(aliphatic) ratio</u>		
		<u>raw coal</u>	<u>THF extn residue</u>	<u>DMF extn residue</u>
01	2.57	0.41	0.84	0.94
02	2.26	0.85	1.80	1.42
03	3.34	0.43	0.78	0.99
04	6.30	0.59	0.64	1.05
05	4.46	0.44	0.80	0.85
06	9.89	0.61	0.64	0.99
07	6.65	0.59	1.37	1.49
08	3.93	0.51	0.93	1.15
09	3.74	0.62	1.27	1.70
10	4.50	0.42	1.47	1.17
11	4.59	0.58	0.78	0.76
12	5.43	0.48	0.56	0.85
13	6.29	0.45	0.71	1.13
14	5.21	0.33	0.63	1.06
15	5.99	0.50	0.84	0.82
16	4.16	0.58	0.86	1.21
17	3.81	0.56	1.43	1.81
18	3.29	0.54	1.05	1.19
19	4.76	0.51	1.04	1.54
20	4.51	0.49	0.64	0.83
21	10.32	0.49	1.14	0.87
22	10.32	0.49	0.64	0.86
23	10.33	0.49	1.11	0.81
24	3.55	0.45	0.61	0.82
25	10.32	0.37	0.66	0.79
26	4.77	0.52	0.94	0.86
27	10.11	0.52	0.57	1.11
28	2.92	0.84	0.86	1.13
30	2.79	0.31	0.95	1.06
31	2.89	0.59	0.97	0.77
32	10.30	0.47	0.73	0.97
33	10.30	0.53	0.93	0.82
34	10.30	0.59	0.72	0.96
35	9.26	0.67	0.75	1.00
36	5.22	0.62	1.27	1.33
37	6.05	0.64	1.35	1.06

Table 18, continued

<u>Coal</u>	<u>ln(max ASTM fluidity</u>	<u>H(aromatic)/H(aliphatic) ratio</u>		
		<u>raw coal</u>	<u>THF extn residue</u>	<u>DMF extn residue</u>
38	5.23	0.51	1.33	1.03
39	5.41	0.48	0.68	0.64
40	3.10	0.46	0.63	0.84
41	5.38	0.35	0.80	0.76
42		0.48	---	1.22
43		0.73	---	1.80

(#22 and #34) were reduced by removal of the volatile solvent and their spectra obtained. The H(aromatic) / H(aliphatic) ratios of the coals, their THF extraction residues, and their THF-extracted material are given in Table 19. As expected, the THF-extracted material has a higher aliphatic content than the parent coal. The unexpected result of this experiment is the constancy of the H(aromatic) / H(aliphatic) ratio of the THF-extracted material, in coals with maximum ASTM fluidities differing by a thousandfold. Clearly the differences in plasticity of coals do not appear to lie in the composition of these extracts.

5.3.5 HPLC Analysis of Extracts

The possibility of systematic chemical differences which may correlate with fluid properties has also been investigated by examination of the THF extracts of the 40 coals.

Preliminary work was carried out by thin layer chromatography (TLC). Five- and ten-microliter portions of the THF extracts were placed on commercial (E. Merck #60 F254) plates coated with a 0.25 mm silica layer. These were developed with hexane and with 20% (v/v) methylene chloride (dichloromethane) in hexane.

Under 254 nm short wave ultraviolet (SWUV) illumination these plates provide a bright green fluorescent background. Any material (such as an aromatic compound) absorbing SWUV light serves to screen this fluorescence and appears as a dark spot on the fluorescent green background. In TLC with coal-derived materials most aromatic species can be 'seen' clearly in SWUV light.

Under 366 nm long wave ultraviolet (LWUV) light those compounds which fluoresce at this lower-energy wavelength can be detected. In TLC with coal-derived materials those polynuclear compounds with three or more fused aromatic rings are generally 'seen' with LWUV light.

Table 19Hydrogen Distribution in Selected THF Coal Extracts and Residues

<u>Coal</u>	<u>ln(max ASTM Fluidity)</u>	<u>H(aromatic)/H(aliphatic) Ratio</u>		
		<u>Raw Coal</u>	<u>THF extn Residue</u>	<u>THF Extract</u>
03	3.34	0.43	0.78	0.33
22	10.32	0.49	0.64	0.33
24	3.55	0.45	0.61	0.33
34	10.30	0.47	0.73	0.33

After the TLC plates are developed with solvent, they are examined under SWUV and LWUV illumination and the appropriate spots marked. The plates are then placed in an enclosed chamber in the presence of iodine crystals. Iodine in the iodine-saturated atmosphere will dissolve in organic phases, producing clearly visible brown spots. This is of particular use in spotting paraffinic (aliphatic) and cycloparaffinic (alicyclic) materials which are not detectable under either SWUV or LWUV light.

Figure 12 shows the patterns obtained with pure hexane (which moves the paraffinic compounds very well) and in 20% methylene chloride in hexane (which moves all of the compound groups well). All extracts examined produce the two aliphatic (iodine-staining) group spots as well as the group of LWUV and SWUV spots, with no clear qualitative differences. Many nonplastic coals when developed in hexane show a third iodine-staining (aliphatic or cycloaliphatic) spot, slightly behind the two main paraffinic spots. Most highly plastic coals in this group do not show this spot. However, several sparingly plastic coals do not exhibit this spot, and about one quarter of the highly fluid coals also exhibit this spot (not present in Figure 12). This does not therefore provide a reliable means of predicting fluid behavior.

In all of the TLC work a strong spot remains stationary at the point of sample loading, indicating the presence also of more highly polar constituents which are substantially insoluble in hexane and in the methylene chloride - hexane mixture.

To undertake quantitative HPLC work a high grade silica phase (E. Merck Silica Kieselgel 60, 230-240 mesh) is dried at 115°C for eight hours, then dry-tapped into a 54 in. x 1/2 in. i.d. stainless steel column

Figure 12

Mobility of Components from THF Extracts on a Silica TLC Plate

and equilibrated with dry pentane, using a Waters 6000A pump. The THF extract to be analyzed is separated from solvent by vacuum evaporation and the residue treated with methylene chloride to dissolve the paraffinic and aromatic components (typically 30-45% of the total extraction residue). This soluble fraction is introduced to the top of the silica column. Then the following three steps are carried out:

(1) Three hundred ml of pentane is added, and 20 15-ml fractions are collected. These fractions are combined as the paraffin fraction. At the end of this stage the paraffin fraction is completely eluted and the first trace of UV-absorbing (aromatic) material is evident.

(2) The solvent is then changed to 100% methylene chloride, which is pumped through (several hundred ml per run) until the effluent, initially quite colored, is lightened to match a very pale yellow standard. The methylene chloride effluent is collected as the aromatic fraction.

(3) Column flow is then reversed, and methanol is backflushed through the column to remove the residual polar organic material. Methanol dissolves silica to a slight extent. In order to quantitate the methanol-soluble polar fraction, therefore, it is necessary to evaporate the methanol, dissolve the organic portion of the residue with THF, dry the organic solution over sodium sulfate, filter with 0.4-micron Millipore to remove dispersed inorganic solids, then dry the THF solution to constant residue weight.

It would seem easier to use THF instead of methanol at the beginning of step 3. However, the solvent power of THF varies from bottle to bottle owing to variations in moisture content. The above procedure, starting with methanol, proves to give more reproducible data.

The result of this quantitative separation is that the THF extract is first divided into a methylene chloride-soluble fraction -- typically

Table 20
Chromatographic Analysis of CH_2Cl_2 -solubles from THF Extracts of Coals

Coal	Extracted by THF	Soluble in CH_2Cl_2^*	Eluted from silica column				ln(max calcd ASTM fluidity)
			pentane	CH_2Cl_2	methanol	total	
02	11.99%	34.35%	4.84%	34.80%	42.74%	82.4%	2.6
01	12.75	38.33	11.95	42.83	40.88	95.7	2.8
30	14.54	45.48	11.82	38.71	40.65	91.2	3.3
31	14.24	10.03	11.21	48.23	43.39	102.8	3.2
28	11.10	43.06	32.77	36.82	30.16	99.8	3.5
40	11.03	37.03	7.91	49.00	43.52	100.4	3.8
18	12.75	27.32	6.35	49.64	39.88	95.9	3.8
03	13.37	47.96	3.32	20.29	55.30	78.9	3.5
24	14.85	29.24	3.68	36.99	52.22	92.9	3.8
09	13.02	29.51	8.58	51.35	39.89	99.8	3.9
17	13.99	31.91	13.14	42.46	42.05	97.7	4.4
08	12.44	31.53	17.02	23.23	57.78	98.0	4.3
05	12.58	37.00	4.22	43.46	48.91	96.6	5.0
10	13.62	30.45	3.68	47.14	47.19	98.0	5.3
11	13.45	39.43	9.49	34.27	56.24	100.0	5.0
19	15.69	27.91	4.62	42.51	54.71	101.8	5.6
26	10.79	39.39	8.45	44.99	39.16	92.6	5.6
14	17.21	31.77	11.02	26.46	63.98	101.5	6.2
36	14.67	25.41	7.30	59.50	35.20	102.0	6.4
38	12.21	46.20	4.71	39.99	60.81	105.5	6.0
39	12.48	41.31	10.91	77.00	47.54	135.4	6.0
15	13.49	33.02	4.21	41.54	63.28	109.0	7.5
12	12.74	---	7.06	44.67	44.50	96.2	6.7
37	13.63	37.98	9.07	47.22	41.61	97.9	7.5
13	14.65	44.00	8.27	58.81	50.87	118.0	7.6
04	14.59	27.20	5.17	48.55	42.59	96.3	7.4
07	19.64	23.60	4.38	52.31	38.31	95.0	8.4
35	15.72	31.83	6.97	49.70	54.90	111.6	11.1
06	17.82	24.72	4.49	52.59	45.07	102.2	12.0
27	16.34	33.16	5.47	66.57	22.41	94.5	12.5
32	18.86	29.97	9.63	56.36	34.74	100.7	14.2
21	16.25	32.85	6.88	45.43	40.35	92.7	14.2
25	10.99	42.68	19.93	49.94	38.26	108.1	14.8

c o n t i n u e d

Table 20, continued

Coal	Extracted by THF	Soluble in CH_2Cl_2 *	Eluted from silica column				ln(max calcd ASTM fluidity)
			pentane	CH_2Cl_2	methanol	total	
22	14.16%	60.63%	5.96%	33.03%	53.06%	92.1%	14.8
34	17.07	37.18	13.17	61.20	30.68	105.1	14.9
23	14.21	36.59	5.25	51.63	43.34	100.2	15.3
33	17.98	39.81	21.00	47.61	31.25	99.9	16.4

* Fraction of material Soxhlet-extracted by THF that, after THF removal, is redissolved by methylene chloride.

30-45% of the total material -- an insoluble fraction. The soluble fraction is then partitioned into three fractions by the above three steps, each fraction assayed gravimetrically after evaporation of the volatile solvent. In view of the number of sample-handling steps involved the material balance is surprisingly good. HPLC assays of the THF extracts of 37 of the 40 coals are given in Table 20. Thirty-two of the 37 balance within 10%, and 22 balance within 5%.

The data in Table 20 are listed in order of increasing ASTM maximum fluidity. The fraction eluted from the silica gel column by methylene chloride shows a positive correlation with fluidity.

5.3.6 Petrographic Aspects of Plasticity

5.3.6.1 Plasticity and Geochemistry

Early analyses (excluding the highest ranked coals) indicated that plasticity increases with increasing coal rank. That factor, however, is obviously not the only parameter contributing to variations in thermoplastic properties. Yarzab et al. (59) note that coals with high organic sulfur may develop plastic properties at lower rank than would ordinarily be expected. They note the study by Ignasiak et al. (6) of an unusual Yugoslavian coal of lignite/subbituminous rank, containing 12% sulfur and exhibiting coking properties.

Analysis of recently published data for two Appalachian coals reveal similar trends. Sentfle and Davis (61) have studied a wide rank range in the Lower Kittanning coal of the northern Appalachian coal field. In Table 21 we have listed partial data for the high volatile bituminous (up to 1.1% $R_{\max}$ vitrinite reflectance) coals in their study. The Gieseler plasticity listed is obtained at one-half normal torque, which yields ddp_m values considerably less than those obtained at the standard 1.4 oz-in torque. For any given vitrinite reflectance value, the higher plasticity

Table 21

Plasticity of the Lower Kittanning Coal*

<u>Whole coal (PSOC)</u>	<u>Vitrinite concentrate</u>	<u>Organic sulfur</u>	<u>Vitrinite R(max)</u>	<u>Plasticity ddpm</u>
1141		0.52%	1.02%	2,195
1142		0.66	0.88	8,951
1143		1.71	0.78	16,634
1146		0.57	1.03	14,163
1166		0.91	0.92	125
1167		0.49	0.84	949
1168		0.49	0.84	649
1169		0.74	0.83	4,271
1170		0.67	0.91	2,590
1171		1.38	0.78	30,000
1193		0.68	1.04	8,013
1266		0.46	0.83	94
1269		0.63	0.71	9
1270		1.96	0.59	5
1274		2.06	0.67	106
1278		0.70	0.64	2
1281		0.77	0.63	2
1286		1.60	0.61	3
1289		1.93	0.66	6
1296		1.09	0.87	30,000
1305		1.48	0.88	21,632
1309		0.71	1.01	5,986
1336		0.86	0.92	7,085
1340		0.44	1.01	11,632
	15	0.67	1.04	3,108
	17	0.93	0.91	15,292
	19	1.20	0.83	24,674
	23	0.70	1.09	3,390
	25	0.91	0.88	6
	26	0.61	0.87	291
	27	0.69	0.83	152
	28	0.83	0.90	13,918
	34	0.79	0.96	425
	35	1.28	0.86	30,000
	43	0.87	1.09	29,956

c o n t i n u e d

Table 21, Continued

<u>Whole coal</u> <u>(PSOC)</u>	<u>Vitrinite</u> <u>concentrate</u>	<u>Organic</u> <u>sulfur</u>	<u>Vitrinite</u> <u>R(max)</u>	<u>Plasticity</u> <u>ddpm</u>
	62	0.43%	0.83%	24
	63	1.32	0.53	21
	64	1.87	0.64	145
	65	0.63	0.61	2
	66	0.83	0.59	2
	67	1.33	0.60	106
	68	1.17	0.91	30,000
	70	1.45	0.90	29,994
	71	0.75	1.04	5,921
	82	0.75	0.96	18

* from J. T. Sentfle and A. Davis, Ref. 61. Samples listed have vitrinite reflectances below 1.1% R(max); plasticity by Gieseler plastometer with torque setting 0.70 oz-in (one-half standard torque).

coals are generally those with higher organic sulfur. Certain coals (e.g., PSOC - 1269) which by rank would fall among the most plastic coals in our study exhibit negligible plasticity.

Cole and Williams (62) studied the Manchester coal of the Southwestern Reserve District of eastern Kentucky. Several of the coals utilized by Williams (63) have also been made available to the Coal Petrology Laboratory at IMMR (Table 22). Our vitrinite reflectance values have proven to be consistently lower than Williams' values. Therefore we can estimate 'IMMR reflectance' for samples which were unavailable to us. As in the study of the Lower Kittanning coals, Manchester samples with ranks similar to our high-plasticity coals are not nearly as plastic unless they also have high organic sulfur contents. The most notable example of this trend is their sample 23-D-64 (their sample numbers correspond to the Carter Coordinate location of the sample site), with 2.08% organic sulfur and an estimated 0.74% $R_{\max}$ vitrinite reflectance. The maximum fluidity of 28,000 ddpm is a little lower than the projected plasticities of coals from plants A, G, and P. In comparison, the low-sulfur coal 19-I-68 has a similar $R_{\max}$ but only 2% of the maximum fluidity of 23-D-64.

Most western Kentucky coals are relatively high in total sulfur and organic sulfur. Therefore little variation should be expected for most of our sample set. Coals 38-41, however, are from a seam known to have low sulfur.

5.3.6.2 Optical Microscopy of Semicokes

Petrographic investigations have centered upon description of the semi-cokes resulting from ASTM Gieseler plasticity runs. The description which follows is roughly ordered in terms of increasing plasticity of the coal and of increasing complexity of the semi-coke.

Table 22
Plasticity of the Manchester Coal*

<u>Sample number</u> <u>Cole &</u> <u>Williams</u> <u>KCER</u>		<u>Organic</u> <u>sulfur</u> <u>%</u>	<u>Vitrinite R(max)</u> <u>Williams</u> <u>(1979)**</u> <u>IMMR</u>		<u>Plasticity</u> <u>Gieseler,</u> <u>ddpm</u>
23-D-64		2.08	0.83%	0.74% ¹	28,000
16-B-64	5047	1.18	0.86	0.78	8,300
21-D-64	5046	1.31	0.83	0.83	5,000
2-F-66		1.04 ² 0.66 ²	0.90	0.81 ¹	1,800
7-C-65		0.84	0.94	0.85 ¹	1,400
3-H-65		0.98	0.71	0.65 ¹	1,000
19-I-68	5040	0.75		0.75	550
21-J-69	5039	0.58	0.93	0.85	350
24-K-67	5033	0.81	0.81	0.71	300
10-H-69	5037	0.84	0.92	0.84	260
4-I-67	5036	0.81	0.90	0.80	225
20-I-68	5038	0.69	0.92	0.80	210
17-J-65	5034	1.16	0.79	0.69	105
15-C-62		0.79	0.88	0.79 ¹	95

* from G. A. Cole and D. A. Williams, Ref. 62.

** from D. A. Williams, Ref. 63.

¹ Estimated value based upon offsets between Williams' and IMMR data on similar coals.

² It is not clear which of these two splits was subjected to the Gieseler plastometer analysis.

The Springfield (KY #9) coal from Daviess Co., KY (Coal #2) is of high volatile C bituminous rank, and exhibits a very low maximum fluidity (ca. 10 ddpm) in ASTM Gieseler runs. The resulting semi-coke (Plate 1) has large intact regions of vitroplast (resolidified melted vitrinite) with no evidence of internal flow. The presence of devolatilization vacuoles indicates that the coal has been brought to a (marginally?) fluid state. The only real visual evidence of flow is the existence of rounded corners on the vitroplast zones. This is seen also in the semi-coke from Coal #40 (Plate 2), another coal exhibiting low maximum fluidity (ca. 20-30 ddpm) in ASTM Gieseler runs. Plate 3 shows for comparison the maceral assemblage of untreated Coal #2. The apparent similarity of value of the vitrinite (Plate 3) and the vitroplast (Plates 1 and 2) is an artifact of the automatic metering of the Leitz Orthomat camera. The vitrinite has a reflectance of $0.42\% R_{\max}$, while the vitroplast is considerably brighter ($1.58\% R_{\max}$ for this coal).

Highly plastic coals are represented by the KY #6 (Coal #22) and KY #11 (Coal #34) coals from Union Co., KY. Coal #34 is a highly plastic high volatile A bituminous coal; under ASTM conditions its fluidity exceeds that measurable by the Gieseler plastometer (greater than 30,000 ddpm). Its semi-coke (Plate 4) shows signs of this high fluidity, with inertinite macerals dispersed throughout the vitroplast. In regions between inertinite fragments and the vacuoles the vitroplast appears to have resolidified as a relatively isotropic mass. This is distinctly different from the semi-coke of another highly plastic coal, Coal #22 (Plate 5), where a fine mosaic structure can be detected. The 'fluid' vitroplasts of the semi-cokes in Plates 4 and 5 can be compared with the relatively intact vitroplast zones of the semi-coke of the sparingly plastic Amos coal (Coal

Plate 1

Gieseler plastometer semi-coke of Coal #2, showing fusinite (F), vitroplast (VP), and devolatilization vacuole (open arrow). Marker bar is 50 microns.

Plate 2

Gieseler plastometer semi-coke of Coal #40, showing vitroplast (VP) and micrinite (M). Marker bar is 50 microns.

Plate 3

Untreated Coal #02, showing vitrinite (V), sporinite (S), cutinite (C) and fusinite (F). Sporinite and cutinite are both grouped as exinite. Marker bar is 50 microns.

Plate 4

Gieseler plastometer semicoke of Coal #34, showing vitroplast (VP), fusinite (F) and pyrite (py). Photograph uses crossed nicols with gypsum plate. Marker bar is 50 microns.

Plate 5

Gieseler plastometer semi-coke of Coal #22, showing vitroplast (VP), fusinite (F) and pyrite (py). Photograph uses crossed nicols with gypsum plate.

Marker bar is 50 microns.

#40, Plate 2). The rank (by vitrinite reflectance) of Coals #22 and #40 is virtually identical.

There are considerable differences in the sulfur contents of these two coals, Coal #22 having 2.91% total S (1.35% organic S), and Coal #40 having 0.80% total S. Several researchers have discussed the interrelationship among rank, sulfur content (particularly organic sulfur) and fluidity.

Comparison of the semi-coke of the highly plastic Coal #22 (Plate 5) with an untreated coal taken from the same preparation plant (Plate 6) shows a much greater contrast between raw coal and semi-coke than was found in comparing the raw coal with the semi-coke of a sparingly plastic coal (Plates 1 and 3).

The next step in the development of semi-cokes is the emergence of a true anisotropic mosaic structure. Coal #25, a high volatile A bituminous Mason seam coal, taken from Bell County in southeastern Kentucky, exhibits this structure in its semi-coke (Plate 7). This is also a highly plastic coal (greater than 30,000 ddpmm).

The Jet Propulsion Laboratory's tapered-screw extrusion pump brings a plastic coal typically to 455°C for a period of time somewhat less than two minutes, in the course of which the coal is brought to a fluid state and is extruded through a small orifice. Plate 8 shows a sample of extrudate of Springfield (KY #9 seam) coal, taken from a previous study by one of us (41,64). The thermal treatment is considerably less severe than that encountered in a normal ASTM Gieseler plasticity analysis. Primary evidence for this is the presence of some residual exinite macerals (Plate 8). Exinites would not be expected to survive the more severe plasticity runs.

Plate 6

Untreated Coal #21, showing vitrinite (V), fusinite (F), semifusinite (SF), micrinite (M) and sporinite (S). Marker bar is 50 microns.

Plate 7

Gieseler plastometer semi-coke of Coal #25, showing anisotropic coke (AC) and fusinite (F). Photograph uses crossed nicols with gypsum plate. Marker bar is 50 microns.

Plate 8

Extrudate of Springfield (KY #9) coal, showing remnant of exinite (E) maceral in field of vitrinite/vitroplast and inertinites. Marker bar is 50 microns.

Residues from thermal hydroliquefaction of hvb coals have zones of anisotropic coke. The fine structure will be in part a function of the temperature/shear stress history of the reacting plastic coal. Plate 9 shows the residue from another sample of Springfield (KY #9 seam) coal, after a liquefaction run in the Sasol hydroliquefaction plant in South Africa. Under these conditions (heating for a relatively long period under pressure, and with an upper temperature limit probably below 460°C), a fine-grained anisotropic coke is the dominant constituent of the residue. This structure is not seen in the semi-cokes from coals of similar rank after subjection to the ASTM Gieseler plasticity analysis.

5.3.6.3 Petrographic Analysis of Semicokes

A tabulation of semicokes from ASTM Gieseler plastometry runs has been completed for all 40 coals and is presented in Table 23. Vitroplast maximum reflectances have been determined on the semicokes of all but a few of the most highly plastic coals.

A number of semicokes from isothermal plastometry runs with five selected coals have also been examined. Three of these coals (nos. 02, 09 and 40) are sparingly plastic, and their residues have been examined after runs at various temperatures in the range $403\text{--}443^{\circ}\text{C}$. The remaining two coals (nos. 25 and 34) are highly plastic; their residues have been examined after isothermal runs at various temperatures in the range $391\text{--}420^{\circ}\text{C}$. The sparingly plastic coals yield semi-cokes with vitroplast reflectances of 1.1-1.3%, increasing moderately with increasing temperature, and in all cases showing evidences of no more than minor flow. The highly plastic coals yield semicokes showing evidence of considerable flow, the extent of flow increasing with temperature. For coal #25 at 420° this extends all the way to formation of anisotropic semi-coke. These results are summarized in Table 24.

Plate 9

Residue fragment from liquefaction (SASOL) of Springfield (KY #9) coal, showing anisotropic coke (AC) and fusinite (F). Photograph uses crossed nicols with gypsum plate. Marker bar is 50 microns.

Table 23

Petrographic Examination of Semi-cokes from ASTM Gieseler Runs

Coal	Vitroplast maximum reflectance		"Flow" type				Anisotropic Coke
	R _{max}	std. dev.	Intact or Minor flow		Flow		
01	1.40	± 0.068	X	.	.	.	.
02	1.58	0.015	X	.	.	.	.
03	1.48	.060	X	.	.	.	.
04	1.75	.096	X	.	.	.	.
05	1.45	.046	X	.	.	.	.
06	1.36	.033	X	.	.	.	.
07	1.47	.038	X	.	.	.	.
08	1.38	.051	X	.	.	.	.
09	1.76	.054	X	.	.	.	.
10	1.48	.066	X	.	.	.	.
11	1.43	.036	.	X	.	.	.
12	1.57	.030	X	.	.	.	.
13	1.59	.034	X	.	.	.	.
14	1.59	.113	X	.	.	.	.
15	1.64	.053	.	.	X	.	.
16	1.43	.047	X	.	.	.	.
17	1.48	.067	X	X	.	.	.
18	1.46	.041	X	.	.	.	.
19	1.69	.119	X	.	.	.	.
20	1.57	.039	.	X	.	.	.
21	---		.	.	X	.	.
22	1.76	.115	.	.	.	X	.

-- continued --

Table 23, cont.Petrographic Examination of Semi-cokes from ASTM Gieseler Runs

Coal	Vitroplast maximum reflectance		"Flow" type				
	R _{max}	std. dev.	Intact or Minor flow		Flow	Anisotropic Coke	
23	1.90	<u>+</u> .015	.	.	.	X	.
24	1.44	.091	X	.	.	.	.
25	---		.	.	.	.	X
26	1.90	.177	.	X	.	.	.
27	---		.	.	.	X	.
28	1.52	.048	X	.	.	.	.
30	1.29	.047	X	.	.	.	.
31	1.80	.042	X	.	.	.	.
32	1.64	.058	X	.	.	.	.
33	1.67	.049	.	.	X	.	.
34	1.68	.034	.	.	X	.	.
35	1.62	.041	.	.	X	.	.
36	1.76	.104	.	.	.	X	.
37	1.58	0.031	.	.	X	.	.
38	1.59	.032	X	.	.	.	.
39	1.50	.049	X	.	.	.	.
40	1.64	.029	X	.	.	.	.
41	1.55	.025	X	.	.	.	.

Table 24

Examination of Semicokes from Selected Isothermal Plastometry Runs

Coal	Temp.	vitroplast maximum reflectance		"Flow" type*					comments
				1	2	3	4	5	
02	407 C	1.09%	± .018%	X	.	.	.	.	little evidence of softening
	411	1.08	.029	X	.	.	.	.	beginning of fusion, some liptinite present
	415	1.14	.032	X	.	.	.	.	oxidation rims forming
	419	1.18	.048	X	.	.	.	.	
	423	1.10	.028	X	.	.	.	.	
09	403	1.12	.041	X	.	.	.	.	relatively intact pieces
	409	1.15	.045	X	.	.	.	.	some liptinite present
	415	1.19	.030	X	.	.	.	.	oxidation rims forming
	421	1.21	.031	X	.	.	.	.	thicker oxidation rims
	427	1.24	.022	X	.	.	.	.	still thicker oxidation rims
25	404	n.a.		.	.	X	.	.	reflectance measurement not possible
	409	n.a.		.	.	X	.	.	
	412	n.a.		.	.	.	X	.	
	416	n.a.		.	.	.	X	.	
	420	n.a.		.	.	.	.	X	
34	391	1.07	.056	.	X	.	.	.	
	397	1.20	.043	.	X	.	.	.	
	400	1.20	.032	.	X	.	.	.	
	403	1.24	.029	.	X	.	.	.	areas of unflowed vitroplast
	409	1.28	.034	.	.	X	.	.	
40	419	1.21	.058	X	.	.	.	.	intact vitroplast, liptinite present
	425	1.31	.046	X	.	.	.	.	
	431	1.30	.031	X	.	.	.	.	better flow developing
	437	1.21	.034	X	.	.	.	.	oxidation rims forming
	443	1.42	.060	X	.	.	.	.	

* On a scale of 1 to 5, where 1 = intact structure or evidence of minor flow, to 5 = extensive flow and conversion to anisotropic coke

Semi-cokes from three plastic coals have been examined after heating to a specified temperature in a Gieseler crucible and then holding at that temperature for 10-45 min. The semi-cokes show liptinites after 10 min but not in general after longer periods of heating. At constant temperature the extent of flow evident in the residual semi-coke increases with time. This is especially clear for Coal #25 (Table 25).

Many of the semi-cokes examined (Tables 24 and 25) exhibit oxidation rims. It has been generally assumed by most users of data obtained from the Gieseler plastometer that coal in its plastic state is continuously outgassing, and that the flow of pyrolysis gases substantially protects the plastic coal from reaction with atmospheric oxygen. This assumption may not be well taken. Further systematic testing with inert gas padding may be indicated.

5.3.7 Additional Experiments

In the course of the main study, several small experiments were conducted to supplement the work reported in the preceding sections. These are briefly noted below. Additional details are given in the Appendix (Part 9).

* * *

Crucible Tests. Five Gieseler crucible-stirrer assemblies were available for the isothermal Gieseler analyses. To check for non-equivalence, a series of 20 isothermal Gieseler determinations was conducted at 411-413°C, on the same coal, using the five crucible-stirrer sets in rotating sequence. Analysis of the results indicates that one crucible-stirrer assembly yields significantly different results (probability greater than 99%). Another is somewhat suspect. The three other crucible-stirrer assemblies give interchangeable results. Data are

Table 25

Effect of Time of Isothermal Heating upon Petrographic Characteristics of Selected Semicokes

coal	temp. °C	time, min.	vitroplast maximum reflectance	Flow type *					comments
				1	2	3	4	5	
25	420	10	n.a.	.	X	.	.	.	some liptinites present
		20	n.a.	.	.	X	.	.	
		30	1.2	.	.	.	X	.	
		45	n.a.	.	.	.	.	X	
28	420	10	0.85	X	.	.	.	.	liptinites present
		20	1.15	X	.	.	.	.	few liptinites remaining
		30	1.25	X	.	.	.	.	oxidation rims developing
		45	n.a.	X	.	.	.	.	slight change from 20-min. sample
32	420	10	n.a.	.	X	.	.	.	some liptinites present
		20	n.a.	.	X	.	.	.	thin oxidation rims
		30	n.a.	.	.	X	.	.	

* see footnote to Table 24

detailed in Part 9.1. Plastometry data obtained in this study are obtained only from the three demonstrably equivalent crucible/stirrer assemblies.

* * *

Weathering and Plasticity. Weathering (low-temperature autoxidation) is well known to result in the diminution of coal fluidity (22, 23, 52-54, 65, 66). A portion of Coal #34 was placed on a laboratory shelf in a wide mouth jar open to the atmosphere, and was periodically sampled and subjected to ASTM Gieseler plastometry over a six-month period. The decrease in $\ln(\text{max intersection fluidity})$ with time is roughly linear, as is the melting slope. During the course of this experiment the coking slope did not appear to change significantly. Data are given in Part 9.2.

* * *

Swelling of Coal Residues. From the viewpoint of polymer science the organic portion of a hvb coal may be viewed as -- primarily -- a three-dimensional network polymer structure of 'infinite molecular weight', encompassing a lesser amount of discrete and extractable molecules. The process of transformation of coal from a refractory solid to a fluid must at the absolute minimum entail the mechanical rupture of sufficient linkages to destroy the three-dimensional network.

When we compare sparingly fluid and highly fluid coals, we may advance two different kinds of structural argument to explain the differences in behavior. The coals may differ chemically, in the distribution and thermal reactivity of their most vulnerable chain segments or crosslinking groups. Or the coals may differ physically in terms of differing effective crosslink densities. (A 'physical' explanation of a highly fluid coal might be that it has a very low crosslink density, so that it requires the rupture of only a very few structural bonds in order to be transformed into a fluid.)

Recent work (67-72) has shown that hvb coals can indeed be viewed as moderately crosslinked networks, and that effective crosslink density can be estimated by the swelling behavior of these coals in contact with appropriate solvents.

Using a simple adaptation of a method described by Larsen (70-71) we have taken the crosslinked network residues from DMF extractions of four selected coals and have determined their equilibrium swelling volume ratios in fresh DMF. The experimental details are given in Part 9.3. Two of the four coals are only sparingly plastic; one other is intermediate, and the fourth is highly plastic. All coal residues underwent a volume expansion of more than 100%. All swelled to very nearly the same degree. There is no indication that the highly plastic coals have perceptibly different crosslink densities than less plastic coals of the same rank.

This observation argues against the 'physical' explanation of differences in fluidity among coals of similar rank.

* * *

6. DATA ANALYSIS

6.1 Plastometry Curves

The shape of a plot of $\ln(\text{Gieseler fluidity})$ against time is, as Fitzgerald has noted (39,40), characterized by a substantially linear coking slope. The initial melting zone, even under ASTM conditions (Figure 3) and very markedly under isothermal conditions (Figure 4), also has a substantially linear character (42). The analysis of plastometry data in terms of slopes and intercepts and slope intersections greatly facilitates the management of the slightly over one thousand Gieseler determinations in the present study.

The raw Gieseler data are loaded into a program (Part 9.4) which sets upper and lower limits for slope calculations, determines the least-squares slopes and intercepts, and also provides a plot of the data, permitting us to verify that the calculated slopes are appropriate to the experimental data. Table 26 illustrates the output of an isothermal Gieseler run with Coal #44. For this run the fluidity data used to calculate slopes were greater than 5 ddpm and less than one-half the highest observed fluidity. The input data printout is labelled to indicate which data are used for slope calculations.

The analysis at the end of Table 26 provides statistics for the two slope calculations. As is typical of highly fluid coals, the melting slope is defined by only a few data and has a relatively large standard deviation. The coking slope is flatter and is determined with considerably better precision.

Figure 13 provides an illustration of a coal sufficiently fluid that the observed maximum fluidity is of little significance: the instrument

Table 26

DEC. 24 1983

 ** GIESELER SLOPE ANALYSIS **
 ** WESTERN KENTUCKY UNIVERSITY **
 ** Revision 2 -- December 83 **

USDOE COAL #44 - KCER #7799

ISOTHERMAL #51: 419.1 +/-0.8C, 375 psig

FOR THE FOLLOWING PARAMETERS...

MINIMUM FLUIDITY FOR SLOPE CALCN = 5.000 D.D.P.M.

MAXIMUM FLUIDITY FOR SLOPE CALCN = .5 OF MAX OBSERVED FLUIDITY

DATA INTERVAL (IN SECONDS) = 60

***** INPUT DATA *****

Time, min. d.d.p.m.

1	2.4	too low
2	8.2	INCLUDED IN SLOPE CALCN
3	45.2	INCLUDED IN SLOPE CALCN
4	302.5	INCLUDED IN SLOPE CALCN
5	4629	INCLUDED IN SLOPE CALCN
6	30276	too high
7	30131	too high
8	30100	too high
9	30437	too high
10	28077	too high
11	13055	INCLUDED IN SLOPE CALCN
12	7125.4	INCLUDED IN SLOPE CALCN
13	3999	INCLUDED IN SLOPE CALCN
14	2348	INCLUDED IN SLOPE CALCN
15	1789	INCLUDED IN SLOPE CALCN
16	1261	INCLUDED IN SLOPE CALCN
17	884.8	INCLUDED IN SLOPE CALCN
18	577.9	INCLUDED IN SLOPE CALCN
19	399.2	INCLUDED IN SLOPE CALCN
20	239.8	INCLUDED IN SLOPE CALCN
21	173.9	INCLUDED IN SLOPE CALCN
22	110.2	INCLUDED IN SLOPE CALCN
23	77.8	INCLUDED IN SLOPE CALCN
24	41.5	INCLUDED IN SLOPE CALCN
25	40.6	INCLUDED IN SLOPE CALCN
26	22.2	INCLUDED IN SLOPE CALCN

Table 26 (Cont.)

USDOE COAL #44 - KCER #7799
 ISOTHERMAL #51: 419.1 +/-0.8C, 375 psig

DEC. 24 1983
 -- PAGE 2 --

27	13.2	INCLUDED IN SLOPE CALCN
28	6.8	INCLUDED IN SLOPE CALCN
29	4.8	too low
30	3.8	too low
31	3	too low
32	2.3	too low
33	1.7	too low
34	1.2	too low
35	1	too low
36	.7	too low

*** END INPUT DATA ***

ANALYSIS OF GIESELER RUN

MAXIMUM OBSERVED FLUIDITY = 30276 DDPM AT 6 MINUTES

SLOPE ANALYSIS DATA

MELTING SLOPE FROM 2 TO 5 MINUTES:

SLOPE	2.090887*	STD DEVN	.167532616
INTERCEPT	-2.30125*	STD DEVN	.615554138
DEGREES OF FREEDOM = 2			

COKING SLOPE FROM 11 TO 28 MINUTES:

SLOPE	-.415829*	STD DEVN	6.47465453E-03
INTERCEPT	13.82469*	STD DEVN	.130647983
DEGREES OF FREEDOM = 16			

INTERSECTION MAXIMUM FLUIDITY = 69537.46 DDPM AT 6.43 MINUTES

Figure 13

ASTM Gieseler Plastometry Run of a Highly Fluid Coal

pegs at 30,000 ddpm. The program calculates the $\ln(\text{maximum intersection fluidity})$ at line 5200. In this case the intersection maximum fluidity is a better descriptor than the conventional "greater than 30,000."

All of these measurements of isothermal fluidity -- melting slope, $\ln(\text{maximum observed fluidity})$ and $\ln(\text{intersection maximum fluidity})$ -- show Arrhenius dependencies when plotted over a range of temperatures. Figure 5 illustrates this for a representative coal. These data, for the 29 coals subjected to series of isothermal measurements, have been reported in Tables 4 and 5. Several generalizations may be tentatively offered regarding the activation energies found for these parameters.

- * Activation energies of the coking slopes do not vary appreciably with fluidity. For these coals, as for a group of English coals (39), they are all in the vicinity of 50 kcal/mole.

- * Activation energies of the melting slopes tend to increase with increasing coal fluidity, typically from 25-30 kcal for sparingly plastic coals to 50-55 kcal for highly plastic coals. The ratio melting slope/coking slope is markedly higher for the highly fluid coals.

- * Activation energies of $\ln(\text{maximum fluidity})$ tend to decrease with increasing plasticity, from 30-35 kcal for sparingly plastic coals to 10-20 for the more highly plastic coals.

Maximum fluidities measured under isothermal conditions and at temperatures near the ASTM temperature of maximum fluidity are substantially greater than the maximum fluidities found in the ASTM determination. The ratio isothermal maximum fluidity/ASTM maximum fluidity is typically 2 to 3 for sparingly fluid coals, and in the range 5 to 8 for moderately plastic (30-300 ddpm) coals. For the highly plastic coals the

isothermal fluidities exceed the instrumental capabilities at temperatures near ASTM maximum fluidity.

The fluidity span (the time interval during which fluidity exceeds a specified value) is easily calculable from slope and fluidity data. The 'melting time', t_m , required for the coal fluidity to increase from 1 ddpm to the intersection maximum fluidity, is a part of the definition of melting slope:

$$m = f/t_m \quad (2)$$

where m is melting slope and f is $\ln(\text{maximum fluidity})$. Since m and f are both determined experimentally, t_m is readily accessible from Eqn. 2. Similarly to total coking time, t_c , is accessible from $\ln(\text{maximum fluidity})$ and the coking slope, c . Since the total fluidity span t_f is equal to $t_m + t_c$,

$$t_f = f(1/m + 1/c) \quad (3)$$

If any fluidity other than 1 ddpm is desired as a minimum in defining fluidity span, then

$$t_f = (f - f')(1/m + 1/c) \quad (4)$$

where f' is the natural logarithm of the desired fluidity in ddpm.

Since melting slope, coking slope and $\ln(\text{intersection maximum fluidity})$ all follow Arrhenius dependencies, this relationship makes it convenient to calculate the fluidity span of a coal at any interpolated temperature (or prudently extrapolated temperature) for any process-determined minimum fluidity and temperature.

For the purposes of prediction of fluid properties, the isothermal data for all 29 coals has been interpolated in Tables 4 and 5 to common reference temperatures. The key variables are:

maximum fluidity (e.g., at 400°C)

melting slope (e.g., at 400°C)

coking slope (e.g., at 400°C)

In addition, from the ASTM data (Table 2) and the ASTM slope and intersection maximum fluidity calculations (Table 27), the key variables are:

ASTM maximum fluidity

ASTM melting slope

ASTM coking slope

and, in addition, the characteristic temperatures of softening, maximum fluidity, and solidification. If all of these variables could be estimated with reasonable accuracy by regression equations, we would be able to provide a means of predicting in some detail the fluid behavior of hvb coals. The following section addresses this task.

6.2 Selection of Candidate Predictors

The independent characterization variables available include seven from Table 8 (moisture, ash, volatile matter, and four elemental assays), five from Table 9 (pyritic sulfur, organic sulfur, ash sulfate, heating value and FSI), five from Table 11 (vitrinite, pseudovitrinite, exinite, resinite, fusinite), three from Table 12 (reactive macerals, Parr mineral matter, vitrinite maximum reflectance), two from Table 13 (DMF and THF-extractables), pyrolysis counts per microgram from Table 16, twelve pyrolysis/GC window signals from Table 17, and one spectroscopic variable from Table 18 (H_{ar}/H_{al} ratio).

In addition to these 36 sets of data there are several derived characterizations which are conceivably of useful predictive power. These include 'preasphaltenes' (the difference between the amounts of material

Table 27

ASTM Gieseler Plasticity: Computed Values*

coal	melting slope		coking slope		max fluidity		(slope intersection)
	(min ⁻¹)		-(min ⁻¹)		ln(max flu)		max fluidity
01	0.219	± .043	0.582	± .118	2.841	± .346	17.1 ddpm
02	0.212	.030	0.563	.033	2.646	.109	14.1
03	0.253	.015	0.776	.015	3.496	.173	33.0
04	0.791	.096	0.759	.011	7.364	.429	1,578.
05	0.398	.071	0.718	.055	4.971	.061	144.
06	1.303	.066	1.009	.041	11.995	.571	161,900.
07	0.902	.056	0.895	.147	8.447	.390	4,662.
08	0.294	.016	0.805	.022	4.285	.220	72.6
09	0.280	.037	0.722	.152	3.925	.110	50.7
10	0.382	.013	0.920	.055	5.254	.044	191.
11	0.407	.003	0.814	.129	5.032	.130	153.
12	0.638	.014	0.808	.059	6.685	.127	801.
13	0.616	.010	0.732	.046	7.596	.120	1,989.
14	0.552	.068	0.706	.015	6.198	.100	492.
15	0.667	.045	0.851	.038	7.515	.043	1,835.
16	0.328	.008	0.790	.034	4.726	.097	113.
17	0.312	.009	0.732	.041	4.403	.055	81.7
18	0.288	.016	0.708	.058	3.795	.094	44.5
19	0.539	.099	0.663	.027	5.557	.109	259.
20	0.334	.018	0.778	.022	4.459	.122	86.4
21	1.298	.020	1.079	.039	14.246	.515	1.54 x 10 ⁶
22	1.148	.084	1.114	.041	14.776	.325	2.61 x 10 ⁶
23	1.289	.104	1.259	.295	15.343	1.121	4.61 x 10 ⁶
24	0.275	.011	0.676	.016	3.814	.092	45.3
25	1.423	.108	1.234	.054	14.767	1.034	2.59 x 10 ⁶
26	0.446	.008	0.874	.016	5.650	.005	284.
27	1.138	.078	0.965	.088	12.550	.246	282,000.
28	0.247	.009	0.850	.062	3.477	.177	32.3

continued

Table 27, continued

coal	melting slope (min ⁻¹)	coking slope (min ⁻¹)	max fluidity ln(max flu)	(slope intersection) max fluidity
29	0.278 ± .014	0.791 ± .018	3.932 ± .333	5.10
30	0.263 .021	0.718 .041	3.349 .100	28.5
31	0.232 .018	0.635 .142	3.216 .212	24.9
32	1.336 .069	1.105 .156	14.227 .908	1.51 × 10 ⁶
33	1.663 .263	1.144 .035	16.395 .577	13.2 × 10 ⁶
34	1.476 .182	1.090 .220	14.860 1.114	2.84 × 10 ⁶
35	1.070 .013	0.964 .020	11.082 .721	64,980.
36	0.694 .242	0.782 .084	6.422 .747	615.
37	0.602 .043	0.957 .056	7.484 .029	1,779.
38	0.607 .036	0.763 .061	6.017 .162	410.
39	0.624 .040	0.750 .068	6.040 .077	420.
40	0.351 .077	0.758 .115	3.828 .479	46.0
41	0.718 .035	0.712 .040	6.379 .189	590.

* Slopes are determined as least-squares fits of ln(fluidity) vs. time in minutes; boundary values are discussed in the text. For each run, ln(maximum fluidity) is calculated by slope intersection. All data are averages of the same runs reported in Table 6. When an outlier value falls more than three standard deviations outside the average of the remaining three data, the reported average is that of the best three data; otherwise all four data are averaged.

extracted with DMF and with THF), two hydrogen/carbon ratios (with and without correction for oxygen present), four additional estimates of reactive macerals (vitrinites and liptinites only, vitrinites and weighted liptinites, all except ash, fusinite, macrinite and two-thirds of the semifusinite, and all except Parr mineral matter, fusinite, macrinite and two-thirds of the semifusinite), eight groupings of selected pyrolysis/GC windows (e.g., a combination of the 2-, 3- and 4-minute window signals), four absolute counts of selected pyrolysis/GC windows, a pyrolysis window ratio, and an empirical formula (in which hydrogen and organic sulfur contents have been used to estimate hydroliquefaction yields). These 21 derived variable sets with the 36 directly measured variable sets make a total of 57 in the initial pool.

Variables which are directly redundant (e.g., fixed carbon) have not been included. Other variables, measuring components present in minor amounts and not believed likely to be of predictive importance, were also excluded: semifusinite, micrinite and macrinite.

Many of the data sets are very strongly correlated with one another. A correlation analysis produces some high correlations between fluidity-related variables. R for $\ln(\text{intersection maximum fluidity})$ and ASTM melting slope is .980, for example, reflecting the systematic variability of melting slope and the comparatively constant coking slope (noted previously). The best single predictive variable for ASTM $\ln(\text{intersection maximum fluidity})$ is the four-minute pyrolysis window measuring the 450° pyrolysis gas peak ($R = .856$), and in the absence of pyrolysis/GC data, by DMF-extractables ($R = .768$).

The importance of recognizing highly correlated variables, however, is mainly in helping to avoid the selection of highly redundant information sets. Thus in the pyrolysis liquids data, the 14- and 15-minute windows

and the 15- and 16-minute windows both show R values of about .95; consequently there would be little incremental value to be gained by including more than one of these data sets in a prediction regression:

The first task in starting with 57 candidate independent variables is to reduce the field. A preliminary regression on $\ln(\text{maximum fluidity})$ led to the dropping of 17 variables showing very little predictive power. Variables dropped here include $H(\text{aromatic})/H(\text{aliphatic})$ ratio, ash sulfate (a measure of mineral alkalinity), both H/C ratios, all estimates of total reactive macerals, both organic sulfur and pyritic sulfur, and two less effective measures of pyrolysis/GC signals.

The remaining 40 independent variables were then grouped with the objective of selecting three chemical variables, four petrographic variables, two extraction variables and two variables each from the 450° pyrolysis gas and pyrolysis liquid signals. Analysis of these variables as predictors of $\ln(\text{maximum fluidity})$, using the standard SAS RSQUARE function (73), are summarized in Tables 28-30.

Table 28 shows two variables, FSI and heating value, with significant predictive value for maximum fluidity. All of the other variables in this table exhibit values of R^2 less than 0.1. The third chemical variable retained for further examination (owing to its utility in slope prediction) is total sulfur.

Table 29 shows two significant petrographic variables, pseudovitrinite and vitrinite maximum reflectance, as well as two other possibly significant variables ($.2 > R^2 > .1$), exinite and resinite. These four are retained.

Among the extraction variables in Table 29, DMF is clearly the strongest in this test of significance. Preasphaltenes shows a higher

Table 28

Chemical Predictors of ln(Maximum Fluidity)*

	<u>ASTM obs</u>	<u>ASTM int</u>	<u>400° obs</u>	<u>400° int</u>	<u>420° obs</u>	<u>420° int</u>	<u>avg. R²</u>	<u>rank</u>
ASH	.000	.000	.010	.014	.007	.008	.007	7
CARBON	.006	.009	.013	.021	.009	.010	.011	5
FSI	.378	.388	.325	.337	.340	.355	.354	1
HEATING VALUE	.094	.106	.135	.156	.100	.110	.117	2
HYDROGEN	.002	.000	.000	.000	.002	.002	.001	9
NITROGEN	.016	.005	.000	.001	.020	.015	.010	6
OXYGEN	.024	.037	.014	.021	.024	.024	.024	3
SULFUR	.000	.000	.003	.002	.037	.029	.012	4
VOLMAT	.010	.012	.001	.002	.000	.000	.004	8

* Numbers are values of R² between the dependent (columns) and independent (row) variables.

Table 29

Petrographic and Extraction Predictors of ln(Maximum Fluidity)*

	<u>ASTM obs</u>	<u>ASTM int</u>	<u>400^o obs</u>	<u>400^o int</u>	<u>420^o obs</u>	<u>420^o int</u>	<u>avg. R²</u>	<u>rank</u>
EXINITE	.105	.103	.145	.148	.162	.173	.139	3
FUSINITE	.008	.006	.004	.006	.000	.000	.004	6
PSEUDOVITRINITE	.295	.277	.260	.287	.266	.273	.276	1
REFLECTANCE	.281	.313	.244	.271	.167	.182	.243	2
RESINITE	.109	.142	.130	.150	.074	.091	.116	4
VITRINITE	.020	.018	.013	.010	.022	.011	.016	5
<hr/>								
DMF	.584	.590	.672	.659	.690	.725	.653	1
THF	.283	.256	.224	.213	.339	.319	.272	3
PREASPHALTENES	.280	.302	.402	.399	.336	.376	.349	2
<hr/>								

* Numbers are values of R² between the dependent (column) and independent (row) variables.

Table 30

Pyrolysis/GC Predictors of $\ln(\text{Maximum Fluidity})^*$

	<u>ASTM obs</u>	<u>ASTM int</u>	<u>400° obs</u>	<u>400° int</u>	<u>420° obs</u>	<u>420° int</u>	<u>avg. R²</u>	<u>rank</u>
Pyrolysis gas:								
2-min window %	.373	.441	.444	.431	.399	.437	.421	11
3-min "	.627	.673	.683	.675	.645	.685	.665	4
4-min "	.682	.733	.754	.751	.678	.722	.720	1
5-min "	.518	.556	.501	.505	.478	.525	.514	10
6-min "	.530	.579	.540	.528	.480	.524	.530	9
2-3 min "	.484	.548	.554	.542	.508	.549	.531	8
2-4 min "	.536	.601	.608	.597	.556	.599	.583	7
2-5 min "	.546	.610	.610	.600	.560	.604	.588	6
2-6 min "	.556	.621	.618	.608	.566	.611	.597	5
2-4 min cts	.673	.757	.727	.731	.619	.678	.698	3
2-5 min cts	.679	.762	.730	.735	.623	.682	.702	2
Pyrolysis liquids:								
13-min window %	.109	.107	.110	.104	.140	.147	.120	12
14-min "	.250	.264	.297	.282	.289	.311	.282	10
15-min "	.344	.361	.483	.464	.457	.483	.432	3
16-min "	.238	.240	.322	.302	.321	.329	.292	9
17-min "	.121	.114	.172	.155	.188	.186	.156	11
13-15 min "	.306	.320	.396	.378	.385	.409	.366	6
13-16 min "	.281	.291	.371	.352	.365	.382	.340	8
14-15 min "	.320	.336	.427	.408	.407	.433	.389	5
14-16 min "	.288	.298	.387	.367	.376	.394	.352	7
14-15 min cts	.669	.731	.731	.728	.617	.672	.691	1
13-16 min cts	.673	.730	.718	.715	.613	.664	.686	2
14-15 min/17-18 min	.376	.406	.437	.430	.412	.446	.418	4

* Numbers are values of R^2 between the dependent (column) and independent (row) variables.

average value of R than THF-extractables. However preasphaltenes and DMF have a high cross-correlation coefficient ($R^2 > .8$), while THF and DMF have a low coefficient ($R^2 < .4$). Therefore THF was selected along with DMF for retention.

Many of the 450°C pyrolysis/GC variables in Table 30 show impressive cross-correlation. We retain the top two from the pyrolysis gas signal region (4-min window % and 2-5 min window counts/microgram), and the top two from the pyrolysis liquids region (14-15 min counts/microgram and 13-16 min counts/microgram). The selection of two measures of the pyrolysis gas signal and two measures of the pyrolysis liquids signal carries forward pairs of variables with high cross-correlations. In the development of the final prediction equations no more than one of each of these pairs will be used in a regression.

The independent variables carried forward to the following sections are:

FSI

Heating value

Sulfur

Exinite

Reflectance

Resinite

Pseudovitrinite

DMF-extractables

THF-extractables

Pyrolysis 4 min %

Pyrolysis 2-5 min cts

Pyrolysis 14-15 min cts

Pyrolysis 13-16 min cts

6.3 Prediction of ASTM Fluidity Characteristics

Using the 13 independent variables identified in the preceding section, a series of R^2 calculations was carried out using 1, 2, 3 and 4 independent variables to estimate the seven characteristics of an ASTM Gieseler plastometry run:

ln(maximum observed fluidity)

ln(maximum fluidity by intersection)

melting slope in min^{-1}

coking slope in min^{-1}

Softening temperature in $^{\circ}\text{C}$

Temperature of maximum fluidity in $^{\circ}\text{C}$

Solidification temperature in $^{\circ}\text{C}$

The results are summarized in Table 31. It is evident that inclusion of a second independent variable results in a very substantial improvement of the correlation coefficient R , an improvement on average of .05. The addition of a third variable results in a further improvement in R , averaging just under .035. The addition of a fourth variable brings about a small incremental improvement, averaging for this set .011. As the three-variable linear regression equations permit the estimation of ln(maximum fluidity) with a value of R of .90 or better, there seems little merit in adding more terms.

When a group of three variables -- reflectance, THF-extractables and the pyrolysis 13-16 min window count -- are used to predict all seven dependent variables, it proves to give satisfactory projections for both of the estimates of maximum fluidity and for both slopes ($R = .86 - .92$). The same three variables are also good estimators of the characteristic temperatures, providing standard errors of estimate of $3-4^{\circ}\text{C}$. The equations are given in Table 32.

Table 31

Prediction of ASTM Fluidity Characteristics with 1-4 Variables

Dependent Variable	Independent Variables				Correlation coeff.
					R (n = 40)
ln(MF observed)	pyr4m				.826
	pyr4m	pseudo			.875
	pyr2-5m	pseudo	THF		.898
	pyr13-16	pseudo	THF	reflect	.907
ln(MF intersection)	pyr2-5m				.873
	pyr2-5m	pseudo			.902
	pyr13-16	reflect	THF		.922
	pyr13-16	reflect	THF	sulfur	.928
melting slope	pyr2-5m				.802
	pyr14-15	pseudo			.858
	pyr14-15	reflect	THF		.889
	pyr14-15	reflect	pseudo	THF	.900
coking slope	pyr2-5m				.800
	pyr13-16	reflect			.854
	pyr13-16	reflect	THF		.860
	pyr13-16	reflect	DMF	pyr4m	.873
T(softening)	pyr13-16				.751
	DMF	sulfur			.785
	THF	reflect	pyr2-5m		.851
T(max fluidity)	pyr14-15				.727
	DMF	sulfur			.791
	sulfur	reflect	pyr2-5m		.851
T(solidification)	reflect				.781
	reflect	pyr13-16			.856
	reflect	pyr14-15	pseudo		.889
	reflect	pyr13-16	pseudo	sulfur	.906

*Variable abbreviations: DMF = DMF-extractables; pseudo = pseudovitrinite; pyr4m = pyrolysis 4 min %; pyr2-5m = pyrolysis 2-5 min cts; pyr13-16 = pyrolysis 13-16 min cts; pyr14-15 = pyrolysis 14-15 min cts; reflect = vitrinite reflectance; sulfur = % total sulfur; THF = THF-extractables.

Table 32

Regression Equations for Estimation of ASTM Fluidity Characteristics*

		<u>R</u>	<u>std error in estimate**</u>
ln(MF observed)	= 1.069E+1 * reflect + 4.190E-1 * THF + 2.288E-3 * pyr13-16m - 9.877	.898	1.25
ln(MF intersection)	= 1.668E+1 * reflect + 5.507E-1 * THF + 3.885E-3 * pyr13-16m - 16.14	.922	1.69
melting slope	= 1.751E0 * reflect + 7.220E-2 * THF + 3.252E-4 * pyr13-16m - 1.897	.888	0.20
coking slope	= 7.984E-1 * reflect + 9.410E-3 * THF + 1.543E-4 * pyr13-16m + 0.0030	.860	0.092
T(softening)	= 2.448E+1 * reflect - 1.309E0 * THF - 6.562E-3 * pyr13-16m + 398.4°	.840	4.0°
T(max fluidity)	= 2.674E+1 * reflect - 7.672E-1 * THF - 4.790E-3 * pyr13-16m + 427.2°	.820	3.0°
T(solidification)	= 5.871E+1 * reflect + 5.574E-1 * THF + 3.647E-3 * pyr13-16m + 404.2°	.858	4.2°

* See footnote to Table 31 for variable abbreviations.

** Standard deviation of the estimated variable

For the equation (Table 32):

$$\ln(\text{MF intersection}) = 1.668\text{E}+1 * \text{reflect} + 5.507\text{E}-1 * \text{THF} \\ + 3.885\text{E}-3 * \text{pyr13-16m} - 16.14 \quad (3)$$

the plot of predicted vs. measured $\ln(\text{maximum fluidity})$ is shown in Figure 14a. Using the best three chemical and petrographic predictors only, the least-squares regression is:

$$\ln(\text{MF intersection}) = 1.462\text{E}0 * \text{FSI} + 2.742\text{E}-1 * \text{pseudo} \\ + 0.357\text{E}0 * \text{reflect} - 5.690 \quad (4)$$

This regression exhibits a correlation coefficient of .768 and a standard error of estimate of 2.80 (cf. $R = .922$, $\sigma = 1.69$ for Eqn. (3)). The plot of predicted vs. measured $\ln(\text{maximum fluidity})$ using Eqn. (4) is shown in Figure 14b.

There is obviously a considerable spread in the goodness of fit of these two equations. For laboratories lacking the pyrolysis/GC capability but equipped to conduct quantitative Soxhlet extractions, a fairly good compromise is attainable:

$$\ln(\text{MF intersection}) = 1.978\text{E}+1 * \text{reflect} + 4.782\text{E}-1 * \text{DMF} \\ + 6.712\text{E}-1 * \text{THF} - 26.583 \quad (5)$$

Eqn. (5) provides a value of R of .873 and a standard error of estimate of 2.13.

For the other measures of ASTM fluidity (slopes, characteristic temperatures) similar patterns obtain. The standard errors using the best three variables and drawing from chemical and petrographic data only are approximately 50% greater than those of Table 32. When Soxhlet extraction data are added to this pool the three-variable regressions yield standard errors which are often only 10-15% greater than those of Table 32.

Figure 14

Three-term Predictions of Ln (Maximum ASTM Fluidity)

14a. Best Three-term Equation

14b. Best three-term Equation Excluding
Pyrolysis/GC and Extraction Data

A collection of three-variable regression equations for the prediction of ASTM Gieseler fluidity characteristics, all based upon this 40-coal data set, is given in Part 9.5.

All of these statistics could be made to look better by eliminating a few coals from the analysis. There are some reasonable and objective criteria for rejection that can be used, for example, Acton's R-test (74). These data, however, give reasonably good predictive correlations without rejection of outliers. All of the statistical calculations summarized in this report are based upon the full set of available data.

6.4 Prediction of Isothermal Fluidity Characteristics

Using the same 13 most influential variables identified in Part 6.2, a series of R^2 calculations was made for expressions using 1, 2, 3 and 4 predictive variables to estimate selected characteristics of an isothermal Gieseler plastometry run:

ln(maximum observed fluidity at 400°C)

ln(maximum observed fluidity at 420°)

ln(intersection maximum fluidity at 400°)

ln(intersection maximum fluidity at 420°)

melting slope at 400°

melting slope at 420°

coking slope at 400°

coking slope at 420°

The results are summarized in Table 33. The correlation coefficient R is significantly improved (by approximately .05 on the average) upon adding the second predictive variable. R is further elevated, typically by .02 - .03, by addition of a third predictive variable. Addition of a fourth predictive variable brings about a marginal additional improvement in R .

Table 33

Prediction of Isothermal Fluidity Characteristics with 1-4 Variables

Dependent Variable	Independent Variables*					Correlation coeff. R (n = 29)
ln(MF observed, 400°)	pyr4m					.868
	BTU	pyr4m				.904
	reflect	THF	pyr14-15			.924
	sulfur	reflect	THF	pyr14-15		.934
ln(MF observed, 420°)	DMF					.831
	pseudo	pyr4m				.864
	pseudo	THF	pyr4m			.905
	exinite	pseudo	THF	pyr4m		.917
ln(MF intersection, 400°)	pyr4m					.867
	pseudo	pyr14-15				.910
	reflect	THF	pyr14-15			.930
	sulfur	reflect	THF	pyr14-15		.939
ln(MF intersection, 420°)	DMF					.851
	pseudo	pyr4m				.888
	pseudo	THF	pyr2-5			.924
	pseudo	DMF	THF	pyr2-5		.931
melt slope, 400°	pyr4m					.849
	THF	pyr4m				.877
	resinite	THF	pyr4m			.906
	sulfur	resinite	THF	pyr4m		.913
melt slope, 420°	pyr4m					.871
	THF	pyr4m				.896
	sulfur	THF	pyr4m			.912
	sulfur	DMF	THF	pyr4m		.916
coke slope, 400°	sulfur					.685
	sulfur	reflect				.796
	sulfur	exinite	reflect			.811
	BTU	sulfur	exinite	reflect		.824
coke slope, 420°	reflect					.852
	sulfur	reflect				.910
	BTU	sulfur	reflect			.913
	BTU	sulfur	reflect	pyr2-5		.918

* See footnote to Table 31 for variable abbreviations.

(.008 on the average). It is possible to estimate most (7 of 8) of these variables with $R > .9$ by using three-variable regressions.

The coefficients for a set of three-variable regression equations are given in Table 34, with the corresponding values of the correlation coefficient R and the standard error in estimate (standard deviation for the prediction). As in the case of ASTM predictions, it is possible in most cases to achieve predictions with values of R greater than .9. Values of R less than .9 are encountered in coking slope estimates; however, the standard errors are quite small (less than $\pm 0.04 \text{ min}^{-1}$).

For the equation (Table 34):

$$\begin{aligned} \ln(\text{MF intersection, } 400^{\circ}) = & 1.228\text{E}+1 * \text{reflect} + 3.866\text{E}-1 * \text{THF} \\ & + 5.243\text{E}-3 * \text{pyr14-15} - 1.214\text{E}-1 \end{aligned} \quad (6)$$

the plot of predicted vs. measured $\ln(\text{maximum fluidity})$ is shown in Figure 15a. Using the best three chemical and petrographic predictors only (i.e., no data from Soxhlet extractions nor from pyrolysis/GC determinations), the best three-term regression on this dataset is:

$$\begin{aligned} \ln(\text{MF intersection, } 400^{\circ}) = & 2.051\text{E}-3 * \text{BTU} + 1.013 * \text{FSI} \\ & - 3.298\text{E}-1 * \text{exinite} - 26.394 \end{aligned} \quad (7)$$

for which $R = .810$ and the standard error of estimate is 1.83 (c.f. $R = .929$ and $\sigma = 1.15$ for Eqn (6)). The plot of predicted vs. measured $\ln(\text{maximum fluidity})$ using Eqn (7) is shown in Figure 15b.

As in the ASTM data, there is a considerable spread in the goodness of fit between these two cases. For laboratories lacking the pyrolysis/GC capability but equipped to conduct quantitative extractions, a fairly good compromise is again attainable:

$$\begin{aligned} \ln(\text{MF intersection, } 400^{\circ}) = & 1.287\text{E}+1 * \text{reflect} + 3.606\text{E}-1 * \text{DMF} \\ & + 3.892\text{E}-1 * \text{THF} - 18.403 \end{aligned} \quad (8)$$

Table 34

Three-Variable Regressions for Estimation of Isothermal Fluidity Characteristics*

			<u>R</u>	<u>std error in estimate</u>
ln(MF observed at 400°)	= 1.136E+1 * reflect + 3.872E-1 * THF + 5.320E-3 * pyr14-15	-12.297	.924	1.19
ln(MF intersec- tion at 380°)	= 5.339E0 * reflect -5.795E-1 * sulfur +6.332E-3 * pyr14-15	- 2.661	.919	1.06
ln(MF intersec- tion at 400°)	= 1.228E+1 * reflect + 3.866E-1 * THF + 5.243E-3 * pyr14-15	-12.140	.929	1.15
ln(MF intersec- tion at 420°)	= 4.594E-1 * pseudo + 5.056E-1 * THF + 3.849E-3 * pyr2-5	- 4.940	.923	1.44
melting slope at 400°	= 1.238E-1 * resinite + 3.34E-2 * THF + 3.220E-1 * pyr4m	- 0.330	.906	0.122
coking slope at 400°	= 2.026E-2 * sulfur - 5.796E-3 * exinite - 3.301E-1 * reflect	- 0.367	.811	0.036

* See footnote to Table 31 for variable abbreviations.

Figure 15

Three-term Predictions of Ln (Maximum Fluidity) at 400°C

15a. Best Three-term Equation

15b. Best Three-term Equation Excluding
Pyrolysis/GC and Extraction Data

Eqn (8) provides a value of R .890 and a standard error of estimate of 1.42.

The estimation of maximum isothermal fluidity by four-variable regressions has been studied for four cases (observed and intersection values at 400° and at 420°C) and for four database assumptions (all data present, no pyrolysis data, no extraction data, and neither pyrolysis nor extraction data). The 16 regression equations providing the best linear fit to these data are given in Table 35. Using all data the correlation coefficients are in the range .90 - .94. When pyrolysis data are excluded the correlation coefficients are slightly lower, in the range .895 - .92. When extraction data are excluded there is a similar slight depression. When both of these subsets of data are excluded, and the regressions are based entirely upon chemical and petrographic data alone the R values drop to .74 - .78.

Table A-5 of Part 9.5 lists a number of other regression equations, including a group of equations predicting intersection fluidity at 380°, 400° and 420°C.

As in the ASTM case, these statistics use the least-squares values generated by all 29 coals subjected to isothermal plasticity measurements. The precision of predictive fit could be substantially improved by elimination of the data from a couple of outlier coals.

Table 35

Four-Variable Regressions on Isothermal Gieseler Fluidity Characteristics*

Dependent	Independents				Intercept	R
ln(MF obs) at 400°	SULFUR -1.024E0	THF +3.239E-1	PYR4m +2.807E0	PYR14-15 +3.213E-3	-2.064	.932
" "	BTU +8.312E-4	Pseudo +2.451E-1	PYR4m +2.396E0	PYR14-15 +3.171E-3	-12.074	.927
" "	RESINITE +6.719E-1	REFLECT +1.083E+1	DMF +3.648E-1	THF +3.703E-1	-18.236	.895
" "	BTU +2.103E-3	FSI +4.426E-1	EXINITE -5.779E-1	RESINITE +1.495E0	-24.238	.743
ln(MF obs) at 420°	PSEUDO +4.354E-1	DMF +1.974E-1	THF +4.653E-1	PYR4m +3.114E0	-9.614	.910
" "	BTU +1.673E-3	SULFUR +9.237E-1	PSEUDO +4.576E-1	PYR4m +4.586E0	-24.063	.885
" "	RESINITE +2.894E-1	REFLECT +1.311E+1	DMF +4.834E-1	THF +6.830E-1	-24.361	.904
" "	BTU +3.113E-3	SULFUR +2.848E0	PSEUDO +5.434E-1	REFLECT +1.181E+1	-53.119	.754
ln(MF int) at 400°	SULFUR -5.552E-1	REFLECT +9.304E0	THF +4.356E-1	PYR14-15 +5.844E-3	-9.715	.939
" "	BTU +9.359E-4	PSEUDO +2.723E-1	PYR4m +2.336E0	PYR14-15 +3.182E-3	-12.831	.937
" "	BTU +7.189E-4	REFLECT +1.027E+1	DMF +3.807E-1	THF +3.287E-1	-25.924	.899
" "	BTU +2.164E-3	FSI +4.272E-1	EXINITE -6.119E-1	RESINITE +1.647E0	-25.583	.775
ln(MF int) at 420°	PSEUDO +4.244E-1	THF +4.371E-1	PYR4m +1.954E0	PYR14-15 +2.321E-3	-4.298	.932
" "	BTU +7.555E-4	PSEUDO +3.439E-1	PYR4m +3.418E0	PYR14-15 +2.633E-3	-8.911	.903
" "	BTU +5.903E-4	REFLECT +9.889E0	DMF +4.821E-1	THF +5.146E-1	-26.865	.919
" "	BTU +2.811E-3	SULFUR +2.496E0	PSEUDO +4.682E-1	REFLECT +1.123E+1	-46.843	.754

* See footnote to Table 31 for variable abbreviations.

7. DISCUSSION

7.1 Prediction of Fluid Properties

The main task of this investigation has been the identification of parameters capable of predicting the fluid properties of mid-ranked coals. Both the ASTM (3 deg/min ramp) and isothermal fluidity characteristics of these hvb coals have been determined, and reasonably good three-term regression equations have been developed, in most cases providing correlation coefficients of .90 or better with all data included.

Gieseler data can be usefully analyzed to provide melting and coking slopes (in log fluidity vs. time plots). From these slopes the $\ln(\text{intersection maximum fluidity})$ is determined. Intersection maximum fluidity, in our experience, is a more consistent measure of fluid characteristics than the traditional 'maximum observed fluidity', in terms of both repeatability of measurements and correlation with other parameters. This may result from its substantial independence from perturbations arising from outgassing of gassy coals in the general region of maximum fluidity.

The examination of isothermal Gieseler plastometer runs over a range of temperatures shows a generally consistent Arrhenius dependency for maximum fluidity, and for melting and coking slopes. This permits an accurate interpolation of fluid behavior at any intermediate temperature of process interest, and a means of extrapolation to other nearby temperatures. The geometry of this analysis permits the determinations of fluidity span -- the interval of time during which fluidity exceeds any desired baseline value -- of a fluid coal as a function of temperature.

Of the nonstandard measurements of these coals, the most useful in our study has been the use of pyrolysis/gas chromatography with a pyrolysis ceiling temperature of 450°C. Highly fluid coals give consistently stronger pyrolysis gas signals and consistently stronger pyrolysis liquids signals than sparingly plastic coals of similar gross composition and rank. Chromatograms furthermore show specific peak regions for which signal strength correlates quite well with $\ln(\text{maximum fluidity})$. Using only the single predictor of the pyrolysis gas signal (Table 31), maximum ASTM fluidity is estimated with $R = .87$ (all 40 coals).

Selection of the ceiling temperature of 450°C is based upon a number of rangefinding runs. Pyrolysis signal strength falls off rapidly at lower temperatures. At substantially higher temperatures the signal strengths are considerably greater but selectivity is rapidly lost.

Among classical and familiar techniques, quantitative Soxhlet extraction with a polar aprotic solvent is a strong single-parameter predictor. A recent report by Ouchi, Tanimoto, Makabe and Itoh (76) notes that the pyridine extraction yields of four hvb coals tend to be proportional to $\log(\text{maximum fluidity})$. In the present study the extraction yields using a similar polar aprotic extractant, DMF, are shown to correlate with $\ln(\text{maximum fluidity at } 420^\circ)$ with $R = .85$ (29 coals). This substantially supports the inference of Ouchi and co-workers.

The best three-variable prediction equations are given in Parts 6.3 and 6.4 of this report. For the prediction of $\ln(\text{maximum fluidity})$ these yield correlation coefficients (Tables 32 and 34) of .90-.93. Other multiple linear regression equations are listed in Part 9.5.

In applying these regression equations to data obtained with other coals, it should be noted that this database covers only hvb coals, and

substantially only coals from a number of western Kentucky locations (Figure 2) in the eastern mid-continent beds.

7.2 The Effect of Pressure

The literature describing the effect of pressure upon the fluid properties of coals is sparse, recent and intriguing. Kaiho and Toda (29) examined the effects of several pressurant gases upon a weakly caking Japanese coal, using a modified Gieseler plastometer operable to about 725 psia. Tests were conducted at a constant heating rate, rather than isothermally. Maximum fluidity in all cases was found to increase sharply with the first couple of hundred pounds of superatmospheric pressure. With helium as the pressurant the curve of $\ln(\text{maximum fluidity})$ vs. pressure tended to flatten but did not give a maximum. With nitrogen as the pressurant a flattish maximum was obtained at about 580 psia.

Lancet and Sim (77) have studied a Pittsburgh #8 hvAb coal as well as others (78), using a research model pressurized Gieseler plastometer similar to that used in the present study. Their tests were carried out at 3 and 6 deg/min temperature ramps, at low torques, and at pressures to 400 psia. The observed maximum fluidity increased with nitrogen pressure, achieving a fivefold increase at the maximum pressure. The initial pressurization with nitrogen -- up to 100 psia -- resulted in a sharp increase in maximum fluidity, while at higher pressures the incremental effect was less.

The first completed isothermal study of the effects of pressure is that of Richard Read (79), who has worked extensively with a Union Co. Kentucky #9 coal similar to our Coal #16. Figure 16, used with the author's permission, illustrates nicely the interactive effects of temperature and pressure upon a fairly fluid hvb coal. Read found that at

RELATIVE FLUIDITY (ln(ddpm)) OF KCER-9080

410°C the maximum fluidity increased from 60 to over 2,000 ddpm as helium pressure was increased to 300 psia. His data indicate that melting slopes increase with increasing pressure, coking slopes are relatively insensitive, and that for all coals in his study the maximum fluidity is sharply responsive to pressure.

M. R. Khan in his study of high pressure dilatometry (80) has noted that swelling is reduced and contraction increased with increasing pressure of nitrogen. He concludes that "The effect of pressure seems to be the inhibition of volatile liberation."

Our results are in general accord with these observations. Figure 7c confirms, with Coal #44, the rapid increase in maximum fluidity with initial pressure increments, and the flattening out of higher pressures. Figures 7a and 7b confirm and extend the observation that melting slope is sensitive to pressure and that coking slope is relatively insensitive; Table 7 extends this to the five other coals examined.

The differences reported in terms of the presence or absence of fluidity maxima may be accounted for, we feel, in terms of significant differences among coals, specifically in the characteristics of the fluid phases of their molten states. A comparison of Figures 6b, 6c and 7c, obtained with the same apparatus using the same techniques in our laboratories, strongly suggests that there is more than one kind of fluidity response to pressure. The proposal of three limiting-case kinds of behavior (Cases A, B and C, illustrated in Figure 6a) is a first effort to provide a rational explanation for these differences.

7.3 Additional Observations

ASTM maximum Gieseler fluidity is substantially lower than isothermally measured maximum fluidity at or near the ASTM temperature of

maximum fluidity. For six sparingly plastic coals with an average ASTM maximum fluidity of 13 ddp_m, the average isothermal fluidity at the same temperatures is 51 ddp_m. Fluidity is even more sharply enhanced by the application of superatmospheric pressure. The maximum fluidity of Coal #44 (Table 6) increases from 1240 ddp_m at atmospheric pressure to 12,240 ddp_m at 115 psia (tenfold), and to 67,800 ddp_m at 415 psia (over fiftyfold).

Among hvb coals variations in $\ln(\text{maximum fluidity})$ are highly cross-correlated with melting slopes ($R = .98$). Coking slopes show relatively little correlation with either melting slopes or maximum fluidities, and are relatively invariant.

Although these freshly mined raw coals show little or no signs of weathering or oxidation, microscopic examination of a number of the Gieseler semi-cokes shows distinct oxidation rims. This suggests a possible weakness in the present Gieseler procedure. Coal laboratory people tend to assume that the heated coal mass is protected from contact with atmospheric oxygen by the outward flow of its own pyrolysis gases and vapors. The gas exit tube ('chimney') of the Gieseler retort barrel may actually need to be padded with an inert gas stream.

The indications of high sensitivity to steric hindrance of extractant base atoms, even by a single ortho-methyl group (Table 14), suggest a highly crowded environment in the micropore structure of hvb coals.

Examination of THF extracts of sparingly fluid and highly fluid coals gives mixed signals. Infrared analysis indicates nearly identical gross compositions and $H(\text{aromatic})/H(\text{aliphatic})$ ratios which are identical within the accuracy of measurement (Table 19). HPLC analysis of the methylene chloride-soluble fraction of THF extracts (Table 20) suggests that there may be a general trend towards more aromatic character (methylene

chloride-elutables) in extracts from highly fluid coals. These data are not sufficiently consistent to support a clear conclusion at this time.

The failure of some candidate predictors to correlate with actual fluidity is itself of interest. Covalent crosslink density, as estimated by equilibrium swelling of extraction residues of highly fluid and sparingly fluid coals (Table A-3, Part 9.3) appears to have nothing to do with fluidity. This eliminates a 'mechanical' theory of fluidity variations. The failure of ash sulfate to correlate detectably with fluidity argues against an old notion that perhaps network decomposition entails a mineral acid-catalyzed depolymerization (Friedel-Crafts dealkylation, retro-Diels-Alder, etc.). The FTIR analysis of THF extracts implies that the differences between highly fluid and sparingly fluid coals do not reside in gross chemical differences between their THF-extractable fractions.

The multiple linear regression analyses developed in Parts 6.3, 6.4 and 9.5 are straightforward groupings of simple first-order terms. Moderate improvements in fit are attainable by changing the order and/or complexity of terms. Larger improvements can be gotten by dropping two or three coals giving 'outlier' values. However, the overall fits -- with correlation coefficients in most cases of .90 or higher -- may be as high as can be reasonably expected, given the problems of sample-to-sample inhomogeneity, adventitious weathering, and the cumulation of normal analytical error.

The results of this study seem to lend support to both of the classical theories of coal plasticity. The role of the extractable 'bitumen' fraction is supported by the importance of total DMF-extractables in predicting fluid properties, and the frequent emergence of total THF-

extractables in multiple linear regression analyses. The role of the primary pyrolysis product ('metaplast') is strongly implied by the very high predictive power of pyrolysis gas signals and (independently) pyrolysis liquids signals for coal fluidity. The extractability (by DMF) of the two groups of compounds providing the 'plasticity peaks', and the failure of THF extracts to provide measurable differences even in FTIR analysis, raises the possibility of a group of polar compounds, strongly H-bonded to the coal structure and not therefore extracted by THF, that may play a key role in the addition/transfer competition which at these temperatures plays a determining role in the extent of development of fluidity.

We are still guessing about the molecular nature of the phenomenon of fluidity. But we are making some progress. We can correlate fluid properties with several other measurable characteristics of coals, especially with pyrolysis/GC signals, THF-extractables, vitrinite reflectance, and the amounts of sulfur and pseudovitrinite present. And, given these other measurements, we can now predict with reasonable confidence both the characteristic ASTM plastometer curve and the isothermal fluidity characteristics of a mid-ranked coal.

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9. APPENDIX

9.1 Crucible Tests

As an additional control to minimize adventitious error, a series of isothermal runs was carried out, using the same coal (#7568, not a part of the present study) at substantially the same temperatures with five different crucible/stirrer assemblies. These crucibles, numbered #0, #1, #3, #4 and #5, were used in sequence for a total of 20 determinations. The observed melting and coking slopes and their standard deviations, and the extrapolated maximum fluidity, were calculated for each run. Results are given in Table A-1.

In the following analysis, temperature differences are not corrected for. The resulting error is significant in run #16.

A preliminary analysis of these data indicates crucibles #1, #3 and #4 to be substantially equivalent overall. The melting slope (10 of 12 pooled data) averages 1.345, std. dev. 0.074. A t-test for crucible #0 does not categorically reject it (probability of systematic differences is 65% by this test). A t-test for crucible #5 indicates it to be clearly different ($t = 3.33$ with 12 df, indicating a probability of difference greater than 99%). The coking slope (11 or 12 pooled data) averages -0.268, std. dev. 0.024. A t-test for crucible #0 and another for crucible #5 both fail to indicate a clear rejection (probability of systematic difference being 62% and 77%, respectively). The maximum fluidity data, like the melting slope data, indicate a clear rejection of crucible #5 and some ambiguity (probability of systematic difference about 60%) for crucible #0.

The conclusion indicated is that crucible #5 should not be used interchangeably with others in this study. Crucible #0 probably could be

Table A-1

Crucible Tests with Coal #7568*

<u>run</u>	<u>crucible</u>	<u>temperature, s.d.</u>		<u>melting slope, s.d.</u>		<u>coking slope, s.d.</u>		<u>extrapolated max flu</u>
1	0	412.3	+ 0.6	1.397	+ .038	-.2686	+ .0010	5,690 ddp _m
2	1	411.6	1.2	1.404	.054	.2849	.0025	5,478
3	3	412.3	0.6	1.132	.021	.2824	.0023	5,848
4	4	412.3	0.7	1.105	.024	.2433	.0045	5,702
5	5	412.4	0.5	1.431	.025	.2909	.0031	10,611
6	0	413.0	0.0	1.008	.048	.2836	.0016	6,850
7	1	413.4	0.6	1.381	.027	.2766	.0020	7,844
8	3	412.9	0.7	1.307	.024	.2993	.0018	9,339
9	4	412.4	1.1	1.392	.031	.2701	.0020	10,547
10	5	411.1	0.4	1.464	.024	.2636	.0028	11,030
11	0	412.1	0.3	1.163	.028	.2574	.0014	6,246
12	1	412.8	0.6	1.233	.017	.2589	.0058	6,246
13	3	412.2	0.4	1.366	.028	.2996	.0024	12,221
14	4	412.3	0.5	1.417	.022	.2705	.0022	9,148
15	5	413.5	0.5	1.474	.043	.4005	.0031	45,584
16	0	418.4	1.9	1.515	.040	.3142	.0016	16,777
17	1	411.1	0.6	1.433	.022	.2316	.0028	7,087
18	3	412.9	0.3	1.243	.022	.3351	.0039	32,598
19	4	413.0	1.2	1.277	.017	.2308	.0031	5,890
20	5	411.4	0.7	1.572	.027	.2349	.0058	13,708

* Melting and coking slopes from $\ln(\text{ddpm})$ vs time, in units of min^{-1} (least-squares fit). Extrapolated maximum fluidity is the intersection of the two slope lines.

used, but as it has given somewhat less consistent results in this study, it too has been rejected. Our isothermal plastometry determinations therefore make use of the three crucible/stirrer assemblies which demonstrably give comparable results.

9.2 Effect of Ageing upon Plasticity

One of the highly plastic coals, coal #34, has been placed in an open jar in the laboratory for six months, with periodic mixing and abstraction of samples for determination of ASTM Gieseler fluidity. This provides a measure of sensitivity of a coal, reduced to -40 mesh, to exposure to air at 20-40% relative humidity and at 22-25°C (72-77°F). The Gieseler data (individual runs) are given in Table A-2.

Overall maximum fluidity shows, as expected, a decrease with time. The slope of $\ln(\text{maximum observed fluidity})$ vs. time is roughly linear, with a least-squares slope of $-.0081 \text{ day}^{-1}$ (std. dev. $\pm .0018$). The melting slope appears to diminish at a significant rate of $-.0031 \text{ min}^{-1} \text{ day}^{-1}$ (std. dev. $\pm .0008$). The coking slope does not change significantly, at least at the present stage of this experiment.

9.3 Swelling of DMF Extraction Residues

If the organic portion of hvb coal is viewed as a three-dimensional network polymer of 'infinite molecular weight' encompassing a soluble and extractable fraction of discrete molecules, then the process of transformation from a refractory solid to a fluid suspension -- as necessarily occurs when a plastic coal is brought to its fluid state -- must entail at least the mechanical rupture of sufficient bridges and chains in the network to break it down to a collection of smaller species. When we compare plastic and nonplastic coals from this point of view, it is evident that there are two qualitatively different kinds of argument to

Table A-2

The Deterioration of Plasticity of Coal #34 on Ageing in Laboratory Air

<u>date</u>	<u>T(soft)</u>	<u>T(max)</u>	<u>T(solid)</u>	<u>max obs flu & ln</u>		<u>melt slope</u>		<u>coke slope</u>	
12/09/82	385°C	420°C	464°C	28,016	10.24	1.338 ± .054		0.808 ± .048	
1/06/83	383	425	472	25,829	10.16	1.176	.020	0.310	.038
1/06	385	428	464	22,856	10.04	1.535	.081	1.068	.020
2/08	378	425	451	13,229	9.49	1.186	.033	1.064	.034
2/09	377	421	462	28,576	10.26	1.425	.037	1.063	.036
3/08	373	417	456	22,192	10.01	1.289	.043	1.070	.032
3/08	372	413	450	15,715	9.66	1.440	.246	0.980	.007
4/07	381	428	461	8,547	9.05	1.066	.035	0.986	.047
4/08	380	425	460	16,073	9.69	1.022	.037	1.063	.025
5/17	382	432	467	9,685	9.18	0.993	.026	0.934	.051
5/17	385	434	468	6,455	8.77	1.007	.037	1.051	.029

account for the observed differences: the coals may differ chemically, in the distribution and thermal reactivity of their chains and bridging groups, for example, or the coals may differ physically in terms of differing crosslink densities. The physical explanation might be that a highly plastic coal actually has a very low crosslink density, so that scission of only a few bridges results in destroying the three-dimensional network, while a nonplastic coal of similar rank may simply have a relatively high crosslink density.

Crosslink densities of network polymers can often be estimated (if the crosslink density is not too high) by swelling the networks in solvents of similar solubility characteristics. For the case of nonpolar networks and ideal 'athermal' solvents (for which $H_{\text{mix}} = 0$) there is a well developed theory to relate degree of swelling to solubility parameters and effective crosslink density. Fortunately, several recent studies (67-72) have demonstrated that coals and coal extraction residues are indeed swelled by appropriate solvents, that the degree of equilibrium swelling can be directly related to effective crosslink density, and that swelling measurements can be easily conducted at room temperature (70).

The DMF extraction residues of four coals have been selected for systematic study, using a simple swelling apparatus. Approximately 3-5 grams of lightly ground residue is mixed with 15 ml of reagent DMF and transferred quantitatively (using additional DMF) into a vertically mounted glass cylinder (9.8 mm i.d.) fitted with a coarse glass disk near its bottom. The bottom of the cylinder is connected to a reservoir of fresh DMF; the top is loosely plugged to prevent contamination and solvent evaporation. Additional DMF is introduced from the bottom until the slurry liquid level is close to the top of the tube (volume above the glass frit

about 25 mL). The slurry is allowed to stand until the coal solids settle to a substantially constant volume. The supernatant solvent (containing dissolved matter from the swollen coal residue) is removed, additional fresh solvent is introduced from the reservoir through the frit at the bottom of the tube, and the slurry is again allowed to settle and the cycle repeated. Eventually the supernatant becomes colorless, and the equilibrium swollen volume of the coal network becomes constant. At this point its volume can be compared with its dry volume V_0 and with the weight of coal residue charged.

The DMF extraction residues from four coals in our main set were selected, nos. 17, 19, 24 and 25. Coals #17 and #24 have low plasticity, with maximum ASTM fluidities less than 50 ddpm. Coal #19 is intermediate, and coal #25 is highly plastic (greater than 30,000 ddpm). Each of these has been subjected to repeated cycles of slurrying, decanting, and restoring fresh solvent, until constant swelling volumes have been attained. The results of this set of experiments are summarized in Table A-3.

These four coals all swell more than 100% in DMF; their swelling ratios (swollen volume / dry volume) fall between 2.07 and 2.45. Their swollen bulk densities are in the range 0.28 - 0.35 g/mL. The first conclusion from these experiments is that, to the extent that these four coals are representative of hvAb - hvBb mid-continent coals, there is no substantial difference in equilibrium swelling among these coals. If we look for small differences within the V/V_0 range of 2.07 to 2.45, we find the most plastic coal near the low end (2.09), with no evidence of a systematic relationship of swelling volume with plasticity.

Swelling equilibrium was reached within two weeks in all cases. One coal (#25) has been slurried, decanted and refilled for over two months, with its volume ratio remaining within ± 0.01 since the first two weeks.

Table A-3Equilibrium Swelling of Extraction Residues in DMF

Coal	<u>ln(maximum fluidity, ASTM)</u>		DMF Swelling Volume, V/V ₀	Bulk Density in DMF
	<u>observed</u>	<u>calculated</u>		
25	10.3+	14.77	2.09	0.325 g/mL
19	4.76	5.56	2.20	.310
17	3.81	4.40	2.07	.348
24	3.55	3.81	2.45	.284

9.4 Gieseler Data Calculations.

Following is the program listing for the calculations made upon raw Gieseler data (Part 5.1, Table 26, Figure 16). This listing is in BASIC, written for an APPLE IIe microcomputer.

PROGRAM GIESELER. 1. INTRODUCTION

```

1000 DA$ = "DEC. 17 1983"
1010 REM *****
1020 REM **                PROGRAM 'GIESELER'                **
1030 REM **  LINES                                           **
1040 REM ** 1000-  INITIATION, CHART OF PROGRAM ANATOMY      **
1050 REM ** 2000-  SUBROUTINE FOR SLOPE CALCULATION          **
1060 REM ** 3000-  SUBROUTINE FOR SLOPE BOUNDARIES           **
1070 REM ** 4000-  MAIN ROUTINE 1. READ AND STORE INPUT DATA **
1080 REM ** 5000-  MAIN ROUTINE 2. CALCULATE AND PRINT OUTPUT **
1085 REM ** 5500-  SUBROUTINE FOR ERROR TRAP IN GRAPHICS     **
1090 REM ** 6000-  SUBROUTINES FOR PAGING, CENTERING        **
1100 REM ** 7000-  SEPARATE TEMPERATURE-AVERAGING ROUTINE   **
1110 REM ** 8000-  DATA INPUT STATEMENTS                    **
1120 REM ** 10000- GRAPHICS 1.  INITIALIZE, SET PARAMETERS   **
1130 REM ** 11000- GRAPHICS 2.  CONVERT RAW TO SCALAR DATA  **
1140 REM ** 12000- GRAPHICS 3.  EXECUTE LO-RES GRAPH        **
1150 REM ** 13000- GRAPHICS 4.  REPEAT GRAPH/TERMINATE       **
1160 REM **
1170 REM *****
1180 HOME : VTAB 5: HTAB 5: INVERSE : PRINT "PROGRAM 'GIESELER'": NORMAL : PRIN
T
1190 REM
1200 REM  revision 1  --  Sept 1983  --  Bill Lloyd
1210 GOTO 4000
1220 REM ===== end
1230 REM
1240 REM

```

SUBROUTINES FOR CURVE FITTING

```

2000 REM ++++++ ++++++ ++++++ SUBROUTINE FOR SLOPE CALCULATION
2010 REM ++++++ ++++++ ++++++ ++++++ ++++++ ++++++ ++++++ ++++++ ++++++ start
2020 S = 0:V = 0:W = 0:X = 0:Y = 0:Z = 0: FOR I = L TO M: IF A > P(I) THEN S = S
+ 1: GOTO 2040
2030 V = V + I / Q:W = W + (I / Q) ^ 2:X = X + P(I):Y = Y + P(I) ^ 2:Z = Z + P(I)
) * I / Q
2040 NEXT I:F = M - L - S + 1:V = V / F:X = X / F:S = Z - F * V * X:T = W - F *
V ^ 2:H = S / T:K0 = X - H * V
2050 IF F < 2.5 THEN H = 0:K0 = 0: PRINT "SLOPE IS NOT CALCULABLE": GOTO 2070
2060 J = Y - F * X ^ 2 - S ^ 2 / T:J0 = SQR ( ABS (J) / (T * (F - 2))) :P0 = J0
* SQR (W / F)
2070 RETURN
2080 REM ----- end
2090 REM
2100 REM

```

```

3000 REM ++++++ ++++++ ++++++ SUBROUTINE FOR SLOPE BOUNDARIES
3010 REM ++++++ ++++++ ++++++ ++++++ ++++++ ++++++ ++++++ ++++++ ++++++ start
3020 I = 1
3030 IF P(I + 1) < P(I) THEN 3050
3040 I = I + 1: GOTO 3030
3050 IF P(I + 2) > P(I + 1) THEN 3040
3055 M3 = I
3060 I = 0: REM M3= POINT OF MAX OBSERVE D
FLUIDITY
3070 I = I + 1: IF A > P(I) THEN 3070
3080 M1 = I: REM M1= INITIAL MELTING SLOPE POINT
3090 I = I + 1: IF P(I) < P(M3) + B THEN 3090
3100 M2 = I - 1:I = M3 + 1: REM M2= FINAL MELTING SLOPE POINT
3110 I = I + 1
3120 IF P(I) > P(M3) + B THEN 3110
3130 M4 = I: REM M4= INITIAL COKING SLOPE POINT
3140 I = I + 1: IF I > 500 THEN 3180
3160 IF A > P(I) THEN M5 = I - 1: GOTO 3180
3165 IF I > = U * Q THEN M5 = I: GOTO 3180
3170 GOTO 3140
3180 REM
3185 RETURN
3190 REM ----- end
3200 REM
3210 REM

```


MAIN ROUTINE - 1 - INPUT DATA

```

4000 REM ***** MAIN ROUTINE, PART 1
4010 REM *****start
4020 D$ = "": PRINT D$;"PR#1"
4030 DIM P(250)
4035 PRINT CHR$(30)
4040 PRINT TAB(24)"*****";DA$
4050 PRINT TAB(24)"** GIESELER SLOPE ANALYSIS **"
4060 PRINT TAB(24)"** WESTERN KENTUCKY UNIVERSITY **"
4070 PRINT TAB(24)"** Revision 1 - September 83 **"
4080 PRINT TAB(24)"*****": PRINT " ": PRINT " "
4090 READ N$,O$:K$ = N$: GOSUB 6500: PRINT CHR$(28);CHR$(31);K$: PRINT " ":
PRINT " "
4100 K$ = O$: GOSUB 6500: PRINT K$: PRINT " ": PRINT CHR$(30)
4110 READ U,A,B,Q:B = LOG(B); IF Q = 2 THEN 4130
4120 FOR I = 1 TO U * Q: READ Y:P(I) = LOG(Y * Q): NEXT I: PRINT : GOTO 4150
4130 FOR I + 1 TO U * 2: READ Y0,Y1,Y2:P(I) = LOG(2 * (Y0 + Y1 + Y2))
4140 NEXT I: PRINT
4150 PRINT "FOR THE FOLLOWING PARAMETERS...":PN = 1:LN = 20: GOSUB 3000
4160 PRINT " MINIMUM FLUIDITY FOR SLOPE CALCN = "; EXP(A);" D.D.P.M."
4170 PRINT " MAXIMUM FLUIDITY FOR SLOPE CALCN = "; EXP(B);" OF MAX OBSERVED F
LUIDITY"
4180 PRINT " DATA INTERVAL (IN SECONDS) = ";60 / Q: PRINT
4185 REM INSERT "GOTO 5000" TO AVOID PRINTOUT OF INPUT DATA
4190 PRINT "***** INPUT DATA *****": PRINT
4200 PRINT "Time, min. d.d.p.m."
4210 PRINT "-----": PRINT
4220 FOR I = 1 TO U * Q: IF A > P(I) THEN S$ = "too low for slope calcn": GOTO
4250
4230 IF P(I) > (P(M3) + B) THEN S$ = "too high for slope calcn": GOTO 4250
4240 S$ = "INCLUDED IN SLOPE CALCN ***"
4250 TX = 100 * I / Q:T = TX / 100:F = 10 * EXP(P(I)):FL = INT(F)
4252 IF F > FL + .5 THEN FL = FL + 1
4254 F = FL / 10
4260 PRINT T; TAB(18);F; TAB(40);S$:J = J + 1:LN = LN + 1
4270 IF Q < 2.5 THEN 4290
4280 IF J > (Q - .5) THEN J = 0: PRINT :LN = LN + 1: GOTO 4300
4290 IF J > 4.5 THEN J = 0: PRINT :LN = LN + 1
4300 IF LN > 55 THEN GOSUB 6000
4310 NEXT I: PRINT : PRINT : PRINT "*** END INPUT DATA ***": PRINT
4312 LN = LN + 4: IF LN > 55 THEN GOSUB 6000
4315 GOTO 5000
4320 REM ===== end
4330 REM
4340 REM

```

MAIN ROUTINE - 2 - CALCULATIONS

```

5000 REM ***** MAIN ROUTINE, PART 2
5010 REM ***** start
5020 M6 = INT (100 * EXP (P(M3))):M6 = M6 / 100:M7 = INT (100 * M3 / Q):M7 =
M7 / 100
5030 PRINT CHR$ (28); CHR$ (31)"ANALYSIS OF GIESELER RUN": PRINT CHR$ (30): P
RINT
5035 LN = LN + 3: IF LN > 55 THEN GOSUB 6000
5040 PRINT "MAXIMUM OBSERVED FLUIDITY = ";M6;" DDPM AT ";M7;" MINUTES": PRINT
5045 LN = LN + 2: IF LN > 55 THEN GOSUB 6000
5050 L = M1:M = M2: GOSUB 2000:MS = H:MI = K0: PRINT TAB( 10)"SLOPE ANALYSIS DA
TA": PRINT
5055 LN = LN + 3: IF LN > 55 THEN GOSUB 6000
5060 M6 = INT (100 * M1 / Q):M6 = M6 / 100:M7 = INT (100 * M2 / Q):M7 = M7 / 1
00
5070 PRINT : PRINT "MELTING SLOPE FROM ";M6;" TO ";M7;" MINUTES:"
5075 IF MI < 0 THEN MI = - MI:F$(1) = "-"
5080 M6 = INT (1E4 * MS):M6 = M6 / 1E4
5082 M7 = INT (1E4 * J0):M7 = M7 / 1E4
5084 M8 = INT (1E4 * MI):M8 = M8 / 1E4
5086 M9 = INT (1E4 * P0):M9 = M9 / 1E4
5090 PRINT "SLOPE "; TAB( 12)M6; TAB( 30)"STD DEVN"; TAB( 45);M7
5100 PRINT "INTERCEPT"; TAB( 12)F$(1);M8; TAB( 30)"STD DEVN"; TAB( 45);M9
5110 PRINT "DEGREES OF FREEDOM ="; TAB( 30)F - 2: PRINT :LN = LN + 5
5120 L = M4:M = M5: GOSUB 2000: IF LN > 58 THEN GOSUB 6000
5125 CS = H:CI = K0
5130 M6 = INT (100 * M4 / Q):M6 = M6 / 100
5135 M7 = INT (100 * M5 / Q):M7 = M7 / 100
5140 PRINT : PRINT "COKING SLOPE FROM ";M6;" TO ";M7;" MINUTES:"
5145 IF CS < 0 THEN CS = - CS
5150 M6 = INT (1E4 * CS):M6 = M6 / 1E4
5152 M7 = INT (1E4 * J0)
5153 M7 = M7 / 1E4
5154 M8 = INT (1E4 * CI):M8 = M8 / 1E4
5156 M9 = INT (1E4 * P0):M9 = M9 / 1E4
5160 PRINT "SLOPE"; TAB( 12);F$(2);M6; TAB( 30);"STD DEVN"; TAB( 45);M7
5170 PRINT "INTERCEPT"; TAB( 12);M8; TAB( 30);"STD DEVN"; TAB( 45);M9
5180 PRINT "DEGREES OF FREEDOM ="; TAB( 30)F - 2: PRINT :LN = LN + 7
5190 IF LN > 58 THEN GOSUB 6000
5192 IF F$(1) = "-" THEN MI = - MI
5194 IF CS > 0 THEN CS = - CS
5200 R = (MS * CI - CS * MI) / (MS - CS):V = (CI - MI) / (MS - CS):R = EXP (R)
5210 M6 = INT (100 * R):M6 = M6 / 100:M9 = INT (100 * V):M9 = M9 / 100
5220 PRINT : PRINT "INTERSECTION MAXIMUM FLUIDITY = ";M6;" DDPM AT ";M9;" MINUT
ES"
5230 PRINT "-----"
5235 PRINT D$;"PR#0"
5240 HOME : HTAB 8: VTAB 8: INVERSE : PRINT "SET PAPER AND THEN TYPE 'CONT'": N
ORMAL
5250 STOP
5260 GOTO 10000
5270 REM ===== end
5280 REM
5290 REM

```

ADDITIONAL SERVICE SUBROUTINES

```

5500 REM ERROR TRAP FOR GRAPHICS
5510 REM +++++ +++++ +++++ +++++ +++++ +++++ +++++ +++++ +++++ start
5520 FOR I = J TO 1 STEP - 1
5530 G$ = "I ";LL = LL + 1
5540 IF LL > 5.5 THEN G$ = "+ ";LL = 1
5550 PRINT G$
5560 NEXT I
5570 GOTO 12040
5580 REM ----- end
5590 REM
5600 REM
6000 REM +++++ +++++ +++++ SUBROUTINE FOR PAGING
6010 REM +++++ +++++ +++++ +++++ +++++ +++++ +++++ +++++ +++++ start
6020 LN = 66 - LN:PN = PN + 1
6030 FOR K = 1 TO 8: PRINT : NEXT K
6040 PRINT N$; SPC( 65 - LEN (N$));DA$
6050 PRINT O$; SPC( 65 - LEN (O$));"-- PAGE ";PN;" --": PRINT
6060 PRINT : PRINT :LN = 6: RETURN
6070 REM ----- end
6080 REM
6090 REM
6500 REM +++++ +++++ +++++ SUBROUTINE TO CENTER TITLES
6510 REM +++++ +++++ +++++ +++++ +++++ +++++ +++++ +++++ +++++ start
6520 Z$ = " "
6530 Z% = LEN (K$): IF Z% > 47 THEN 6570
6540 Z% = (48 - Z%) / 2: REM SET FOR 6 CPI
6550 Z$ = LEFT$ (Z$,Z%)
6560 K$ = Z$ + K$
6570 RETURN
6580 REM ----- end
6590 REM
6600 REM
7000 REM +++++ +++++ +++++ TEMPERATURE-AVERAGING ROUTINE
7010 REM +++++ +++++ +++++ +++++ +++++ +++++ +++++ +++++ +++++ start
7020 PR# 0: HOME : VTAB 3: DIM X(15)
7030 PRINT "UTILITY TO CALCULATE AVERAGE OF FIFTEEN TEMPERATURES": PRINT
7040 PRINT "ENTER VALUES:": PRINT : FOR I = 1 TO 15
7050 PRINT I;: INPUT X(I):S = S + X(I): NEXT I:S = S / 15
7060 FOR I = 1 TO 15:D = D + (S - X(I)) ^ 2: NEXT I:D = SQR (D / 14): PRINT
7070 INVERSE : PRINT "AVERAGE TEMPERATURE = ";S: PRINT
7080 PRINT "STANDARD DEVIATION = ";D: PRINT : NORMAL
7090 GET A$: IF A$ = "" THEN 7090
7100 END
7110 REM ----- end
7120 REM
7130 REM

```

INPUT DATA

```

8000 REM ***** DATA INPUT STATEMENTS
8010 REM ***** start
8020 DATA "USDOE COAL #44 - KCER #7799"
8030 DATA "ISOTHERMAL #12: 419.9 +/-0.3C, 745 psig"
8040 DATA 30 : REM NUMBER OF MINUTES' DATA
8050 DATA 0 : REM LN(MINIMUM D.D.P.M. TO BE USED IN SLOPE CALCN)
8060 DATA .50 : REM FRACTION OF MAX D.D.P.M. TO BE USED IN SLOPE CALCN
8070 DATA 1 : REM NUMBER OF DATA PRINTOUTS PER MINUTE
8080 REM
8090 REM DATA FOLLOWS .....
8100 DATA 0.9, 1.3, 3.1, 15.5, 56.9 , 276.2, 1016, 1609, 1992, 1776
8110 DATA 1475, 1157, 856.4, 614.2, 434.4, 291.4, 190.4, 126.1, 75.4, 55.3
8120 DATA 26.4, 25.6, 17.0, 10.2, 5.8, 3.4, 2.4, 1.4, 1.1, 0.7
8130 DATA 1.5, 1.0, 0.8
8140 DATA 1418, 1397, 1259, 1142, 1054, 997.8, 991.8, 1056, 959.8, 880.1
8150 DATA 851.5, 781.6, 738.2, 705.9, 643.7, 616.6, 624.0, 615.6, 607.5, 611.9
8160 DATA 620.2, 627.3, 586.0, 530.0, 467.0, 414.5, 358.2, 310.8, 283.5, 269.0
8170 DATA 250.7, 234.9, 222.7, 223.0, 205.6, 195.2, 188.2, 183.0, 166.3, 150.5
8180 DATA 148.2, 140.3, 131.7, 126.8, 122.1, 108.9, 99.8, 97.2, 92.7, 81.8
8190 DATA 74.9, 73.4, 69.8, 61.5, 62.9, 62.9, 58.2, 60.0, 54.7, 53.6
8200 DATA 48.3, 47.8, 42.8, 42.0, 36.5, 37.3, 34.4, 26.1, 28.3, 25.1
8210 DATA 22.8, 16.7, 15.3, 16.0, 15.2, 14.4, 13.6, 11.8, 9.00, 8.00
8219 DATA 5.1, 4.6, 4.2, 3.7, 3.2, 3.0, 2.8, 2.6, 2.4, 2.0
8310 DATA
8320 DATA
8330 DATA
8340 DATA
8350 DATA
8360 DATA
8370 DATA
8380 DATA
8390 DATA
8400 REM ===== end
8410 REM
8420 REM

```

GRAPHICS - PART 1

```

10000 REM ***** GRAPHICS 1.  INITIALIZE
10010 REM *****
10020 DIM X%(250),Y%(250)
10025 DIM F%(25),Z%(25)
10030 DIM T%(120),U%(120),V%(120)
10040 HOME : VTAB 4: PRINT "MAX EXPERIMENTAL TIME IN MINUTES = ";U * Q
10050 PRINT : INPUT "HORIZONTAL SPACES (MAX=135)? ";H
10060 IF H > 135 THEN FLASH : PRINT "MAXIMUM IS 135!!": NORMAL : PRINT : GOTO 10050
10070 PRINT : INPUT "MAX VALUE OF TIME AXIS ? ";X
10080 PRINT : PRINT : PRINT "TABLE OF VALUES FOR LN(MAX FLUIDITY)": PRINT
10090 FOR I = 1 TO 7: PRINT "LN(10^";I;") = ";LOG (10 ^ I): NEXT
10100 PRINT : PRINT : PRINT "LN(MAX OBSERVED FLUIDITY) = ";P(M3)
10110 PRINT : PRINT "LN(MAX INTERSECTION FLU) = ";LOG (R)
10120 PRINT : INPUT "VERTICAL SPACES (MAX= 90) ? ";VS
10130 IF VS > 90 THEN FLASH : PRINT "MAXIMUM IS 90!!": NORMAL : PRINT : GOTO 10120
10140 PRINT : INPUT "MAX VALUE OF LN(FLU) AXIS ? ";YM
10180 PRINT D$;"PR#1"
10190 PRINT CHR$ (27);"X9"; CHR$ (14)
10200 K$ = N$: GOSUB 6500: PRINT CHR$ (28); CHR$ (31);K$: PRINT " ": PRINT " "
10210 K$ = O$: GOSUB 6500: PRINT K$: PRINT " ": PRINT CHR$ (30)
10220 REM =====
10230 REM
10240 REM

```

GRAPHICS - PART 2(A)

```

11000 REM ***** GRAPHICS 2.  CONVERSION TO SCALAR DATA
11010 REM ***** start
11020 FOR I = 1 TO U * Q:YX(I) = INT (P(I) * VS / YM)
11030 X(I) = INT (I * H / (Q * X))
11040 IF X(I) > H OR X(I) < 0 THEN X(I) = 0:YX(I) = 0
11050 NEXT I
11100 REM ----- TANGENTS
11110 FOR I = 1 TO VS:TX(I) = I:UX(I) = INT (((I * YM / VS - MI) / MS) * H / X
)
11120 IF UX(I) > H OR UX(I) < 0 THEN UX(I) = 0
11130 VX(I) = INT (((I * YM / VS - CI) / CS) * H / X)
11140 IF VX(I) > H OR VX(I) < 0 THEN VX(I) = 0
11150 NEXT I
11160 REM ----- end tangents
11170 REM ===== end
11180 REM
11190 REM
11200 REM ----- ORGANIZE STRINGS
11210 LL = 5
11215 PRINT CHR$(29)
11220 FOR J = VS TO 1 STEP -1
11240 F = 0: FOR I = 1 TO U * Q
11250 IF J = YX(I) THEN F = F + 1:ZX(F) = X(I) + 3:FX(F) = 0
11260 NEXT I
11300 REM ADD TANGENTS
11310 IF UX(J) = 0 THEN 11330
11320 F = F + 1:FX(F) = 1:ZX(F) = UX(J) + 3
11330 IF VX(J) = 0 THEN 11350
11340 F = F + 1:FX(F) = 1:ZX(F) = VX(J) + 3
11350 REM NODE
11360 IF F < 2 THEN 11540

```

GRAPHICS - 2(B)

```

11400 REM SEQUENCING
11410 FOR K = 1 TO F: FOR L = 2 TO F
11420 IF ZX(L) < ZX(L - 1) THEN 11440
11425 IF ZX(L) = ZX(L - 1) AND FX(L) = 1 THEN ZX(L) = 0:FX(L) = 2: GOTO 11470
11428 IF ZX(L) = ZX(L - 1) AND FX(L - 1) = 1 THEN ZX(L - 1) = 0:FX(L - 1) = 2:
GOTO 11470
11430 GOTO 11470
11440 YX = ZX(L):FLX = FX(L)
11450 ZX(L) = ZX(L - 1):FX(L) = FX(L - 1)
11460 ZX(L - 1) = YX:FX(L - 1) = FLX
11470 NEXT L
11480 NEXT K
11500 REM ELIMINATE REDUNDANT SPACES
11510 FOR K = F TO 1 STEP - 1
11515 IF ZX(K) < 1 THEN ZX(K) = 0: GOTO 11530
11520 ZX(K) = ZX(K) - ZX(K - 1) - 1
11530 NEXT K
11540 G$ = "I"
11545 LL = LL + 1
11550 IF LL > 5.5 THEN G$ = "+" :LL = 1
11600 REM ASSEMBLE STRINGS
11605 ONERR GOTO 5500
11610 BB$ = "
"
11615 BB$ = BB$ + "
"
11620 W$ = G$: IF F = 0 THEN 11670
11625 FOR K = 1 TO F
11630 IF ZX(K) = 0 THEN 11635
11630 W$ = W$ + LEFT$(BB$,ZX(K))
11635 ON FX(K) + 1 GOTO 11640,11645,11650
11640 W$ = W$ + "o": GOTO 11670
11645 W$ = W$ + ".": GOTO 11670
11650 W$ = W$ + " "
11670 NEXT K
11800 FOR K = 1 TO 10
11810 ZX(K) = 0:FX(K) = 0
11820 NEXT K
11840 REM ===== end
11850 REM
11860 REM

```


9.5 Notes on Regression Equations

The analysis of ASTM and isothermal Gieseler plasticities in terms of multiple linear regression equations is found in Parts 5.3 and 5.4, and in Tables 31-35. A number of additional regression equations have been developed in the course of the analysis. Table A-4 presents a listing of further equations for prediction of ASTM Gieseler fluid properties. Table A-5 presents a similar listing for isothermal Gieseler fluid properties.

In making selections of variables to reject in order to simplify a particular multiple linear regression equation, for SAS analyses (73) we have relied mainly upon the Type III/Type IV sum of squares, which measures the incremental contribution of each independent variable to the overall predictive fit when all other variables are included. This measure is independent of the order in which variables are entered, a critically important consideration.

Exploratory regression analysis has been carried out with an APPLE IIe microcomputer using a modified multiple regression analysis program (75) which also provides an order-independent measure of the contribution of each independent variable, namely a T-ratio (closely akin to the β' values of statistical texts).

An example of the Type IV ss test is in the reduction of the ASTM maximum fluidity by intersection from four to three variable terms. For the four-variable analysis the Type IV sums are:

pyrolysis liquids (13-16 min window)	151.02
THF-extractables	32.47
vitronite reflectance	22.87
pseudovitronite content	4.65

The probabilities of significance in this regression range from the pyrolysis variable ($P > 99.99\%$) to pseudovitrinite ($P = 79\%$). The latter variable is dropped to form the three-variable regression equation.

Table A-4

Multiple Linear Regression Equations for the Prediction of ASTM Gieseler Fluid Properties

					R	std error
<u>ln(maximum observed fluidity):</u>						
=	1.069E+1 * reflect	+ 4.190E-1 * THF	+ 2.288E-3 * pyr13-16	- 9.877	.898	1.25
=	1.208E+1 * reflect	+ 3.054E-1 * DMF	+ 4.682E-3 * THF	- 16.04	.867	1.41
=	9.441E-1 * FSI	+ 2.617E-1 * pseudo	+ 3.123E0 * reflect	- 1.468	.760	1.84
=	9.605E-1 * FSI	+ 3.172E-1 * pseudo	+ 3.397E-1 * resinite	- 0.095	.759	1.85
=	3.798E-1 * pseudo	+ 3.125E0 * pyr4m	+ 2.812E-3 * THF	- 2.024	.898	1.56
=	3.683E-1 * pseudo	+ 3.634E0 * pyr4m		+ 1.629	.875	1.83
=	4.133E0 * pyr4m			+ 2.611	.826	2.42
=	2.151E-1 * pseudo	+ 3.769E-1 * THF	+ 6.863E0 * reflect			
			+ 2.317E-3 * pyr13-16	- 7.721	.907	1.21
=	-3.613E-1 * sulfur	+ 8.727E0 * reflect	+ 4.476E-1 * THF			
			+ 2.461E-3 * pyr13-16	- 8.215	.902	1.24
<u>ln(maximum intersection fluidity):</u>						
=	1.668E+1 * reflect	+ 5.507E-1 * THF	+ 3.385E-3 * pyr13-16	- 16.14	.922	1.69
=	1.978E+1 * reflect	+ 4.782E-1 * DMF	+ 5.712E-1 * THF	- 26.58	.873	2.13
=	1.460E0 * FSI	+ 1.126E+1 * reflect	+ 9.367E-1 * resinite	- 7.295	.768	2.80
=	1.462E0 * FSI	+ 2.742E-1 * pseudo	+ 8.357E0 * reflect	- 5.690	.768	2.80
=	2.142E-1 * pseudo	+ 5.090E+1 * THF	+ 1.287E+1 * reflect			
			+ 3.916E-3 * pyr13-16	- 13.99	.926	1.67
=	-6.645E-1 * sulfur	+ 1.306E+1 * reflect	+ 6.026E-1 * THF			
			+ 4.202E-3 * pyr13-16	- 13.06	.928	1.65
=	5.126E-1 * pseudo	+ 5.914E0 * pyr13-16		+ 0.810	.895	
=	6.609E0 * pyr13-16			+ 2.176	.856	

--continued--

Table A-4 (Cont.)

						<u>R</u>	<u>std error</u>
<u>melting slope:</u>							
=	1.751E0	* reflect	+ 7.220E-2 * THF	+ 3.252E-4 * pyr13-16	- 1.897	.888	.203
=	6.313E-2	* pseudo	+ 4.897E-2 * THF	+ 7.683E-4 * pyr14-15	- 0.739	.887	.204
=	2.099E0	* reflect	+ 3.521E-2 * DMF	+ 8.666E-2 * THF	- 2.768	.842	.238
=	1.166E-1	* FSI	+ 5.450E-2 * pseudo	+ 1.336E-1 * resinite	- 0.199	.712	.310
=	1.178E-1	* FSI	+ 4.640E-2 * pseudo	+ 6.321E-1 * reflect	- 0.453	.702	.314
<u>coking slope:</u>							
=	7.984E-1	* reflect	+ 9.410E-3 * THF	+ 1.543E-4 * pyr13-16	+ .0030	.860	.092
=	1.038E0	* reflect	+ 1.266E-2 * DMF	+ 1.995E-2 * THF	- .4080	.770	.115
=	4.643E-2	* FSI	+ 8.344E-1 * reflect	+ 2.035E-2 * THF	- .1848	.816	.104
=	5.034E-2	* FSI	- 1.334E-2 * exinite	+ 7.330E-1 * reflect	+ .2006	.793	.110
=	5.697E-2	* FSI	+ 3.012E-3 * pseudo	+ 6.414E-1 * reflect	+ .1660	.782	.113
<u>softening temperature:</u>							
=	3.120E+1	* reflect	- 1.303E0 * THF	- 8.724E-3 * pyr2-5	+ 390.9	.851	3.84°
=	2.448E+1	* reflect	- 1.309E0 * THF	- 6.562E-3 * pyr13-16	+ 398.4	.840	3.98°
=	2.176E+1	* reflect	- 9.449E-1 * DMF	- 1.388E0 * THF	+ 416.2	.815	4.25°
=	-2.944E0	* sulfur	- 6.602E-1 * DMF	- 1.244E0 * THF	+ 429.3	.844	3.93°
=	-3.170E0	* FSI	+ 5.579E-1 * pseudo	+ 2.825E+1 * reflect	+ 381.3	.642	5.62°
=	-1.938E0	* FSI	+ 4.221E-1 * pseudo	- 3.765E0 * sulfur	+ 404.9	.707	5.18°

--continued--

Table A-4 (Cont.)

					<u>R</u>	<u>std error</u>
<u>temperature of maximum fluidity:</u>						
=	3.162E+1 * reflect	- 7.632E-1 * THF	- 6.361E-3 * pyr2-5	+ 421.7	.831	2.95°
=	2.674E+1 * reflect	- 7.672E-1 * THF	- 4.790E-3 * pyr13-16	+ 427.2	.820	3.04°
=	2.404E+1 * reflect	- 6.507E-1 * DMF	- 8.601E-1 * THF	+ 440.1	.781	3.32°
=	-2.868E0 * sulfur	+ 5.600E-1 * pseudo	- 6.406E-1 * DMF	+ 449.1	.804	3.16°
=	-1.810E0 * FSI	+ 5.076E-1 * pseudo	+ 2.289E+1 * reflect	+ 418.8	.572	4.36°
=	-3.218E0 * sulfur	+ 1.934E-1 * pseudo	+ 5.748E-1 * exinite	+ 433.2	.701	3.79°
<u>solidification temperature:</u>						
=	3.522E+1 * reflect	+ 1.185E0 * pseudo	+ 8.798E-3 * pyr14-15	+ 421.9	.883	3.87°
=	-2.358E0 * sulfur	+ 4.157E+1 * reflect	+ 9.515E-1 * DMF	+ 410.8	.867	4.10°
=	1.078E0 * pseudo	+ 3.840E+1 * reflect	+ 6.492E-1 * DMF	+ 409.4	.872	4.03°
=	1.355E0 * FSI	+ 1.092E0 * pseudo	+ 3.673E+1 * reflect	+ 420.4	.853	4.29°
=	5.871E+1 * reflect	+ 5.574E-1 * THF	+ 3.647E-2 * pyr13-16	+ 404.2	.858	4.23°
=	5.986E+1 * reflect	+ 5.441E-1 * DMF	+ 5.840E-1 * THF	+ 394.3	.853	4.29°

Table A-5

Multiple Linear Regression Equations for the Prediction of Isothermal Gieseler Fluid Properties

<u>ln(maximum observed fluidity at 400°):</u>					<u>R</u>	<u>std error</u>			
=	4.66E0	* pyr4m		+ 2.270E-1	.860	2.22			
=	2.993E-1	* pseudo	+ 4.247E0	* pyr4m	- 7.014E-1	.899	1.80		
=	2.652E-1	* pseudo	+ 2.695E0	* pyr4m	+ 3.519E-2 * pyrtotal	- 2.833E0	.921	1.48	
=	-1.024E0	* sulfur	+ 3.239E-1	* THF	+ 2.807E0	* pyr4m			
				+ 3.213E-3	* pyrl4-15	- 2.064E0	.932	1.15	
=	6.719E-1	* resinite	+ 1.083E+1	* reflect	+ 3.648E-1	* DMF			
				+ 3.703E-1	* THF	- 1.824E+1	.895	1.42	
=	8.321E-4	* BTU	+ 2.451E-1	* pseudo	+ 2.396E0	* pyr4m			
				+ 3.171E-3	* pyrl4-15	- 1.207E+1	.927	1.19	
=	2.013E-3	* BTU	+ 4.426E-1	* FSI	- 5.779E-1	* exinite			
				+ 1.495E0	* resinite	- 2.435E+1	.743	2.12	
=	3.867E-1	* THF	+ 1.977E0	* pyr4m	+ 3.424E-3	* pyrl4-15			
			- 6.924E-1	* sulfur	+ 6.221E0	* reflect	- 7.377E0	.942	1.09
=	4.367E-1	* THF	+ 8.357E0	* reflect	+ 5.913E-3	* pyrl4-15			
				- 5.602E-1	* sulfur	- 9.849E0	.934	1.14	
=	3.872E-1	* THF	+ 1.136E+1	* reflect	+ 5.320E-3	* pyrl4-15	- 1.230E+1	.924	1.19
=	3.203E-1	* THF	- 1.021E0	* sulfur	+ 4.665E0	* pyr4m	- 1.481E0	.921	1.21
=	3.713E-1	* THF	- 9.954E-1	* sulfur	+ 7.208E-3	* pyrl4-15	- 3.128E0	.912	1.28
=	1.423E-1	* THF	+ 2.617E0	* pyr4m	+ 3.149E-3	* pyrl4-15	- 2.216E0	.885	1.45
=	5.116E0	* pyr4m	- 7.232E-1	* sulfur		+ 1.909E0	.897	1.35	

--continued--

TABLE A-5 (CONT.)

<u>ln(intersection maximum fluidity at 380°):</u>					<u>R</u>	<u>std error</u>
= 2.284E-1 * FSI	- 1.021E0	* sulfur	+ 4.504E0	* reflect - 9.465E-2*DMF		
+ 2.257E-1 * THF	+ 1.825E0	* pyr4m	- 1.647E-3 * pyr2-4			
			+ 5.228E-3 * pyr14-15	- 3.048E0	.947	0.97
= -8.176E-1 * sulfur	+ 5.462E0	* reflect	- 8.960E-2 * DMF			
+ 2.148E-1 * THF	+ 1.744E0	* pyr4m	+ 4.291E-3 * pyr14-15	- 2.968E0	.942	0.96
= -6.402E-1 * sulfur	+ 6.771E0	* reflect	+ 2.203E-1 * THF			
+ 5.911E-3 * pyr14-15	+ 1.512E-4	* Btu	- 2.988E-2 * DMF	- 7.555E0	.935	1.01
= -8.101E-1 * sulfur	+ 5.210E0	* reflect	+ 1.925E-1 * THF			
	+ 1.319E0	* pyr4m	+ 4.035E-3 * pyr14-15	- 4.277E0	.940	0.96
= -7.219E-1 * sulfur	+ 6.636E0	* reflect	+ 2.259E-1 * THF			
			+ 5.696E-3 * pyr14-15	- 5.926E0	.935	0.97
= -5.795E-1 * sulfur	+ 5.339E0	* reflect	+ 6.332E-3 * pyr14-15	- 2.661E0	.919	1.06
= -1.067E0 * sulfur	+ 1.740E-1	* THF	+ 6.724E-3 * pyr14-15	- 5.895E-1	.916	1.07
= -8.981E-1 * sulfur	+ 7.074E-3	* pyr14-15		+ 1.203E0	.906	1.11
<u>ln(intersection maximum fluidity at 400°):</u>						
= -4.565E-1 * sulfur	+ 8.272E0	* reflect	+ 3.680E-1 * THF			
+ 4.791E-3 * pyr14-15	+ 2.529E-4	* BTU	+ 1.086E-1 * DMF	- 1.381E+1	.943	1.11
= -5.801E-1 * sulfur	+ 8.479E0	* reflect	+ 3.974E-1 * THF			
	+ 4.913E-3	* pyr14-15	+ 1.040E-1 * DMF	- 1.061E+1	.942	1.09
= -5.558E-1 * sulfur	+ 9.305E0	* reflect	+ 4.357E-1 * THF			
			+ 5.381E-3 * pyr14-15	- 9.709E0	.939	1.10
= 1.228E+1 * reflect	+ 3.866E-1	* THF	+ 5.243E-3 * pyr14-15	- 1.214E+1	.929	1.15
= 8.551E0 * reflect	+ 6.668E-3	* pyr14-15		- 5.092E0	.893	1.38

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Table A-5 (Cont.)

						<u>R</u>	<u>std error</u>
<u>ln(intersection maximum fluidity at 420°):</u>							
=	6.338E-4	* BTU	+ 3.244E-1	* pseudo	+ 3.819E-1 * THF		
	+ 1.670E0	* pyr4m	+ 1.606E-3	* pyr2-5	+ 1.538E-1 * DMF	- 1.467E+1	.938
							1.38
=	2.375E-2	* sulfur	+ 9.309E0	* reflect	+ 4.925E-1 * THF		
	+ 2.978E-3	* pyr14-15	+ 5.820E-4	* BTU	+ 2.963E-1 * DMF	- 2.329E+1	.932
							1.45
=	5.414E-4	* BTU	+ 3.813E-1	* pseudo	+ 4.217E-1 * THF		
			+ 2.263E0	* pyr4m	+ 1.967E-3 * pyr2-5	- 1.108E+1	.935
							1.39
=	5.625E-4	* BTU	+ 3.280E-1	* pseudo	+ 4.146E-1 * THF		
			+ 2.205E-1	* DMF	+ 2.605E-3 * pyr2-5	- 1.526E+1	.934
							1.40
=	4.340E-1	* pseudo	+ 4.373E-1	* THF	+ 1.982E0 * pyr4m		
					+ 2.241E-3 * pyr2-5	- 4.301E0	.931
							1.40
=	3.915E-1	* pseudo	+ 4.339E-1	* THF	+ 1.863E-1 * DMF		
					+ 2.838E-3 * pyr2-5	- 7.633E0	.930
							1.41
=	4.594E-1	* pseudo	+ 5.056E-1	* THF	+ 3.849E-3 * pyr2-5	- 4.940E0	.923
							1.44
=	4.824E-1	* THF	+ 4.498E-3	* pyr2-5		- 3.150E0	.875
							1.78
<u>melting slope at 400°:</u>							
=	8.139E-2	* reflect	+ 1.157E-1	* resinite	+ 3.466E-2 * THF		
	+ 2.640E-1	* pyr4m	+ 8.901E-4	* pyr14-15	- 4.014E-4 * pyr13-16	- 3.493E-1	.910
							0.127
=	1.180E-1	* resinite	+ 3.313E-2	* THF	+ 2.745E-1 * pyr4m		
			+ 8.619E-4	* pyr14-15	- 3.899E-4 * pyr13-16	- 2.838E-1	.910
							0.125
=	1.224E-1	* resinite	+ 3.343E-2	* THF	+ 2.962E-1 * pyr4m		
					+ 4.523E-5 * pyr14-15	- 3.368E-1	.906
							0.124
=	1.238E-1	* resinite	+ 3.343E-2	* THF	+ 3.220E-1 * pyr4m	- 3.300E-1	.906
							0.122
=	3.037E-2	* THF	+ 3.661E-1	* pyr4m		- 2.082E-1	.877
							0.136

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Table A-5 (Cont.)

coking slope at 400°:											R	std error	
=	4.225E-5	*	BTU	+	4.584E-2	*	sulfur	-	1.463E-2	*	exinite		
-	3.227E-1	*	reflect	+	2.038E-2	*	resinite	+	4.937E-2	*	DMF		
-	6.303E-3	*	THF	-	6.229E-2	*	pyr4m	+	4.951E-4	*	pyr14-15		
								-	2.573E-4	*	pyr13-16	- 1.981E-1	.876
													0.035
=	2.495E-5	*	BTU	+	3.723E-2	*	sulfur	-	9.071E-3	*	exinite		
-	2.547E-1	*	reflect	+	2.872E-3	*	DMF	-	5.132E-2	*	pyr4m		
+	4.474E-4	*	pyr14-15	-	2.233E-4	*	pyr13-16					- 5.462E-2	.857
													0.036
=	2.575E-5	*	BTU	+	3.205E-2	*	sulfur	-	8.056E-3	*	exinite		
-	3.073E01	*	reflect	-	5.540E-3	*	pyr4m	-	1.343E-5	*	pyr13-16	+ 7.158E-3	.835
													0.036
=	2.540E-5	*	BTU	+	3.165E-2	*	sulfur	-	7.922E-3	*	exinite		
				-	3.115E-1	*	reflect	-	1.687E-5	*	pyr13-16	+ 1.553E-2	.835
													0.036
=	1.787E-5	*	BTU	+	2.490E-2	*	sulfur	-	6.308E-3	*	exinite		
								-	3.581E-1	*	reflect	+ 1.359E-1	.824
													0.036
=	2.026E-2	*	sulfur	-	5.796E-3	*	exinite	-	3.301E-1	*	reflect	+ 3.665E-1	.811
													0.036
=	2.878E-2	*	sulfur	-	2.809E-1	*	reflect					+ 2.887E-1	.796
													0.037