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PREDICTORS OF PLASTICITY IN BITUMINOUS COALS

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1. SUMMARY

In the second quarter of this study a second dozen coals from western Kentucky have been identified and samples obtained. The nominal ranks of these plastic coals range from hvAb to subA. Classical chemical and petrographic characterizations have been completed on all 24 coals. ASTM Gieseler plastometric analysis has been carried out in quadruplicate on all coals. Pyrolysis gas chromatography has been completed on a half-dozen coals, using a procedure affording reproducible pyrograms. Quantitative extractions have been completed on a half-dozen coals, using THF and DMF extractants. Method development work on FTIR analysis has been completed, with indications of high sensitivity for several organic functional groups.

During the third quarter it is planned to complete acquisition of the last dozen coals -- mostly non-Kentucky coals of varying rank and plasticity -- and to obtain substantially more data on all coals. Classical analyses and ASTM Gieseler plastometric analyses are expected to be completed. Work on the nonclassical characterization procedures (pyrolysis GC, quantitative extractions, and FTIR), which has thus far been focussed upon development of reproducible and reliable techniques, will be directed to the generation of characterization data for the coals under study. Work will commence on coal extract chromatography, and the systematic organization of the data for statistical analysis will be undertaken.

2. INTRODUCTION

2.1 Purpose and Approach. The plastic properties of mid-ranked coals are potentially important for next-generation coal handling and coal conversion technologies. Yet coal plasticity in the scientific sense is poorly understood. We have a little empirical knowledge about the modification of plasticity, but no quantitative or semiquantitative basis for inferring plastic behavior from other properties.

The approach of this study is to secure three dozen (or more) coals of varying rank, composition and plasticity, and to analyze these coals carefully by standard chemical and petrographic techniques. The bitumen fractions will be determined, both by THF (asphaltenes but not preasphaltenes) and DMF (everything). Pyrolysis gas chromatography on both whole coals and extracted residues will compare capacities to generate 'metaplast'. Extracts from coals with plasticities differing by at least four orders of magnitude will be examined for identifiable differences; extraction residues will be subjected to differential FTIR analysis. All of the data will be combined and subjected to systematic statistical analysis with the objective of identifying predictors of coal plasticity.

This report describes the work in the first six months of the study. During this period equipment and instrumentation has been obtained, 24 coal samples have been obtained, the nonclassical methods have been developed and checked out, and an appreciable amount of experimental data has been obtained.

2.2 Coals Used in This Study. The first two dozen coals have been obtained from various coal preparation plants in western Kentucky, all in coarse sizes, and all from well defined seams and mines. These represent seven seams, 12 sources, and five counties. Nominal ranks range from hvAb to subA. These sources are given in Table 1. The accession number for this study (right hand column in Table 1) is used to identify the coals in subsequent tests.

The remaining coal samples will be obtained mainly from eastern Kentucky, Pennsylvania and Wyoming. These are expected to provide a wider range of ranks.

2.3 Work Schedule. Phase 1 of this study is planned to be completed by the end of calendar 1982. The second and final phase will be a detailed examination of a subset of six to eight coals, to be selected at the end of Phase 1.

Figure 1 shows schematically the projected time flow of the principal tasks in Phase 1 of this study. The project is generally on schedule. Specifically:

Tasks 1.1, 1.6 and 1.8 are on schedule, and task 1.9 is ready to go on schedule.

Tasks 1.2, 1.3 and 1.5, which have received major attention in this first six months, are now 6 to 12 coals ahead of schedule.

Task 1.4 is mixed: ASTM analysis is complete on 24 coals, but isothermal data is not yet under way. The isothermal study will commence during the coming quarter.

Task 1.7 is coupled to task 1.4.

During the coming three months the work schedule calls for initiation of tasks 1.8, 1.10 and 1.12. We expect all of these to commence on schedule.

Table 1

Sources of Western Kentucky Coals

<u>no.</u>	<u>IMMR 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	G2	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

Figure 1

Work Schedule for Phase 1

	1981.....	1982.....	
	<u>S</u> <u>O</u> <u>N</u> <u>D</u>	<u>J</u> <u>F</u> <u>M</u> <u>A</u> <u>M</u> <u>J</u> <u>J</u> <u>A</u> <u>S</u> <u>O</u> <u>N</u> <u>D</u>	
1.1 Selection/Acquisition of Coals	AAAAAAAAAAAA	BBBBBBBBBBBBCCCCCCCCCCCC.	.
1.2 Prep/Distribution of Coals	. AAAAAAAAAA.	AAABBBBBB. BBBBCCCC. CCCCCCCC.	.
1.3 Prox/Ultimate/ASTM Analyses	. AAAAAAAAAA.	AAABBBBBB. BBBBCCCC. CCCCCCCC.	.
1.4 ASTM and Isothermal Plastometry	.	. AAAAAAAAAA. AAABBBBBB. BBBBCCCC. CCCCCCCC.	.
1.5 Petrographic/Reflectance Anal.	.	AAAAAAAAAAAAABBBBBBBBBBCCCCCCCCCCCC.	.
1.6 Quantitative Extraction	.	. AAAAAAAAAAAAA BBBBCCCCCCCC.	.
1.7 Plastometry Analysis	.	. AAAAAAAAAAAAA BBBBCCCCCCCC.	.
1.8 Pyrolysis/GC Analysis	.	. AAAAAAAAAAAAA BBBBCCCCCCCC.	.
1.9 F.T. Infrared Analysis	.	. AAAAAAAAAAAAA BBBBCCCCCCCC.	.
1.10 Chromatography of Extracts	.	. AAAAAAAAAAAAA BBBBCCCCCCCC.	.
1.11 Quantitative Fluorescence	.	. AAAAAAAAAABBBBBBBBCCCCCccc	.
1.12 Statistical Analysis	.	. XXXXXXXXXXXXXXXXXXXXXXXXXXXX	.
1.13 Select Coals for Phase 2	.	. XXXXX	.

A = first 12 selected coals. B = second 12 selected coals. C = third 12 selected coals.

3. CLASSICAL CHARACTERIZATION

3.1 Proximate and Ultimate Analyses. Data for the first 24 coals are given in Table 2. The standard methods used have been identified elsewhere.¹ Ultimate data are on an as-is basis (moisture and mineral matter present).

3.2 Sulfur, Free Swelling Index, and Heating Values. These data are given in Table 3. While these eastern mid-continent coals are all high in total sulfur (1.9-3.7%), the ash sulfate as SO_3 varies considerably (0.4-9.0%), and the organic S : pyritic S ratio varies from 2:1 to 1:2. Swelling characteristics (by FSI) vary from moderately low (2.5) to high (8+). Heating value is very substantially dependent upon chemical composition.²

3.3 Maceral Analysis. Maceral compositions of these coals are given in Table 4. These values are not corrected for the mineral matter present.

3.4 Maceral and Mineral Composition and Vitrinite Reflectance. The maceral contents from Table 4 are summarized in Table 5, along with the estimate of mineral matter (Parr procedure) and the vitrinite maximum reflectance data. The sum of maceral and mineral contents is in most cases close to 100%. Mineral matter by this procedure is (as expected) consistently higher than furnace ash residues (Table 2).

Table 2

Proximate and Ultimate Analyses

<u>Coal no.</u>	<u>Mois- ture</u>	<u>Ash</u>	<u>Vol. matter</u>	<u>Fixed carbon</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%S</u>
1	10.03	7.82	38.6	43.6	66.46	4.87	1.56	3.69
2	7.86	9.93	39.3	42.9	66.04	4.66	1.50	3.15
3	6.75	5.04	38.8	49.4	72.37	5.02	1.50	1.89
4	5.33	6.10	44.4	44.2	72.41	5.09	1.52	3.12
5	4.08	6.24	43.2	46.5	71.51	5.12	1.35	2.68
6	5.02	7.47	42.3	45.2	68.57	4.84	1.06	3.50
7	5.21	6.15	42.5	46.1	72.48	4.54	0.99	3.04
8	7.76	8.11	38.2	45.9	67.49	5.01	1.41	2.89
9	7.08	8.41	38.6	45.9	69.69	5.19	1.44	3.14
10	6.32	7.96	39.1	46.6	70.34	4.03	1.06	2.95
11	5.94	16.66	36.2	41.2	59.56	4.34	1.18	3.20
12	4.72	16.92	36.9	41.6	63.15	4.60	1.22	3.29
13	6.92	7.86	39.0	46.2	69.02	4.88	1.15	2.99
14	6.70	7.10	38.4	47.8	69.16	4.87	1.26	2.57
15	6.31	9.73	38.7	45.3	68.57	5.13	1.45	3.54
16	6.20	7.90	38.5	47.4	70.38	5.27	1.37	2.85
17	7.97	7.75	38.0	46.2	68.97	4.64	1.28	3.32
18	7.09	7.77	37.8	47.3	68.83	4.75	1.40	3.34
19	7.55	9.40	38.1	44.9	67.75	4.81	1.22	2.94
20	7.77	8.95	40.2	43.0	68.31	4.87	1.13	2.70
21	2.57	8.46	39.3	49.6	73.48	5.14	1.05	3.27
22	2.45	9.37	38.5	49.6	74.12	5.29	1.41	2.84
23	2.61	8.04	39.1	50.3	75.03	5.30	1.44	2.60
24	7.87	6.59	39.5	46.0	69.73	5.12	1.40	3.28

Table 3

Analyses for Sulfur, Free Swelling Index and Heating Value

Coal no.	Total sulfur	% SO ₃ in ash	Forms of Sulfur			F S I	Heating value Btu
			Pyritic	Sulfate	Organic		
1	3.69%	5.58%	1.84%	0.06%	1.79%	2 1/2	11,650
2	3.15	5.96	1.32	0.02	1.81	4 1/2	11,630
3	1.89	0.42	0.92	0.01	0.96	4	12,790
4	3.12	0.74	2.11	0.13	0.88	3 1/2	12,920
5	2.68	0.77	1.64	0.24	0.80	3 1/2	12,930
6	3.50	0.37	1.32	0.02	2.16	6	12,630
7	3.04	0.72	1.03	0.03	1.98	3 1/2	12,880
8	2.89	4.30	1.07	0.05	1.77	5	12,080
9	3.14	2.89	1.17	0.12	1.85	4 1/2	12,130
10	2.95	2.83	1.11	0.10	1.74	4	12,490
11	3.20	1.14	1.52	0.14	1.54	2 1/2	11,070
12	3.29	0.72	1.70	0.09	1.50	2 1/2	11,200
13	2.99	3.97	1.25	0.04	1.70	4 1/2	12,410
14	2.57	9.02	0.87	0.05	1.65	4	12,510
15	3.54	6.63	1.52	0.05	1.97	4 1/2	12,040
16	2.85	4.18	1.10	0.05	1.70	4 1/2	12,510
17	3.32	0.48	1.45	0.12	1.75	5	12,110
18	3.34	1.13	1.37	0.24	1.73	4 1/2	12,100
19	2.94	2.88	1.33	0.14	1.47	4	11,910
20	2.70	2.30	0.85	0.27	1.58	5	11,910
21	3.27	2.16	1.30	0.68	1.89	8 1/2	13,190
22	2.84	2.04	1.42	0.10	1.32	8	13,160
23	2.60	3.14	1.19	0.05	1.36	8 1/2	13,360
24	3.28	1.23	1.13	0.05	2.10	4	12,250

Table 4

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	75.7	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

continued

Table 4, 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
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
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

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 5

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

* 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 4) are counted as inert.

4. PLASTOMETRY

4.1 ASTM Gieseler Plasticities. The first twenty-four coals in this study have been subjected to ASTM Gieseler plastometry measurements in quadruplicate, under carefully controlled conditions, as described previously.¹ Results of these determinations are summarized in Table 6. The individual data are given in Appendix Tables A-1 and A-2.

The first four columns of Table 6 present the usual characterization data, e.e., softening temperature (1 ddpm achieved), maximum fluidity temperature, solidification temperature, and maximum observed fluidity (in dial divisions per minute - ddpm). The numbers given are (for each of the three temperatures) the arithmetic averages of the four replicate determinations, after testing the raw data (Table A-1) for rogue values. Where one value differs from the average of the remaining three by more than three standard deviations that value is rejected and the average shown is that of the remaining three values. Each value is followed by a standard error (see footnote to Table 6) as an estimate of repeatability.

The maximum fluidity values are averages of the logarithms of the individual observed values: these are geometric averages. The same test for rogue values is used. The standard errors for these data are in logarithmic units, however. For example, the standard error of 0.227 for an average fluidity of 13.0 ddpm (coal 1) applies to the natural logarithm, 2.565: the value is expected to be between 2.338 (9.9 ddpm) and 2.792 (16.3 ddpm). For three coals (number 21, 22, and 23) the ASTM maximum fluidity is immeasurably high and is reported as greater than 30,000 ddpm.

Table 6

ASTM Gieseler Plasticities of Coals*

<u>coal</u>	<u>T(softening)</u>		<u>T(max flu)</u>		<u>T(solidifcn)</u>		<u>max fluidity</u>		<u>melting slope</u>		<u>coking slope</u>		<u>max flu (intersectn)</u>	
01	386.0	+ 1.5	418.3	+ 1.3	437.4	+ 1.1	13.0	x .227	.2192	+ .0216	.5821	+ .0588	17.1	x .173
02	384.6	0.2	422.7	0.3	437.8	0.2	9.6	.017	.2123	.0151	.5627	.0190	14.1	.063
03	390.4	1.8	432.0	0.0	450.3	0.7	28.3	.026	.2533	.0087	.7755	.0086	33.0	.087
04	382.8	0.4	429.0	0.4	452.5	1.0	544.	.057	.4156	.0208	.9589	.0132	459.	.031
05	390.9	1.0	430.8	0.8	452.8	0.3	86.2	.013	.3167	.0125	.8228	.0039	85.7	.139
06	381.7	0.6	421.0	0.6	457.3	0.3	19689.	.147	.6783	.0405	1.0463	.0174	19087.	.179
07	383.0	0.0	425.5	1.4	453.2	0.4	772.	.013	.4628	.0367	.9315	.0215	1662.	.157
08	387.0	2.1	427.5	2.2	448.1	0.7	50.7	.068	.2939	.0082	.8053	.0130	72.6	.110
09	389.3	1.4	426.3	0.3	446.9	0.1	42.3	.051	.2797	.0183	.7219	.0764	50.7	.064
10	389.8	1.1	426.3	0.3	450.0	0.6	90.2	.008	.3825	.0077	.9204	.0274	191.	.026
11	390.8	0.4	424.5	1.2	448.5	0.1	98.9	.025	.4069	.0019	.8145	.0647	153.	.065
12	387.8	0.3	423.0	0.0	450.5	0.2	228.	.006	.4724	.0069	.8951	.0700	442.	.056
13	376.4	0.2	422.3	0.3	451.8	0.3	529.	.101	.4294	.0129	.8411	.0081	1136.	.082
14	385.7	2.0	425.0	2.3	452.7	1.9	184.	.021	.3832	.0133	.8441	.0278	302.	.141
15	378.9	0.5	424.0	0.0	449.9	0.6	400.	.067	.3990	.0010	.9230	.0138	628.	.052

continued

Table 6, continued

<u>coal</u>	<u>T(softening)</u>		<u>T(max flu)</u>		<u>T(solidifcn)</u>		<u>max fluidity</u>		<u>melting slope</u>		<u>coking slope</u>		<u>max flu (intersectn)</u>	
16	384.1	± 2.1	423.5	± 0.6	445.7	± 0.9	64.3	x .061	.3280	± .0049	.7903	± .0171	113.	x .056
17	392.8	1.9	430.0	2.7	448.7	1.5	45.3	.160	.3122	.0050	.7323	.0235	72.2	.079
18	388.3	1.5	428.0	0.4	446.5	0.2	26.8	.053	.2879	.0082	.7083	.0289	44.5	.054
19	383.3	0.7	428.0	0.6	450.4	1.3	116.	.026	.3204	.0025	.8271	.0069	153.	.081
20	383.2	0.9	423.3	0.9	448.8	0.1	91.2	.068	.3338	.0104	.7780	.0128	86.4	.070
21	374.8	0.2	(419-428)		463.4	0.3	30000.	--	.6492	.0050	1.0694	.0020	102,740.	.025
22	375.7	0.3	(422-435)		467.0	0.2	30000.	--	.6135	.0099	1.1116	.0390	115,790.	.157
23	383.5	0.9	(422-434)		467.1	1.0	30000.	--	.6502	.0608	1.2471	.1138	75,180.	.170
24	384.8	1.0	423.7	0.3	444.6	0.6	34.9	.032	.2746	.0063	.6758	.0091	45.3	.053

* Raw data in Appendix Table A-1 and calculated data in Appendix Table A-2. Average values are from quadruplicate determinations except when a single value differs from the average of the remaining three values by more than three standard deviations. Range given is the standard error, $(\sigma^2/n)^{1/2}$. As fluidities are averaged as their logarithms, the standard error associated with fluidities is the standard error of the logarithm.

4.2 Maximum Fluidity by Slope Intersection. The ASTM plastometry curves are skewed, owing to the progressively increasing temperature during the course of the determination. The maximum fluidity is approached relatively slowly, and the subsequent loss of fluidity on the 'coking' side of the curve is quite abrupt. Nevertheless, it is possible to achieve a fair fit of the experimental plot on $\ln(\text{fluidity})$ vs. time to a straight line tangent to much of the curve on the 'melting' side -- a melting slope -- and another straight line tangent to much of the curve on its coking side -- a coking slope. Figure 2 illustrates the fit, using averaged data for coal no. 1.

These slopes are of possible utility for a study of plastic behavior, for two reasons. First, they provide measures of relative reactivities of coals, specifically relative rates of melting and coking when subjected to the ASTM gradient of 3°C per minute. Secondly, the intersection of these slopes provides an estimate of maximum fluidity that is not perturbed by outgassing phenomena and other changes which often make observed fluidities near the maximum fluidity subject to considerable uncertainty. These slopes, and the intersection maximum fluidity, have been calculated for each ASTM run, as described in the footnote to Table A-2. The average values are shown in the three right-hand columns of Table 6, along with their standard errors.

Figures 2-4 show calculated slope lines and the experimental points (asterisks) for a sparingly plastic coal (no. 1, max fluidity 13 ddpm), a moderately plastic coal (no. 5, max fluidity 86 ddpm), and a highly plastic coal (no. 22, max fluidity greater than 30,000 ddpm). The slope fits and the intersection fluidity are good for the sparingly plastic coal, fair for the moderately plastic coal, and rather poor for the highly plastic coal,

USDOE COAL #01 - ASTM RUN #4

HORIZONTAL AXIS: TIME IN MINUTES Maximum Value = 22
 VERTICAL AXIS : LN(FLUIDITY IN GIESELER DDPM) Maximum Value = 4
 Tangents are least-squares slopes.
 Experimental data: ■
 Calculated slopes: *

Figure 2

USDOE COAL #05 - ASTM RUN #2

HORIZONTAL AXIS: TIME IN MINUTES Maximum Value = 27

VERTICAL AXIS: LN(FLUIDITY IN GIESELER DDPM) Maximum Value = 6

Tangents are least-squares slopes.

Experimental data: $\square$

Calculated slopes: $*$

Figure 3

LSDOE COAL #22 - ASTM RUN #1

HORIZONTAL AXIS: TIME IN MINUTES Maximum Value = 35

VERTICAL AXIS : LN(FLUIDITY IN GIESELER DDPM) Maximum Value = 15

Tangents are least-squares slopes.

Experimental data: ■

Calculated slopes: *

Figure 4

which the actual melting curve is distinctly concave-upwards. The intersection for maximum fluidity thus appears to be a good measure in Figure 2, while in Figure 4 it seriously underestimates the probable true maximum fluidity. Even with this limitation this analysis has the advantage for highly plastic coals of providing a numerical estimate -- in this case an estimated minimum value -- for intersection maximum fluidity. For coal no. 22 this value is approximately 116,000 ddpm.

5. NONCLASSICAL CHARACTERIZATION

5.1 Pyrolysis Gas Chromatography. A Chemical Data Systems Model 100 Pyroprobe (coil probe) is interfaced with a Varian Model 3700 gas chromatograph (dual FID) and a Laboratory Data Control Model 308 computing integrator for this system. Results of some exploratory runs have been described.¹

The chromatograph is fitted with a 50 cm x 1/8 in stainless steel column containing 5% OV-101 (an inert silicone phase) with a flow of nitrogen carrier of approximately 46 ml/min. The GC injection and detector stages are set at 270° and the Pyroprobe interface unit is held at 200°C.

Approximately 4-mg samples of the coals are pyrolyzed in quartz tubes 2.4 mm o.d. x 25 mm in length. Pyrolysis ceiling temperatures of 450°C and 650°C have been used in the present work.

Pyroprobe temperature calibration has been undertaken, using the "molecular thermometer" technique of Levy³ and Walker⁴. When Kraton 1107 copolymer (Shell Chemical Co., Houston, TX) is pyrolyzed under the conditions of the coal samples -- in the 2.4 x 25 mm quartz tube -- the ratio of the isoprene peak area to the dipentene peak area is sensitive to temperature. Using the calibration curve and a 4 ft x 1/4 in Porapak Q column, the results of six runs at a nominal pyrolysis temperature of 650°C indicate an effective temperature of 636°C, stand. dev. $\pm 27^\circ$. When an extreme low value is discarded, the average of the remaining five determinations is 645°C, stand. dev. 19°. Therefore the 650°C setting for the Pyroprobe is believed to be reasonably accurate.

After the coal sample in the Pyroprobe unit is dried at 200°, it is brought rapidly (at a temperature ramp of 500°C/min) to the ceiling temperature (450° or 650°C in the present work). The nitrogen sweep carries volatilized matter onto the OV-101 column, which is held at 60° for

10 min. A substantial amount of volatile product passes through the OV-101 column and is measured by the detector during the first few minutes -- typically 5,000 counts per mg (setting X32) at 450°, and tenfold more at 650°. By the end of the ten-minute period this volatile fraction is virtually completely through the column, and the pen has returned to the baseline. At ten minutes after pyrolysis the GC is brought at 20°C/min to 250°C, and is then held at this temperature for 30 min. A larger amount of less volatile material passes through the OV-101 column at these elevated temperatures -- typically 60,000 counts per mg (setting X32) at 450°, and 90,000 to 120,000 counts per mg at 650°. Under these conditions all of the low-volatile material appears to have passed completely through the column by the end of each analytical run.

This procedure thus provides an opportunity to measure separately a "high-volatile" product group and a "low-volatile" product group for each pyrolysis run. In addition, with somewhat less sensitivity it is possible to estimate the mass volatilized by weighing the quartz tube again after the pyrolysis has been completed. A summary of the results obtained with the first several coals examined is shown in Table 7. The data here are averaged from 3 to 7 replicate runs, and are shown with the associated standard errors. Individual run data are given in Appendix Tables A-3 and A-4.

Most of the coals studied thus far are very similar, and this appears to be reflected in the data obtained by pyrolysis-GC. Coal no. 6, the only notably plastic coal in this early group, gives the largest total response in this group -- over 200,000 counts per mg coal charged. Other plastic coals need to be examined to determine if this is a reliable indicator of

Table 7

Initial Performance of Coals in GC/Pyroprobe System*

Coal	Pyroprobe Ceiling T	runs	% High- volatile	% Low- volatile	Yield, integrator counts per mg	Weight loss, percent
01	450 C	3	8.1 $\pm$.4	91.9	66,550 $\pm$ 1,440	17.5 $\pm$ 2.8%
	650	5	32.6 $\pm$.7	67.4	133,470 $\pm$ 10,240	23.8 $\pm$ 2.4%
02	450	4	8.3 $\pm$.7	91.7	72,550 $\pm$ 3,510	18.0 $\pm$ 1.3%
	650	7	30.7 $\pm$.9	69.3	175,190 $\pm$ 9,560	43.2 $\pm$ 3.5%
03	450	4	5.9 $\pm$.7	94.1	65,080 $\pm$ 9,290	---
	650	4	33.6 $\pm$.3	66.4	177,120 $\pm$ 3,820	---
06	450	-	--	--	---	---
	650	3	32.5 $\pm$.1	67.5	206,090 $\pm$ 12,270	25.1 $\pm$ 3.1%
09	450	4	5.8 $\pm$.9	94.2	86,030 $\pm$ 11,350	11.7 $\pm$ 1.5%
	650	5	29.3 $\pm$.9	70.7	141,930 $\pm$ 8,210	24.0 $\pm$ 1.2%

* With approximately 4-mg samples dried at 200°, then pyrolyzed at a ramp of 500°C/sec to a ceiling temperature of 450 or 650°C. 'High-volatile' material is collected in the first ten minutes (passing through a 50-cm OV-101 column at 60°C). 'Low-volatile' material is collected during the following 40 minutes during which the column temperature is raised to and held at 250°C. Experimental details are given in the text. All data are averages, with standard errors given. Raw data are given in Tables A-3 and A-4.

high plasticity. It is of interest that the high plasticity of coal no. 6 is not reflected in either overall weight loss or high-volatile / low-volatile ratio.

5.2 Quantitative Extractions. The extraction data have been obtained in standard Soxhlet assemblies, at the reflux temperatures of the two solvents employed, tetrahydrofuran (THF) and N,N-dimethylformamide (DMF). The procedure has been described in detail.¹ Approximately 10-g samples of -60 mesh coal are dried at 110°C and then at 60°C under vacuum; the dried coal in dry cellulose thimbles is then extracted for 24 hours with refluxing solvent. The residue is then extracted for six hours with refluxing methanol, to remove original solvent, and the coal residues dried overnight in a vacuum desiccator and for six hours at 60° under approximately 1 mm pressure. Samples are then subjected to several additional two-hour drying cycles and the weights checked. The results from the first half dozen coals are summarized in Table 8.

All coal extractions have been run in triplicate, although in several instances one of the coal samples has been 'lost', most often by blowout of coal powder during vacuum drying. The averaging program used calculates precision as standard error:

$$\text{STD ERROR} = \text{SQR} \left((\text{STD DEVIATION})^2 / N \right)$$

This program also discards rogue data, on the following basis: if the suspected datum lies more than four standard deviations from the average of the other two data, it is discarded. In most cases the rejected datum shows very high apparent extractables; i.e., the datum may arise from handling losses. All extraction run results are recorded in Appendix Table A-5.

Three preliminary observations may be made from these data.

Coal 06, the only pronouncedly plastic coal in this group, affords the highest extractable fractions for both solvents. This is particularly evident with THF.

Table 8

Coal Fractions Extractable by THF and DMF*

coal	% Loss of Dry Coal with THF		% Loss of Dry Coal with DMF	
	avg. loss	standard error	avg. loss	standard error
01	12.41%	± 0.06	13.26%	± 0.93
02	11.85%	± 0.33	19.47%	± 0.36
03	7.23%	± 0.65	15.12%	± 0.42
04	9.85%	± 0.06	18.42%	± 0.32
05	7.27%	± 0.56	16.59%	± 2.08
06	17.76%	± 0.01	23.81%	± 1.52

* Soxhlet extractions at atmospheric reflux with tetrahydrofuran (THF) and with N,N-dimethylformamide (DMF) upon predried coal samples. Procedure is described in text and in a previous report.¹ Averaged results of duplicate or triplicate extractions. Individual extraction data are given in Appendix Table A-5.

The highly polar DMF consistently extracts more than THF, as expected. However, the proportional increase with DMF is quite variable, from less than 10% (coal 01) to more than 100% (coals 03 and 05). This seems likely to reflect compositional differences among the extraction fractions.

FT-IR analysis (next section) of the DMF-extracted residue from coal 06 clearly reveals bands assignable to DMF, at 1680 and 1095 cm^{-1} . This supports indications by Fort (noted previously¹) that residual DMF is tenaciously adsorbed by coal residues. Future DMF extractions will entail final drying at 150° under vacuum. The import for the DMF extraction data in Table 8 is that these numbers may all be somewhat low. If the procedural modification results in significantly higher values for the extracted fraction, DMF extractions will be repeated for these first half dozen coals.

5.3 Fourier Transform Infrared Spectrometry. The Nicolet MX-1 instrument has been put into satisfactory working condition, and our study of the coals, coal extraction residues and coal extracts is beginning.

The possible procedures for handling coal have been examined. The approach which in our hands gives the strongest signals and the best resolution is that of Painter and coworkers.⁵ The procedure, which we are currently using, entails reduction of the -60 mesh coal or coal residue to -200 mesh, and mixing thoroughly with finely reduced KBr, in the proportion (approximately) of 1 to 200. Typically 1.5 mg of coal or coal residue, finely pulverized, is blended with 300 mg of KBr for the preparation of the pellet. The spectrum is run for 16 minutes (512 scans at 32 scans/min) and the spectrum plotted.

Figure 5 shows the spectrum (transmittance plot) of coal 06. After THF extraction (Figure 6) several small differences can be seen, both in removal of functionality and sharpening resolution. Further work will indicate whether these small differences are significant. After DMF extraction the residue (Figure 7) shows two significant peaks at 1680 and 1095 cm^{-1} , both major peaks for DMF. This has led to a modification (see preceding section) in our post-extraction procedure.

Another indication of the sensitivity of this system is that we have had no trouble detecting polymer pickup when using the standard mortar and pestle of the Wig-L-Bug mixer to reduce -60 mesh coal. We are now fine-grinding by hand (agate) to avoid this contamination.

This appears to be sensitive, reproducible and a fast-throughput system. We expect to generate a significant volume of FT-IR data in the coming quarter, and to commence development of a standard spectrum subtraction procedure.

NICOLET MX-1

SAMPLE - RAW COAL - KCER 9045

Figure 5

Infrared Spectrum of Coal 06 (KBr pellet)

NICOLET MX-1

SAMPLE - KCER 9045 - AFTER EXTRACTION WITH THF

NICOLET MX-1

SAMPLE - KCER 9045 - AFTER EXTRACTION WITH DMF

6. DISCUSSION

This study is directed to the explanation/prediction of the plastic properties of bituminous coals, in terms of other measurable parameters. This is by no means the first such study. Plastic properties have been known since the nineteenth century, and have generally been explained in terms of one of two widely accepted, plausible and insufficient mechanisms.

R. V. Wheeler, in one of his earliest papers⁶ and in many subsequent ones, articulated the view that coals which swell and exhibit plastic properties contain a fusible portion, or bitumen, which is responsible for these properties. This portion was early identified as the portion which is extractable with organic solvents.⁷ This view was supported by Audibert's theory of true melting,⁸ by the early observation that the extractable 'fusible fraction' when added to nonplastic coals confers plasticity,⁹ and by evidence that initial melting is (more or less) a reversible phenomenon.^{10,11} Certain physical properties, such as pore structure and surface area, are not substantially changed by bringing a plastic coal to the molten state and then cooling it. These observations, however, could be accounted for by assuming a microstructure including large micelles or 'nuclei',^{12,13} which retain their integrity even though enough interstitial or surface melting occurs to permit fluid behavior.

The other major view, and certainly the predominantly accepted interpretation for the past three decades, is due mainly to van Krevelen and his associates.¹⁴⁻¹⁶ In this view bituminous coal undergoes irreversible pyrolytic reaction upon being heated to the plastic state, and plasticity itself is intimately associated with the formation of an unstable or metastable fluid pyrolysate or 'metaplast'. This view is supported by the work of many others. Fitzgerald studied the isothermal

plastic behavior of coals and demonstrated the irreversible nature of the transformations.¹⁷ Brown and Brown have shown the substantial effects of heating rates upon plasticity,¹⁸ effects which are consistent with pyrolytic reactions but not with simple melting. Russell and Perch¹⁹ -- and many others -- have shown an extremely sharp suppression of plastic behavior by very mild partial oxidation, an observation hard to reconcile with simple mass melting. In their comprehensive review of plastic behavior for Lowry, Loison and his coworkers strongly support the metaplast view.²⁰

It is our view that -- as often occurs in the development of theory -- there are important truths in both approaches. The evidence for the formation of small molecules via pyrolysis is overwhelming. At the same time, fluid behavior in a solid/liquid mixture requires a critical minimum volume fraction of liquid phase, an important part of which is initially present as extractable small molecules in plastic coals. Finally, if the dynamics of pyrolysis involve the critical competition between H-transfer and coking condensation, as Neavel²¹ suggests, then the presence of bitumen in a 'melting' coal will promote the formation of a larger amount of 'metaplast' product than would otherwise occur.

We are reexamining this old problem from this eclectic viewpoint, and with the aid of two newly available tools. The amount of pyrolysate generated by a coal, whole or after pretreatment, can be conveniently measured with the Pyroprobe/GC system discussed in part 5.1. Analysis of extracts and residues by FT-IR is expected to provide significant information on functional group distributions, and may even identify thermally labile bridging structures in the residues of highly plastic coals. Examination of the data from these sources, along with the

comprehensive physical, petrographic and chemical characterization of the coals in this study, will (we believe) provide significant insights into plasticization phenomena.

In the coming quarter we expect to obtain and commence characterization of the third and last group of coals to be used in this study. These coals will cover a somewhat wider range of ranks than those we are now working with. We will obtain our first substantial volume of data by Pyroprobe/GC and by quantitative extraction, and our first quantitative infrared data, and will commence HPLC/GLC examination of coal extracts, as well as isothermal plastometry. We expect to expand greatly the amount of quantitative extraction data. Midway in this quarter we plan to commence organization of the statistical analysis procedure to be used for the balance of the study.

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8. APPENDICES

8.1 Tables.

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Table A-1*

Individual ASTM Gieseler Plastometry Determinations

Coal	T(softening)				T(max fluidity)				Max fluidity, ddpm				T(solidification)			
1	383	388	387	...	421	420	416	416	22.4	15.7	8.2	9.9	435	436.4	438.6	439.7
2	385	379.6	348.2	384.5	422	419	423	423	9.9	9.3	9.3	9.8	440.3	437.3	438	438
3	385.6	391	394.6	390.5	431	432	432	432	33.6	27.9	29.8	27.3	451.2	449.4	451.8	448.9
4	388 389.7	383.5	382.4	382.5	428 429	429	427	430	610.4 333.4	515.8	1334.7	512.6	451.5 455.6	451.9	451.0	455.5
5	391	380.7	392.7	389.1	432	430	432	429	87.3	87.3	71.4	83.9	453	452.2	453.3	450.8
6	382	376.4	382.5	380.6	422	420	426	421	16086	18115	8851	26190	458.0	457.5	457.1	456.7
7	383	...	383	383.1	422	425	429	426	787.7	753.7	876.3	774.3	452.2	453.2	453.2	454.0
8	390.1	390.7	382	385	429	433	423	425	42.5	56.0	56.8	49.0	448	452.7	447	449.3
9	391.1	392	388	386	427	426	426	430	47.3	37.0	43.1	42.3	447	446.6	447	448
10	390.4	387	392.3	389.5	426	427	426	429	89.0	90.0	91.5	103.5	450.4	448.6	449.6	451.3
11	390.3	391.5	390.5	387.3	426	427	422	423	102.8	94.3	82.1	99.7	448.7	448.3	448.4	...
12	385	387.4	388.4	387.5	423	423	423	423	231.1	257.3	227.8	226.4	450.9	448.6	450.5	450.4
13	376	379.8	376.6	376.6	422	426	422	423	648.8	437.4	452.4	611.0	451.2	457.6	452.4	451.7
14	387.4	382.9	382.1	390.4	430	421	421	428	176.2	187.5	187.9	162.9	456.1	449.5	449.4	455.9
15	379.8	378.9	378	388.7	424	424	424	433	423.5	350.0	432.0	227.1	448.8	449.8	451	456.4
16	379	383.7	384.5	389.1	423	422	425	424	70.1	71.7	61.8	55.1	447.6	446.5	445.2	443.5
17	390	394	389.4	397.6	426	433	425	436	53.1	63.5	40.8	30.5	449.9	452.4	447.1	445.5
18	388	397.6	386	391	427	428	428	429	25.1	23.9	30.0	28.5	445	446.7	446.7	446
19	382.6	387.6	382.6	384.7	422	428	429	427	146.5	122.2	115.4	111.6	447.4	452	453.1	449.0
20	385	382.5	382	396.5	425	423	422	434	101.3	93.2	80.4	61.5	449	448.6	448.8	453.6

continued

Table A-1, continued

<u>Coal</u>	<u>T(softening)</u>				<u>T(max fluidity)</u>			<u>Max fluidity, ddpm</u>				<u>T(solidification)</u>			
21	376.4	375	375	374.5	419	419-428	425	29825	30000	29666	30000	466	464	463.1	463
					419-427										
22	376	376	379	375.2	423	429	422-435	30000	29718	30000	30000	468.4	467	466.6	467.4
					422-431										
23	385	378.4	382	383.4	422	422-427		29920	30000	30000	30000	468.6	465.3	467.4	473
					428-434	430-445									
24	382.8	391.5	385.7	385.8	421-425	433	424	36.1	23.9	35.9	32.7	443.6	449.2	445.6	444.5
					424										

* These data are summarized in Table 6.

Table A-2

Calculated Properties from ASTM Gieseler Plastometry Runs*

<u>coal</u>	<u>slope</u>					<u>average</u>	<u>std error</u>	<u>average of best 3</u>	<u>std error</u>
01	melt	.1976	.1696	.2630	.2466	<u>.2192</u>	<u>+</u> .0216	.2357	<u>+</u> .0196
	coke	.6395	.7171	.4587	.5132	<u>.5821</u>	.0588	.5371	.0535
	ln(max)	3.290	2.448	2.789	2.838	<u>2.841</u>	0.173	2.692	0.123
02	melt	.1913	.1855	.2215	.2507	<u>.2123</u>	.0151	.1994	.0112
	coke	.5278	.5935	.5669	.7542	<u>.6106</u>	.0497	<u>.5627</u>	.0190
	ln(max)	2.556	2.616	2.767	3.073	2.753	.1155	<u>2.646</u>	.0628
03	melt	.1875	.2466	.2706	.2428	.2369	.0176	<u>.2533</u>	.0087
	coke	.7823	.7858	.7585	.7094	.7590	.0176	<u>.7755</u>	.0086
	ln(max)	3.280	3.490	3.704	3.508	<u>3.496</u>	.0867	3.567	.0685
04	melt	.3633	.4011	.4499	.3516	<u>.4156</u>	.0208	.4330	.0160
	coke	.9370	.9806	.9829	1.0332				.0149
	ln(max)	5.912	6.190	6.753	6.090				.0307
04 cont	melt	.4481							.0149
	coke	.9350				<u>.9589</u>	.0132	.9509	.0149
	ln(max)	6.109				<u>6.075</u>	.0586	<u>6.130</u>	.0307
05	melt	.3152	.2297	.2959	.3390	.2950	.0235	<u>.3167</u>	.0125
	coke	.8295	.7638	.8228	.8160	.8080	.0150	<u>.8228</u>	.0039
	ln(max)	4.637	4.112	4.340	4.713	<u>4.451</u>	.1386	4.563	.1138
06	melt	.5958	.6400	.6933	.7840	<u>.6783</u>	.0405	.6430	.0282
	coke	1.0223	1.0601	1.0888	1.0139	<u>1.0463</u>	.0174	1.0321	.0142
	ln(max)	9.421	9.945	9.778	10.283	<u>9.857</u>	.1792	10.002	.1485
07	melt	.5422	.3740	.4363	.4985	<u>.4628</u>	.0367	.4923	.0307
	coke	.8891	1.1142	.9593	.9460	<u>.9772</u>	.0482	.9315	.0215
	ln(max)	7.367	6.446	7.709	7.171	7.173	.2667	<u>7.416</u>	.1572
08	melt	.3134	.2954	.2937	.2732	<u>.2939</u>	.0082	.3008	.0063
	coke	.8243	.8111	.7805	.6525	<u>.7671</u>	.0393	<u>.8053</u>	.0130
	ln(max)	4.171	4.574	4.326	4.067	<u>4.285</u>	.1102	4.188	.0752

continued

Table A-2, continued

<u>coal</u>	<u>slope</u>					<u>average</u>	<u>std error</u>	<u>average of best 3</u>	<u>std error</u>
09	melt	.3243	.2393	.2912	.2640	<u>.2797</u>	+ .0183	.2648	+ .0150
	coke	.8957	.5312	.7712	.6896	<u>.7219</u>	.0760	.7855	.0599
	ln(max)	4.399	3.993	3.985	3.798	<u>4.044</u>	0.127	3.925	.0637
10	melt	.3670	.3208	.3895	.3909	<u>.3671</u>	.0164	<u>.3825</u>	.0077
	coke	.9007	.9871	.9360	.8576	<u>.9204</u>	.0274	<u>.8981</u>	.0227
	ln(max)	5.272	4.827	5.204	5.287	<u>5.148</u>	1.083	<u>5.254</u>	.0255
11	melt	.4086	.4032	.4090	.3723	<u>.3983</u>	.0088	<u>.4069</u>	.0019
	coke	.6616	.8784	.7618	.9561	<u>.8145</u>	.0647	<u>.8654</u>	.0565
	ln(max)	5.086	5.174	5.000	4.867	<u>5.032</u>	.0654	5.087	.0502
12	melt	.3199	.4826	.4592	.4754	<u>.4343</u>	.0384	<u>.4724</u>	.0069
	coke	.7110	1.0494	.8906	.9292	<u>.8951</u>	.0701	<u>.9564</u>	.0478
	ln(max)	5.997	6.447	6.089	6.192	<u>6.181</u>	.0971	<u>6.093</u>	.0563
13	melt	.4177	.4631	.4028	.4339	<u>.4294</u>	.0129	<u>.4181</u>	.0090
	coke	.8515	.8467	.7975	.8252	<u>.8302</u>	.0123	<u>.8411</u>	.0081
	ln(max)	6.939	7.198	6.587	6.968	<u>6.923</u>	.1261	<u>7.035</u>	.0819
14	melt	.3979	.3733	.3510	.4107	<u>.3832</u>	.0133	<u>.3940</u>	.0110
	coke	.8313	.7775	.9115	.8561	<u>.8441</u>	.0278	<u>.8216</u>	.0232
	ln(max)	5.883	5.404	5.544	6.005	<u>5.709</u>	.1409	5.811	.1379
15	melt	.4008	.3991	.3972	.3267	<u>.3810</u>	.0181	<u>.3990</u>	.0010
	coke	1.0087	.9459	.8981	.9250	<u>.9444</u>	.0236	<u>.9230</u>	.0138
	ln(max)	6.395	6.373	6.538	5.355	<u>6.165</u>	.2725	<u>6.435</u>	.0517
16	melt	.3221	.3242	.3377	.2746	<u>.3147</u>	.0138	<u>.3280</u>	.0049
	coke	.7577	.8116	.7646	.8271	<u>.7903</u>	.0172	<u>.7780</u>	.0169
	ln(max)	4.762	4.800	4.616	3.755	<u>4.483</u>	.2460	<u>4.726</u>	.0561
17	melt	.3196	.3143	.3026	.4736	<u>.3525</u>	.0405	<u>.3122</u>	.0050
	coke	.7047	.8876	.7132	.7790	<u>.7711</u>	.0422	<u>.7323</u>	.0235
	ln(max)	4.352	4.461	4.103	4.202	<u>4.2795</u>	.0792	<u>4.219</u>	.0723

continued

Table A-2, continued

coal	slope					average	std error	average of best 3	std error
18	melt	.3029	.2666	.2985	.2836	<u>.2879</u>	+ .0082	<u>.2950</u>	+ .0058
	coke	.6498	.6698	.7432	.7705	<u>.7083</u>	.0289	<u>.6876</u>	.0284
	ln(max)	3.715	3.207	3.899	3.771	<u>3.648</u>	.1520	<u>3.795</u>	.0545
19	melt	.3168	.3253	.2975	.3191	<u>.3147</u>	.0060	<u>.3204</u>	.0025
	coke	.8237	.7888	.8173	.8404	<u>.8176</u>	.0107	<u>.8271</u>	.0069
	ln(max)	5.194	5.137	4.913	4.869	<u>5.028</u>	.0806	<u>4.973</u>	.0830
20	melt	.3513	.3153	.2734	.3348	<u>.3187</u>	.0168	<u>.3338</u>	.0104
	coke	.7526	.6882	.7933	.7881	<u>.7556</u>	.0242	<u>.7780</u>	.0128
	ln(max)	4.992	4.570	4.329	4.477	<u>4.592</u>	.1423	<u>4.459</u>	.0702
21	melt	.6392	.6545	.6118	.6539	<u>.6399</u>	.0200	<u>.6492</u>	.0050
	coke	1.0925	1.0659	1.0729	1.0695	<u>1.0752</u>	.0059	<u>1.0694</u>	.0020
	ln(max)	11.508	11.523	10.912	11.589	<u>11.383</u>	.1580	<u>11.540</u>	.0249
22	melt	.6072	.6309	.5883	.6275	<u>.6135</u>	.0099	<u>.6219</u>	.0074
	coke	1.0820	1.0175	1.1518	1.1952	<u>1.1116</u>	.0391	<u>1.1430</u>	.0330
	ln(max)	11.504	11.294	11.875	11.965	<u>11.660</u>	.1575	<u>11.781</u>	.1411
23	melt	.7559	.5370	.7546	.5532	<u>.6502</u>	.0608	<u>.6879</u>	.0674
	coke	.9603	1.4507	1.1701	1.4074	<u>1.2471</u>	.1138	<u>1.3427</u>	.0872
	ln(max)	11.567	11.036	12.315	11.080	<u>11.500</u>	.2973	<u>11.228</u>	.1701
24	melt	.2665	.2338	.2870	.2704	<u>.2644</u>	.0111	<u>.2746</u>	.0063
	coke	.6900	.5384	.6787	.6587	<u>.6415</u>	.0350	<u>.6758</u>	.0092
	ln(max)	3.832	3.193	3.896	3.715	<u>3.659</u>	.1598	<u>3.814</u>	.0530

* Least-squares slopes, ln(ddpm) vs. time, using all data between 0.4 ddpm and one half the highest observed ddpm. Best values are underlined. 'Best' is determined by a test calculation using the closest three of four data; when the fourth datum differs from the average of the closest three by more than three standard deviations, then the average of the closest three is taken as 'best.'

Table A-3

Coal Pyrolysis Data at 450 °C

<u>coal</u>	<u>measurement</u>	<u>determinations</u>				<u>average*</u>	<u>std error</u>	
01	gases: cts/mg	4950	5751	9114		5350	+	400
	% cts	7.28	8.53	8.57		8.1%	+	0.42%
	liquids cts/mg	61373	63040	97789		62206	+	833
	wt loss	12.50	17.66	22.19		17.45%	+	2.8%
02	gases: cts/mg	4360	5718	6178	8166	5419	+	772
	% cts	6.83	7.84	8.54	10.08	8.3%	+	0.68%
	liquids cts/mg	59515	66164	67226	72881	66446	+	2741
	wt loss	15.56	16.05	19.04	21.16	17.95%	+	1.3%
03	gases: cts/mg	3202	3502	3719	7302	3474	+	212
	% cts	4.11	5.72	6.62	7.08	5.88%	+	0.66%
	liquids cts/mg	52448	57674	74704	95795	61608	+	9502
	wt loss					(na)	-	
09	gases: cts/mg	4240	5278	5383	6747	5411	+	514
	% cts	4.81	5.47	6.98	9.00	5.75%	+	0.91%
	liquids cts/mg	56501	68187	91167	106606	80615	+	11265
	wt loss	8.91	9.28	14.20	14.37	11.7%	+	1.5%

* The data for both Tables A-3 and A-4 are combined and summarized in Table 7.

Table A-4

Coal Pyrolysis Data at 650°C

coal	measurement	Determinations					average*	std error	
01	gases: cts/mg	39881	43707	44711	49255	53836	46278	+	2408
	% cts	30.1	32.5	32.8	33.5	34.2	32.6%	+	0.7%
	liquids: cts/mg	82688	85956	86655	101040	125125	89085	+	7063
	wt loss:	19.7	24.7	25.0	25.8	34.3	23.8%	+	2.4%
02	gases: cts/mg	44836	45328	46988	49688	50081	54101	+	4406
		69832	71961					+	
	% cts	28.1	29.4	29.7	29.8	30.2		+	0.9%
		32.5	35.0				30.7%	+	
	liquids: cts/mg	104986	106208	116968	120448	120515	121083	+	5395
		133490	144969					+	
	wt loss:	27.1	38.3	39.5	45.8	47.8	43.2%	+	3.5%
		48.8	55.2					+	
03	gases: cts/mg	55857	61209	61748	62549		60341	+	1520
	% cts	33.22	33.76	33.76	35.53		33.58%	+	0.26%
	liquids: cts/mg	112021	112308	120082	122700		116778	+	2717
	wt loss:						(na)		
06	gases: cts/mg	59498	67247	74046			66930	+	4203
	% cts	32.21	32.58	32.59			32.46%	+	0.12%
	liquids: cts/mg	125167	139174	153136			139159	+	8074
	wt loss:	19.8	25.0	30.4			25.1%	+	3.05%
09	gases: cts/mg	31702	42249	43983	48186	48684	42961	+	3069
	% cts	28.3	29.1	29.8	30.0	33.7	29.3%	+	0.94%
	liquids: cts/mg	80311	94590	102741	103754	113459	98971	+	5542
	wt loss:	19.8	24.1	24.1	24.9	27.1	24.0%	+	1.2%

* The data for both Tables A-3 and A-4 are combined and summarized in Table 7.

Table A-5

Coal Fractions Removed by Soxhlet Extractions*

<u>coal</u>	<u>extraction by tetrahydrofuran</u>			<u>average</u>	<u>extraction by dimethylformamide</u>			<u>average</u>
01	11.22%	12.35%	12.47%	<u>12.41%</u> (a)	14.19%	12.33%		<u>12.36%</u> (a)
02	11.76	12.47	11.33	<u>11.85</u>	19.11	19.82		<u>19.47</u> (a)
03	6.21	8.43	7.05	<u>7.23</u>	15.05	15.88	14.42	<u>15.12</u>
04	9.79	10.47	9.91	<u>9.85</u>	18.10	21.81	18.73	<u>18.42</u> (a)
05	7.83	10.50	6.71	<u>7.27</u> (a)	14.51	18.66		<u>16.59</u> (a)
06	17.77	17.75	16.36	<u>17.76</u> (a)	23.60	26.54	21.59	<u>23.81</u>

* data summarized in Table 8

a average of two determinations