

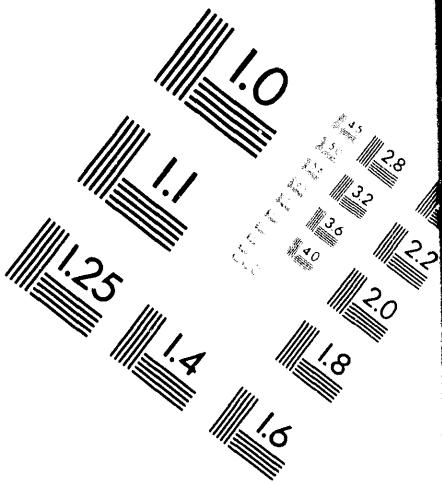
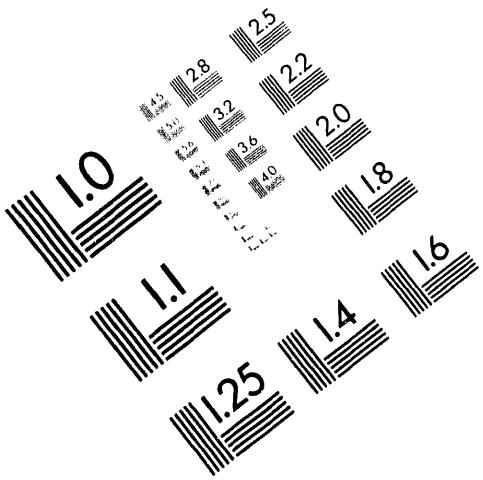


**AIIM**

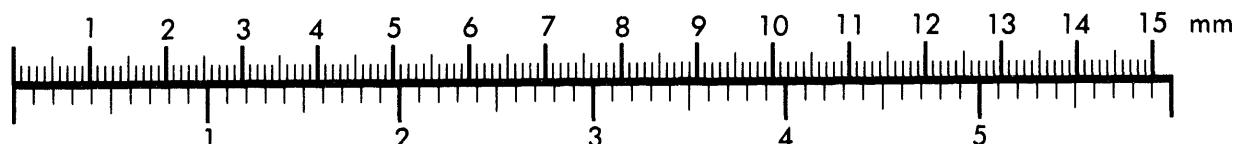
**Association for Information and Image Management**

1100 Wayne Avenue, Suite 1100  
Silver Spring, Maryland 20910

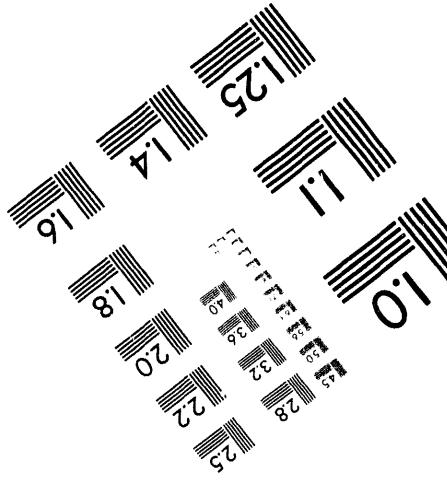
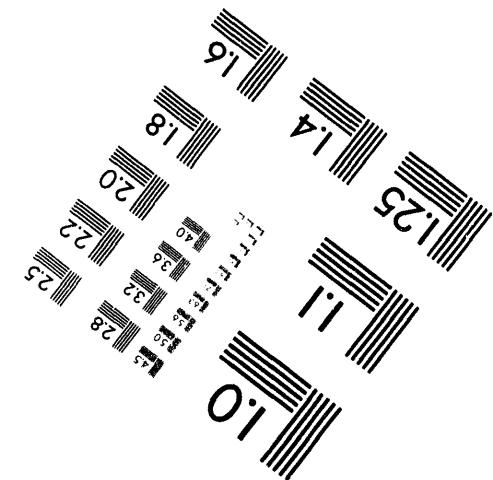
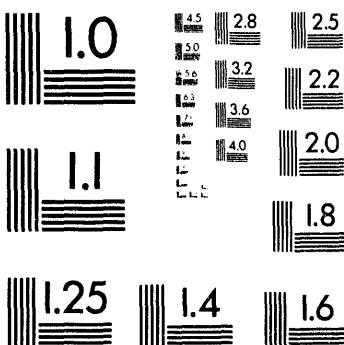
301/587-8202



**Centimeter**



**Inches**



MANUFACTURED TO AIIM STANDARDS  
BY APPLIED IMAGE, INC.

1 of 1

DOE/PC/88654--T15

COMBUSTION CHARACTERIZATION  
OF BENEFICIATED COAL-BASED FUELS

QUARTERLY REPORT NO. 15 FOR THE PERIOD OCTOBER TO DECEMBER 1992

PREPARED BY

ABB POWER PLANT LABORATORIES  
COMBUSTION ENGINEERING, INC.  
1000 PROSPECT HILL ROAD  
WINDSOR, CT. 06095

PROJECT MANAGER  
MICHAEL J. HARGROVE

PRINCIPAL INVESTIGATORS  
OSCAR K. CHOW  
N. Y. NSAKALA

MARCH 1993

PREPARED FOR

U.S. DEPARTMENT OF ENERGY  
PITTSBURGH ENERGY TECHNOLOGY CENTER  
UNDER CONTRACT NO. DE-AC 22-89 PC 88654

MASTER  
-88  
DISTRIBUTED BY THE UNITED STATES GOVERNMENT

#### **DISCLAIMER**

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor Combustion Engineering, Inc., nor any of their employees, subcontractors, suppliers, or vendors make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

#### **ACKNOWLEDGEMENTS**

The authors gratefully acknowledge the following contributors to this report: B. F. Griffith, K. W. Johnson and R. L. Patel of Combustion Engineering, Inc; and S. A. Benson, J. P. Hurley and T. M. Strobel of the University of North Dakota Energy and Environmental Research Center.

**QUARTERLY REPORT**

**TABLE OF CONTENTS**

<b>INTRODUCTION</b>	<b>1</b>
<b>SUMMARY</b>	<b>2</b>
<b>Task 1 - FUEL PREPARATION</b>	<b>3</b>
<b>Task 2 - BENCH SCALE TESTS</b>	<b>4</b>
<b>Task 3 - PILOT-SCALE TESTING</b>	<b>24</b>
<b>Task 4 - SCALE-UP TESTS</b>	<b>25</b>
<b>Task 5 - TECHNO-ECONOMIC EVALUATION</b>	<b>25</b>
<b>Task 6 - TECHNICAL REPORTING</b>	<b>25</b>
<b>WORK PLANNED FOR NEXT QUARTER</b>	<b>25</b>
<b>BIBLIOGRAPHY</b>	<b>26</b>
<b>APPENDIX</b>	<b>30</b>

## INTRODUCTION

The Pittsburgh Energy Technology Center of the U.S. Department of Energy has contracted with Combustion Engineering, Inc. (CE) to perform a five-year project on "Combustion Characterization of Beneficiated Coal-Based Fuels." The beneficiated coals are produced by other contractors under the DOE Coal Preparation Program. Several contractor-developed advanced coal cleaning processes are run at pilot-scale cleaning facilities to produce 20-ton batches of fuels for shipment to CE's laboratory in Windsor, Connecticut. CE then processes the products into either a coal-water fuel (CWF) or a dry microfine pulverized coal (DMPC) form for combustion testing.

The objectives of this project include: 1) the development of an engineering data base which will provide detailed information on the properties of BCFs influencing combustion, ash deposition, ash erosion, particulate collection, and emissions; and 2) the application of this technical data base to predict the performance and economic impacts of firing the BCFs in various commercial boiler designs.

The technical approach used to develop the technical data includes: bench-scale fuel property, combustion, and ash deposition tests; pilot-scale combustion and ash effects tests; and full-scale combustion tests. Subcontractors to CE to perform parts of the test work are the Massachusetts Institute of Technology (MIT), Physical Science, Inc. Technology Company (PSIT) and the University of North Dakota Energy and Environmental Research Center (UNDEERC).

Twenty fuels will be characterized during the five-year base program: three feed coals, fifteen BCFs, and two conventionally cleaned coals for full-scale tests. Approximately nine BCFs will be in dry ultra fine coal (DUC) form, and six BCFs will be in coal-water fuel (CWF) form. Additional BCFs would be characterized during optional project supplements.

## SUMMARY

During the fourth quarter of 1992, the following technical progress was made.

- Completed analyses of drop tube furnace samples to determine devolatilization kinetics.
- Re-analyzed the samples from the pilot-scale ash deposition tests of the first nine feed coals and BCFs using a modified CCSEM technique.
- Updated the Topical Summary Report.
- Prepared for upcoming tests of new BCFs being produced.

## TASK 1 - FUEL PREPARATION

Beneficiated coals (BCs) and feed coals are acquired from other DOE projects and shipped to CE. These fuels are then processed into either a dry pulverized coal form by CE or a coal-water fuel (CWF) form using OXCE Fuel Company technology. The feed coals are fired as standard grind (70% minus 200 mesh) pulverized coal (PC), while the dry beneficiated fuels are generally dry microfine pulverized coal (DMPC).

Thirteen twenty-ton batches of test fuel have been produced under the DOE-PETC Coal Preparation program since 1987. These fuels include:

1. Illinois #6 feed coal
2. Pittsburgh #8 feed coal
3. Upper Freeport feed coal
4. Illinois #6 microbubble flotation product
5. Pittsburgh #8 microbubble flotation product
6. Upper Freeport microbubble flotation product
7. Illinois #6 spherical oil agglomeration product
8. Pittsburgh #8 spherical oil agglomeration product
9. Upper Freeport spherical oil agglomeration product
10. Fresh Upper Freeport feed coal
11. Upper Freeport microagglomerates
12. Illinois #5 microagglomerates
13. Pittsburgh #8 microagglomerates

The first nine fuels were tested in the pilot-scale facility between October 1989 and June, 1990. Bench-scale testing continued through this quarter. Since the first six fuels had been stored in sealed drums for approximately eighteen months, a fresh 20-ton sample of Upper Freeport parent coal was tested in the fourth quarter of 1991 to evaluate the effects of aging or "weathering". The next three BCFs were produced during the second and third quarters of 1992.

## **TASK 2 - BENCH-SCALE TESTS**

### **2.1 Background**

All test fuels are fully characterized using various standard and advanced analytical techniques. These tests evaluate the impacts of parent coal properties and beneficiation process on the resulting BCF's qualities.

A few selected fuels are tested in a laminar flow drop tube furnace to determine fly ash particle size and chemical composition. Results include mineral matter measurements and modeling of fly ash history and have been reported in previous quarterly reports and in the paper by Barta, et alia, 1991.

A swirl-stabilized, entrained flow reactor is used to characterize the surface compositions and the states of ash particles formed during combustion. Deposition rates on a target are determined, and the size and compositions of the deposits from different fuels are compared. Results were reported in the Quarterly Report for the period January to March, 1991.

The first ten coal and BCF samples received to date have been completely analyzed for: (1) complete chemical analyses; (2) flammability index measurements; (3) weak acid leaching; (4) TGA reactivities and BET surface areas of chars, and (5) combustion kinetics. All these data have been reduced and reported in the Quarterly Reports for July to September, 1990, January to March 1991, and October to December, 1991, as well as in papers by Nsakala, et alia, 1990 and 1991, and the draft Topical Report issued in June, 1991.

Work during this quarter focused on completing the CE Drop Tube Furnace System-1 (DTFS-1) devolatilization testing of the BCFs. The analyses of the samples collected during the tests were completed and are discussed in the next section. These results were also added to the Topical Summary Report.

UNDEERC re-analyzed the samples from the pilot-scale ash deposition tests done in 1989 using a modified CCSEM technique. Results are discussed in the Appendix.

## 2.2.2 DTFS-1 Pyrolysis Kinetic Parameters of Fuels

CE's Drop Tube Furnace System-1 (DTFS-1) was used in this study to derive the pyrolysis and combustion kinetic parameters of beneficiated coal-based fuels. This system is comprised of a 1-inch inner diameter horizontal tube gas pre-heater and a 2-inch inner diameter vertical tube test furnace for providing controlled temperature conditions to study pyrolysis, gasification and/or combustion phenomena (Figure 2.2.5). This entrained flow reactor, which is electrically heated with silicon carbide elements, is capable of heating reacting particles to temperatures of up to 2650°F and sustaining particle residence times of up to about one second to simulate the rapid suspension firing conditions encountered in pulverized coal-fired boilers.

The DTFS-1 testing procedure entails the following: (1) the fuel is fed at a precisely known rate through a water-cooled injector into the test furnace reaction zone; (2) the fuel and its carrier gas are allowed to rapidly mix with a pre-heated down-flowing secondary gas stream; (3) devolatilization, gasification or combustion is allowed to occur for a specific time (dictated by the transit distance); (4) reactions are rapidly quenched by aspirating the mixture into a water-cooled sampling probe; (5) the solids are separated from gaseous products in a filter medium; and; (6) an aliquot of the effluent gas stream is sent to a dedicated Gas Analysis System for on-line determination of the concentrations of NO<sub>x</sub>, SO<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CO, and THC (total hydrocarbons). A data acquisition system records all relevant test data for subsequent retrieval and processing.

An ash tracer technique (Nsakala, et al., 1977) is used in conjunction with the proximate analyses of feed samples and chars subsequently generated in the DTFS-1 to calculate the devolatilization, gasification or combustion efficiency as a function of operational parameters (particle temperature, particle residence time, fuel fineness, reaction medium, etc.). Alternatively, the information on concentrations of CO<sub>2</sub>, CO and THC in the effluent gas streams can be used to calculate carbon conversion rates under prevailing combustion conditions.

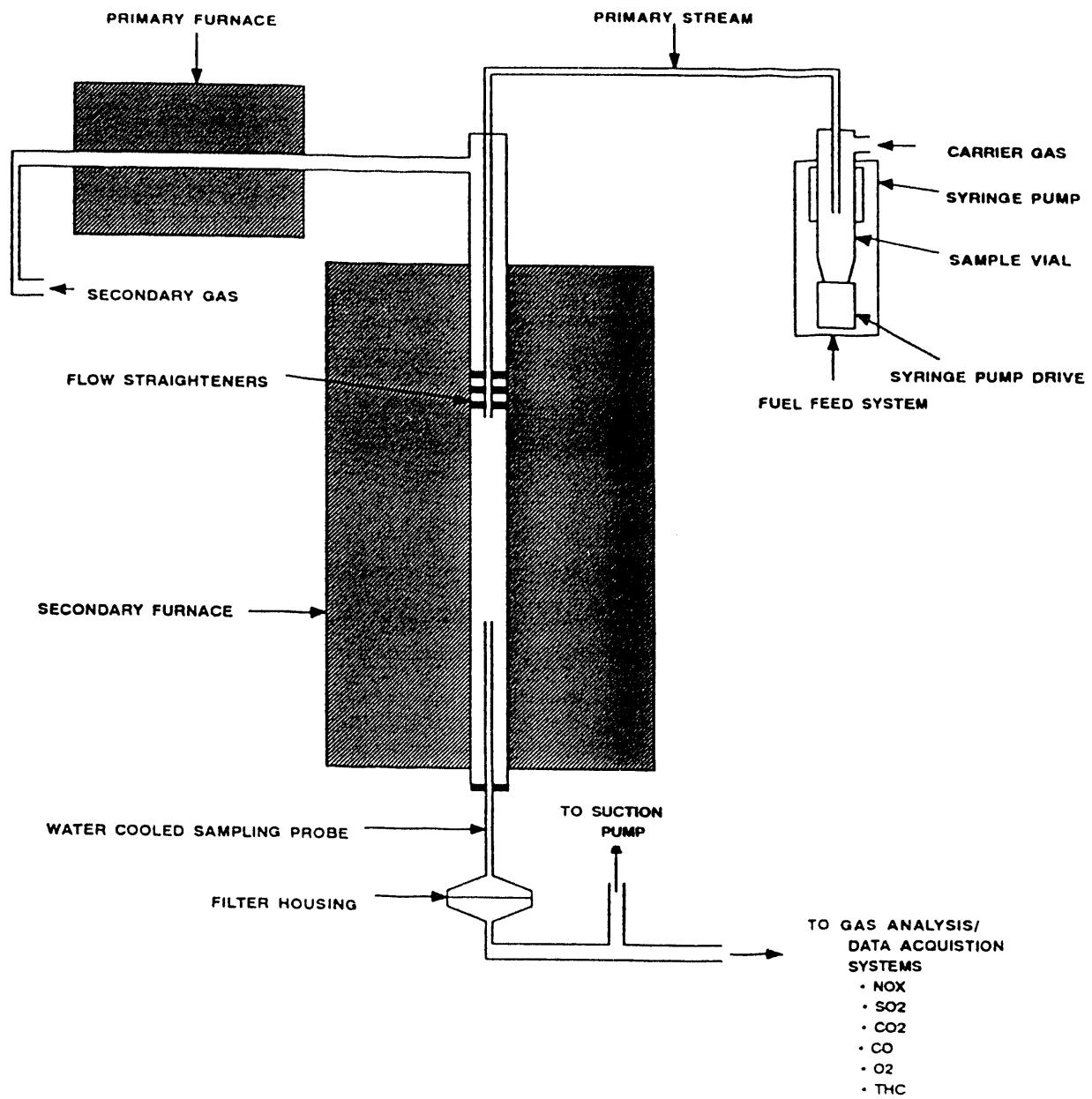


Figure 2.2.5 Schematic of Drop Tube Furnace System-1

Pyrolysis Kinetic Parameters of Fuels. The test fuel samples were size-graded to 325x0 mesh beforehand. The ASTM proximate and ultimate analyses of these size-graded products are given in Table 2.2.3. These values are fairly comparable to those of un-sized products given in Tables 2.2.1 and 2.2.2.

Data to determine the devolatilization kinetic parameters [apparent activation energy (E) and frequency factor (A)] of each BCF were obtained from the DTFS-1 in accordance with the test procedure depicted in Figure 2.2.6. The size-graded sample was subjected to thermal decomposition in nitrogen atmosphere at four temperatures (1900, 2150, 2400 and 2650 °F) and residence times (dictated by transit distances) ranging up to 0.75 sec.

Due to the fact that the initial ash contents of the feed stocks were so low (3.4-7.2% on as received basis and 5.9-11.9% on moisture and volatile matter-free basis), the calculated pyrolysis weight losses using the ash tracer technique yielded widely scattered data. Therefore, for each case, an average ash content was used for all its test chars (e.g.,  $A_c = 5.9 \pm 0.6\%$  for Illinois No. 6 MFP, Table 2.2.4). The volatile matter remaining in a char ( $V_c$ ) was subsequently expressed as a percentage of the original dry-ash-free fuel feed stock, as shown in Eq.(1)

$$V_c = \{[A_o/(1-M_o-A_o)](VM_c/A_c)\}100 \quad (1)$$

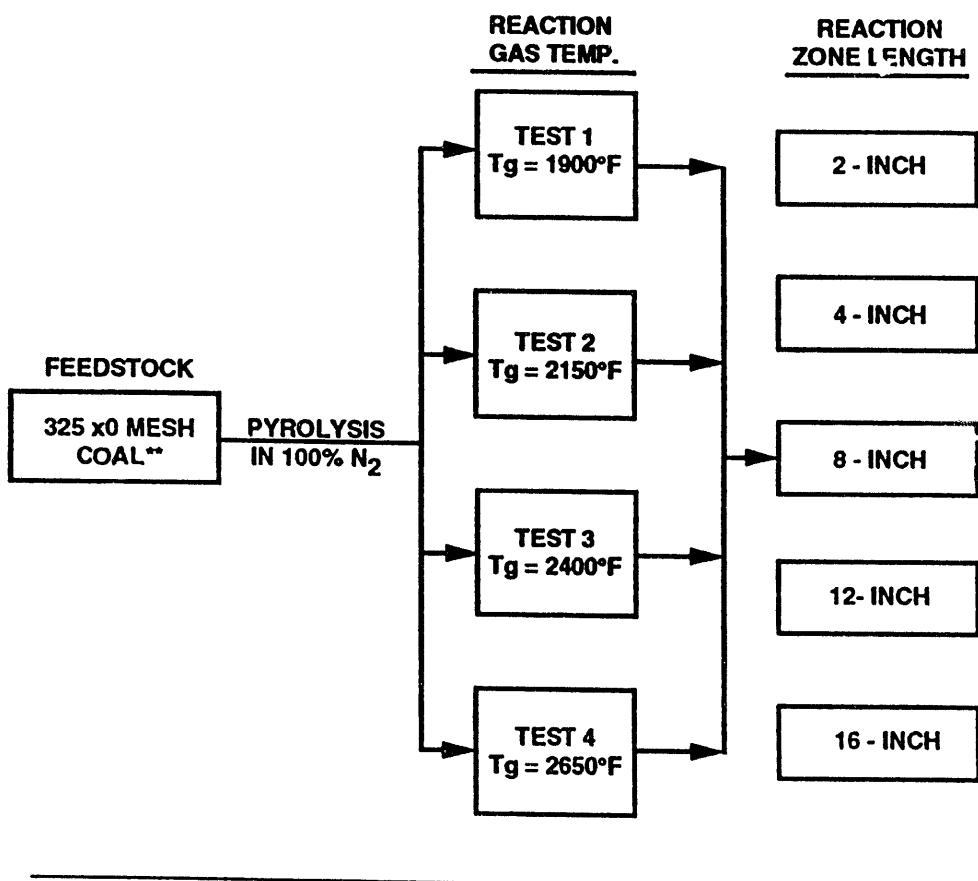
where  $M_o$  and  $A_o$  are, respectively, the fractional moisture and ash contents of the feed stock and  $VM_c$  and  $A_c$  are the fractional volatile matter and ash contents of the char.

Subtracting  $V_c$  from the dry-ash-free volatile matter of the feed stock ( $VM_o$ ) yielded a corresponding weight loss ( $\Delta V$ ), as

Table 2.2.3  
SELECTED ANALYSES OF SIZE-GRADED BENEFICIATED COAL-BASED FUELS

QUANTITY	ILLINOIS # 6 MFP		PITTSBURGH # 8 MFP		UPPER FREEPORT MFP		ILLINOIS #6 SOAP		PITTSBURGH #8 SOAP		UPPER FREEPORT SOAP	
	As Rec'd	daf	As Rec'd	daf	As Rec'd	daf	As Rec'd	daf	As Rec'd	daf	As Rec'd	daf
<b>Proximate, WT.%</b>												
Moisture	5.4	--	2.3	--	1.3	--	2.8	--	1.5	--	1.0	--
Volatile Matter	40.1	44.2	40.5	42.9	27.7	29.6	43.0	46.2	38.5	41.0	37.2	40.6
Fixed Carbon (Diff.)	50.6	55.8	53.8	57.1	65.9	70.4	50.0	53.8	56.8	59.0	55.4	59.4
Ash	3.9	--	3.4	--	5.1	--	4.2	--	4.7	--	7.4	--
<b>Ultimate, WT.%</b>												
Moisture	5.4	--	2.3	--	1.3	--	2.8	--	1.5	--	1.0	--
Hydrogen	5.0	5.5	5.5	5.8	5.5	5.9	5.6	6.0	5.8	6.2	5.4	5.8
Carbon	68.9	76.0	74.5	79.0	79.6	85.0	72.5	78.0	77.6	82.7	78.2	84.4
Sulfur	2.6	2.9	3.3	3.5	1.3	1.4	2.7	2.9	1.9	2.0	1.7	1.8
Nitrogen	1.3	1.4	1.3	1.4	1.3	1.4	1.3	1.4	1.5	1.6	1.4	1.5
Oxygen (Diff.)	12.9	14.2	9.7	10.3	5.9	6.3	10.9	11.7	8.5	9.1	4.9	5.3
Ash	3.9	--	3.4	--	5.1	--	4.2	--	4.7	--	7.4	--

daf = dry-ash-free



\*\* A 200x400 mesh size grade is used in CE standard procedure

Figure 2.2.6 DTFS-1 determination of BCF pyrolysis kinetic parameters

shown in Eq.(2):

$$\Delta V = VM_0 - V_c \quad (2)$$

All the  $\Delta V$  values obtained from this study are presented in Tables 2.2.4-2.2.6 as a function of temperature and time. The results are plotted in Figure 2.2.7. The use of average ash contents in chars (e.g.,  $A_c = 5.9 \pm 0.6\%$  for Illinois #6 MFP,

Table 2.2.4) necessarily introduces errors in the values of pyrolysis weight losses ( $\Delta V$ ) calculated per Eq.(2). Hence, it was deemed necessary to evaluate the impact of  $A_c$  on  $\Delta V$  and, ultimately, on the kinetic parameters. This is illustrated on the Illinois No. 6 MFP and SOAP fuels (Figure 2.2.8). As would be expected, the error bands are more accentuated at 1900 °F than they are at 2650 °F.

Figure 2.2.9 is a re-plot of Figure 2.2.7 to directly illustrate the impact of temperature-time history on the pyrolysis of these fuels. The following is indicated: (1) pyrolysis weight loss depends significantly on both temperature and residence time in each case, the higher the temperature and/or time, the higher the pyrolysis efficiency; (2) pyrolysis at the highest temperature tested (2650 °F) is complete within about 0.25 sec.; and (3) pyrolysis at the lowest temperature tested (1900 °F) is never complete even at the longest residence time (~0.75 sec.) evaluated.

Results in Figure 2.2.8 were used to derive the pyrolysis kinetic parameters of each fuel. The results in Figure 2.2.9 were also used to determine the impact of  $\Delta V \pm \sigma$  (where  $\sigma$  is the standard deviation due to  $A_c = A_{avg} \pm \sigma$ ) on the kinetic parameters. The derivation method used by Nsakala, et al.

(1977), Scaroni, et al. (1981) and Walker, et al. (1983) was

Table 2.2.4  
DTFS-1 PYROLYSIS DATA FOR SIZE-GRADED ILLINOIS No. 6 BCFS

FUEL TYPE	TEST NO.	M'	VM'	A'	DIST. (in.)	TIME (sec.)	TEMP. (°F)	Vc	ΔV	ln(1-(ΔV/VMo))
ILLINOIS #6 MFP	ILMP-1	0.9	36.0		2	0.098	1795	26.1	18.1	-0.5273
		1.7	31.0		4	0.193	1824	22.5	21.7	-0.6768
		2.0	26.8		8	0.383	1858	19.4	24.8	-0.8224
		1.6	16.6		12	0.569	1898	12.0	32.2	-1.3014
		1.1	13.1		16	0.754	1899	9.5	34.7	-1.5382
	ILMP-1R	0.8	21.6		8	0.383	1858	15.7	28.5	-1.0381
		2.1	19.7		12	0.569	1898	14.3	29.9	-1.1302
		3.0	15.3		16	0.754	1899	11.1	33.1	-1.3830
	ILMP-2	2.6	32.6		2	0.089	2030	23.6	20.6	-0.6265
		3.8	23.8		4	0.176	2077	17.2	27.0	-0.9411
		3.7	18.2	0.6	8	0.346	2131	13.2	31.0	-1.2094
		3.0	14.5	0.9	12	0.513	2156	10.5	33.7	-1.4367
		4.8	10.5	5.0	16	0.680	2147	7.6	36.6	-1.7595
	ILMP-3	0.2	16.9		2	0.082	2243	12.2	32.0	-1.2835
		2.0	20.3		4	0.162	2273	14.7	29.5	-1.1002
		2.5	11.2		8	0.321	2314	8.1	36.1	-1.6949
		1.9	5.4		12	0.477	2363	3.9	40.3	-2.4244
		1.5	3.3		16	0.631	2392	2.4	41.8	-2.9169
	ILMP-4	2.4	21.9		2	0.076	2473	15.9	28.3	-1.0243
		4.8	13.7		4	0.149	2554	9.9	34.3	-1.4934
		4.5	1.4		8	0.292	2624	1.0	43.2	-3.7744
		3.3	1.2		12	0.434	2636	0.9	43.3	-3.9285
		2.5	1.2		16	0.575	2637	0.9	43.3	-3.9285
ILLINOIS #6 SOAP	ILSP-1	2.7	36.8		2	0.098	1795	27.1	19.2	-0.5356
		2.7	35.5		4	0.193	1824	26.1	20.2	-0.5716
		3.3	25.8		8	0.383	1858	19.0	27.3	-0.8907
		3.8	20.3		12	0.569	1898	14.9	31.4	-1.1305
		4.8	15.2		16	0.754	1899	11.2	35.1	-1.4198
	ILSP-2	2.6	32.5		2	0.089	2030	23.9	22.4	-0.6599
		3.4	27.6		4	0.176	2077	20.3	26.0	-0.8233
		4.9	19.7		8	0.346	2131	14.5	31.8	-1.1605
		5.9	14.0		12	0.513	2156	10.3	36.0	-1.5021
		5.0	8.0	0.8	16	0.680	2147	5.9	40.4	-2.0617
	ILSP-3	3.6	29.5	6.3	2	0.082	2255	21.7	24.6	-0.7567
		4.0	22.7	+	4	0.162	2290	16.7	29.6	-1.0188
		3.5	12.5	+	8	0.321	2338	9.2	37.1	-1.6154
		4.8	6.2	+	12	0.477	2387	4.6	41.7	-2.3166
		5.0	4.0	+	16	0.631	2397	2.9	43.4	-2.7548
	ILSP-4	2.9	27.0		2	0.076	2473	19.9	26.4	-0.8453
		3.8	20.6		4	0.149	2554	15.2	31.1	-1.1158
		4.8	4.0		8	0.292	2624	2.9	43.4	-2.7548
		3.1	3.9		12	0.434	2636	2.9	43.4	-2.7801
		2.2	2.8		16	0.575	2637	2.1	44.2	-3.1115

Table 2.2.5

## DTFS-1 PYROLYSIS DATA FOR SIZE-GRADED PITTSBURGH NO. 8 BCFs

FUEL TYPE	TEST NO.	M'	VM'	A'	DIST.	TIME	TEMP.	Vc	$\Delta V$	$\ln(1-(\Delta V/VM_0))$
					(in.)	(sec.)	(°F)			
PITTSBURGH #8 MFP	PTMP-1	0.7	29.3		2	0.098	1795	20.3	22.6	-0.7482
		1.3	25.7		4	0.193	1824	17.8	25.1	-0.8793
		1.2	22.6		8	0.383	1858	15.7	27.2	-1.0078
		0.5	23.1		12	0.569	1898	16.0	26.9	-0.9859
		0.1	18.1		16	0.754	1899	12.5	30.4	-1.2298
	PTMP-1R	1.2	29.1		8	0.383	1858	20.2	22.7	-0.7551
		0.8	23.7		12	0.569	1898	16.4	26.5	-0.9603
		1.2	18.3		16	0.754	1899	12.7	30.2	-1.2188
	PTMP-2	3.6	27.2		2	0.089	2030	18.8	24.1	-0.8226
		2.7	28.8	5.0	4	0.176	3077	20.0	23.0	-0.7654
		3.2	21.8	4.4	8	0.346	2131	15.1	27.8	-1.0439
		4.8	13.0	5.2	12	0.513	2156	9.0	33.9	-1.5607
		3.8	8.0	5.6	16	0.680	2147	5.5	37.4	-2.0461
	PTMP-3	0.5	21.7		2	0.082	2255	15.0	27.9	-1.0485
		1.8	15.6		4	0.162	2290	10.8	32.1	-1.3785
		0.7	8.7		8	0.321	2338	6.0	36.9	-1.9623
		1.2	4.3		12	0.477	2387	3.0	39.9	-2.6666
		0.7	2.7		16	0.631	2397	1.9	41.0	-3.1316
	PTMP-4	2.0	22.3		2	0.076	2473	15.5	27.5	-1.0212
		3.5	15.3		4	0.149	2554	10.6	32.3	-1.3979
		2.8	2.1		8	0.292	2624	1.5	41.5	-3.3826
		1.4	1.1		12	0.434	2636	0.8	42.1	-4.0280
		1.7	1.1		16	0.575	2637	0.8	42.1	-4.0280
PITTSBURGH #8 SOAP	PTSP-1	1.1	35.7		2	0.098	1795	25.3	15.7	-0.4831
		0.7	32.0		4	0.193	1824	22.7	18.3	-0.5925
		0.6	23.0		8	0.383	1858	16.3	24.7	-0.9227
		1.4	20.3		12	0.569	1898	14.4	26.6	-1.0476
		3.8	19.4		16	0.754	1899	13.7	27.3	-1.0929
	PTSP-1R	2.0	26.3		8	0.383	1858	18.6	22.4	-0.7886
		2.1	22.0		12	0.569	1898	15.6	25.4	-0.9672
		2.5	16.8		16	0.754	1899	11.9	29.1	-1.2368
	PTSP-2	0.4	29.4		2	0.089	2030	20.8	20.2	-0.6772
		1.1	33.3		4	0.176	2077	23.6	17.4	-0.5527
		2.5	19.7		8	0.346	2131	14.0	27.0	-1.0776
		3.8	42.8	2.0	12	0.513	2156	30.3	10.7	-0.3017
		3.9	10.9	1.1	16	0.680	2147	7.7	33.3	-1.6694
	PTSP-3	2.2	23.6	7.1	2	0.082	2255	16.7	24.3	-0.8970
		2.4	20.9		4	0.162	2290	14.8	26.2	-1.0185
		4.2	10.9		8	0.321	2338	7.7	33.3	-1.6694
		3.3	5.1		12	0.477	2387	3.6	37.4	-2.4290
		2.3	2.7		16	0.631	2397	1.9	39.1	-3.0650
	PTSP-4	2.3	19.3		2	0.076	2473	13.7	27.3	-1.0981
		2.0	19.5		4	0.149	2554	13.8	27.2	-1.0878
		2.9	4.8		8	0.292	2624	3.4	37.6	-2.4896
		1.4	3.1		12	0.434	2636	2.2	38.8	-2.9268
		1.6	2.6		16	0.575	2637	1.8	39.2	-3.1027
	PTSP-4R	3.1	4.2		8	0.292	2624	3.0	38.0	-2.6231
		1.4	3.7		12	0.433	2636	2.6	38.4	-2.7499
		1.3	3.6		16	0.574	2637	2.6	38.4	-2.7773

**Table 2.2.6**  
**DTFS-1 PYROLYSIS DATA FOR SIZE-GRADED UPPER FREEPORT BCFs**

FUEL TYPE	TEST NO.	M'	VM'	A'	DIST. (in.)	TIME (sec.)	TEMP. (°F)	Vc	ΔV	ln(1-(ΔV/VMo))
UPPER FREEPORT MFP	UFMP-1	0.1	18.7		4	0.193	1824	15.0	14.6	-0.6823
		0.7	17.3		8	0.383	1858	13.8	15.8	-0.7601
		1.4	13.5		12	0.569	1898	10.8	18.8	-1.0081
		0.5	12.3		16	0.754	1899	9.8	19.8	-1.1012
	UFMP-1R	0.6	18.7		8	0.383	1858	15.0	14.6	-0.6823
		0.9	14.4		12	0.569	1898	11.5	18.1	-0.9436
		0.6	11.0		16	0.754	1899	8.8	20.8	-1.2129
	UFMP-2	1.2	23.7		2	0.098	2030	19.0	10.6	-0.4453
		1.3	21.4		4	0.193	2077	17.1	12.5	-0.5474
		2.9	15.6		8	0.383	2131	12.5	17.1	-0.8635
		3.1	9.4	6	12	0.569	2156	7.5	22.1	-1.3701
		2.5	6.1	0	16	0.754	2147	4.9	24.7	-1.8025
	UFMP-3	0.8	15.5	8	2	0.098	2255	12.4	17.2	-0.8699
		1.1	16.3	6	4	0.193	2290	13.0	16.6	-0.8196
		0.4	8.2		8	0.383	2338	6.6	23.0	-1.5066
		0.5	2.9		12	0.569	2387	2.3	27.3	-2.5461
	UFMP-4	0.3	2.1		16	0.754	2397	1.7	27.9	-2.8688
	UFMP-4R	2.2	18.2		2	0.098	2473	14.6	15.0	-0.7094
		3.3	14.7		4	0.193	2554	11.8	17.8	-0.9229
		0.8	3.6		8	0.383	2624	2.9	26.7	-2.3298
		0.5	1.6		12	0.569	2636	1.3	28.3	-3.1408
		0.2	1.2		16	0.754	2637	1.0	28.6	-3.4285
UPPER FREEPORT SOAP	UFSP-1	0.4	2.7		8	0.383	2624	2.2	27.4	-2.6175
		0.1	3.6		12	0.569	2636	2.9	26.7	-2.3298
		0.3	2.8	7	16	0.754	2637	2.2	27.4	-2.5812
	UFSP-2	0.4	28.0		2	0.098	1795	22.6	18.0	-0.5867
		0.8	25.4		4	0.193	1824	20.5	20.1	-0.6842
		0.5	24.5		8	0.383	1858	19.8	20.8	-0.7203
		2.3	17.0		12	0.569	1898	13.7	26.9	-1.0857
		3.2	12.9		16	0.754	1899	10.4	30.2	-1.3617
	UFSP-3	0.4	26.3		2	0.098	2030	21.2	19.4	-0.6494
		0.3	20.7		4	0.193	2077	16.7	23.9	-0.8888
		0.5	12.3		8	0.383	2131	9.9	30.7	-1.4094
		3.2	8.6		12	0.569	2156	6.9	33.7	-1.7672
		0.9	3.7	6	16	0.754	2147	3.0	37.6	-2.6106
	UFSP-4	1.0	19.5	9	2	0.098	2255	15.7	24.9	-0.9485
		3.4	10.6	9	4	0.193	2290	8.5	32.1	-1.5581
		3.2	7.2		8	0.383	2338	5.8	34.8	-1.9449
		0.9	3.3		12	0.569	2387	2.7	37.9	-2.7250
		0.9	2.9		16	0.754	2397	2.3	38.3	-2.8893
	UFSP-4	1.5	17.5		2	0.098	2473	14.1	26.5	-1.0568
		3.5	9.5		4	0.193	2554	7.7	32.9	-1.6677
		0.5	2.1		8	0.383	2624	1.7	38.9	-3.1770
		0.6	4.2		12	0.569	2636	3.4	37.2	-2.4839
		0.2	1.3		16	0.754	2637	1.0	39.6	-3.6566

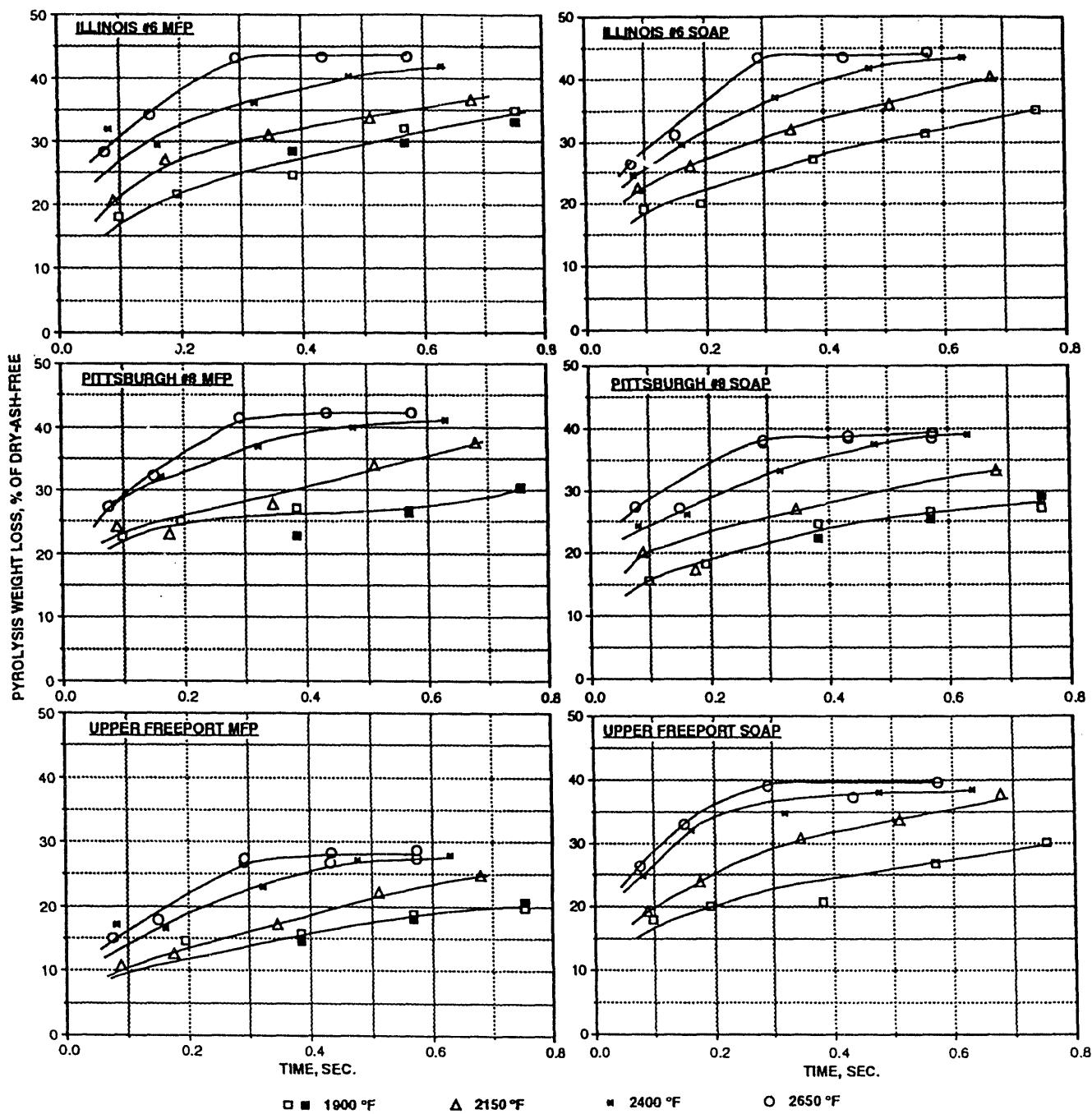


Figure 2.2.7 DTFS-1 pyrolysis weight losses of 325x0 mesh BCFs in nitrogen atmosphere at various temperatures

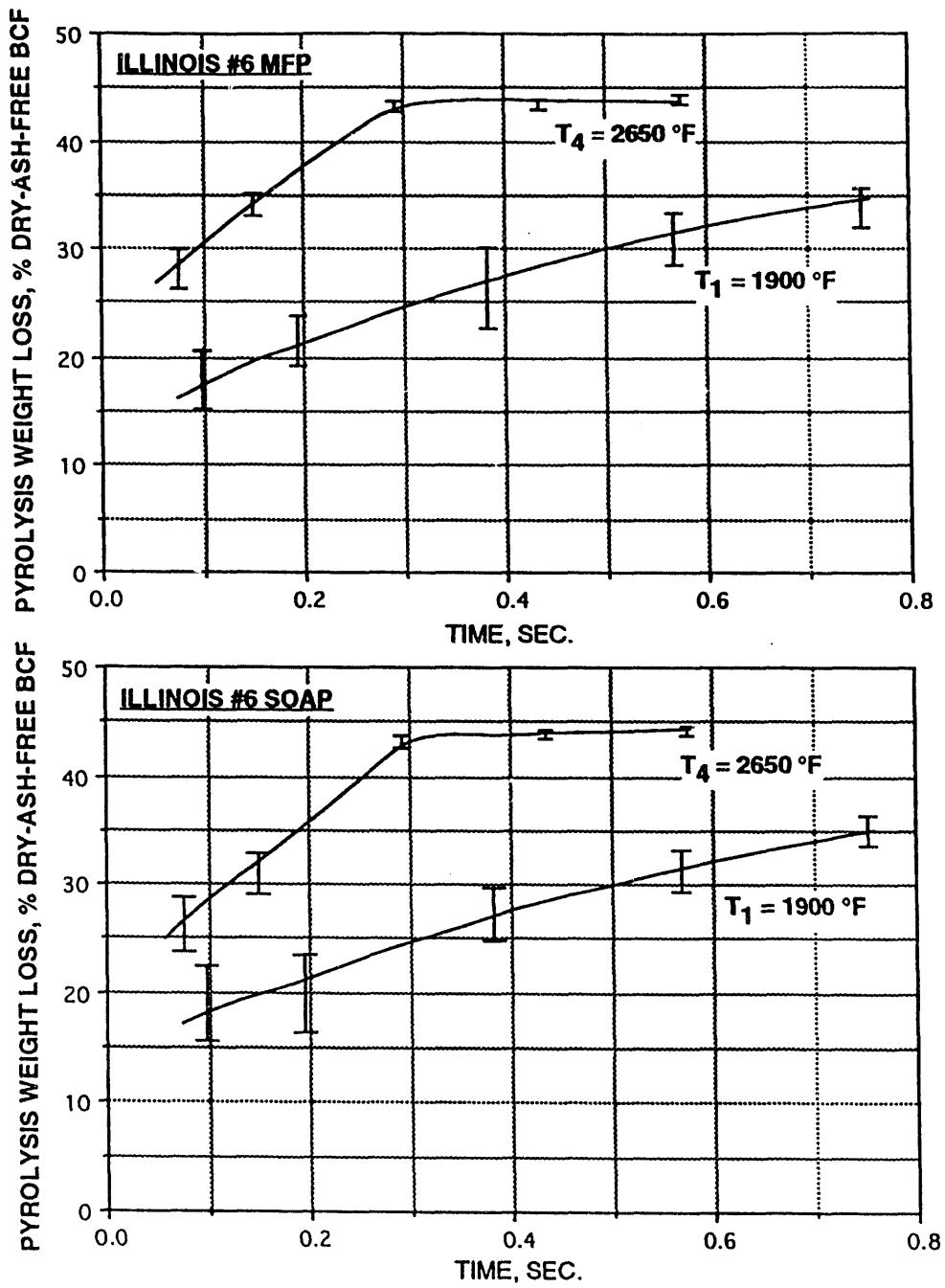


Figure 2.2.8 Error bands for DTFS-1 pyrolysis weight losses of 325x0 mesh Illinois No. 6 BCFs

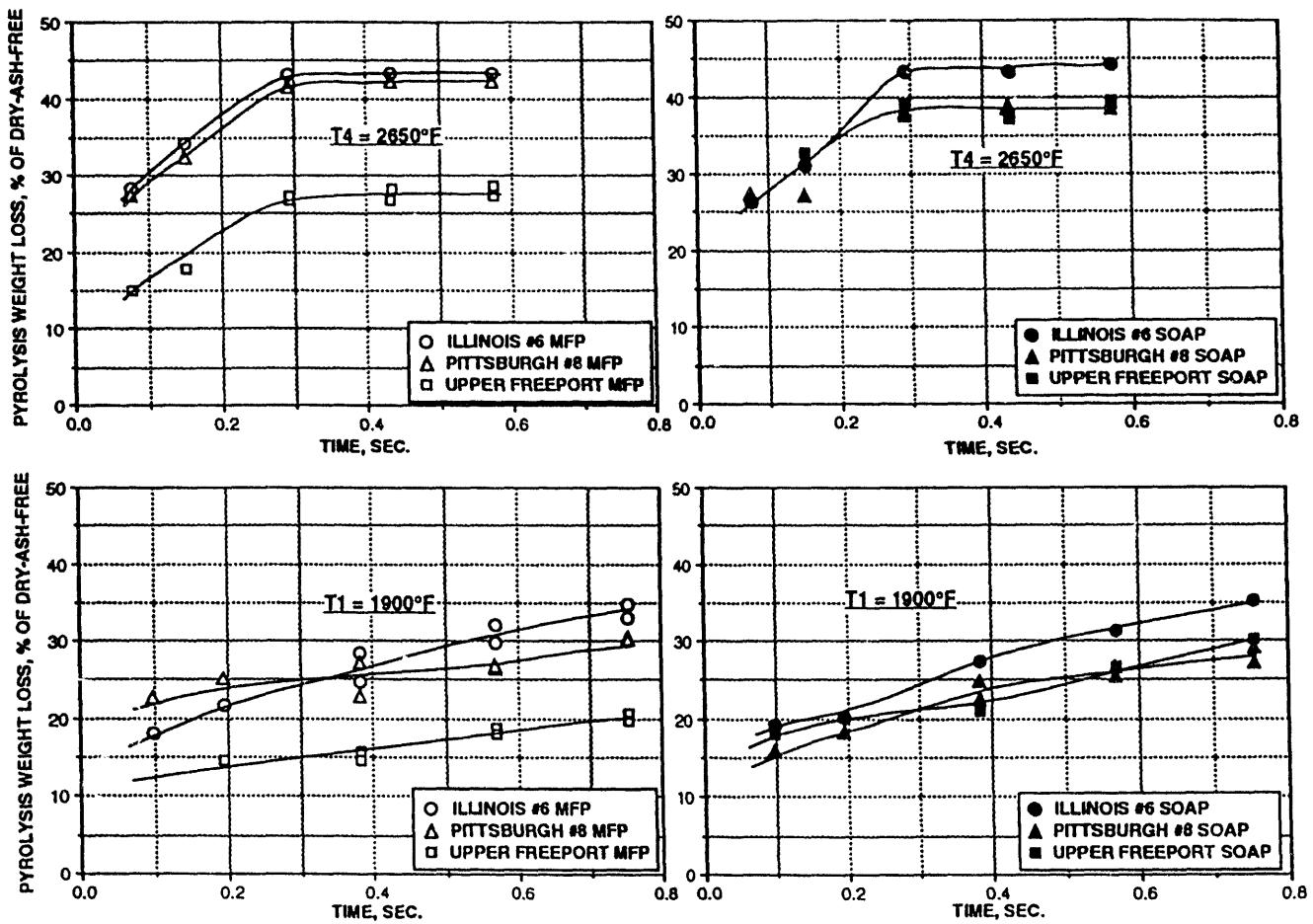


Figure 2.2.9 Effect of fuel type on DTFS-1 pyrolysis weight losses of 325x0 mesh BCFs in nitrogen atmosphere at various temperatures

generally followed here. That is, briefly:

$$C = C_0 \exp(-kt) \quad (3)$$

where  $C_0$  is the maximum obtainable weight loss ( $\Delta W_0$ ),  $C$  is the remaining pyrolyzable material at time  $t$  and  $k$  is a pyrolysis rate constant. None of the maximum weight loss values in this experiment exceeded  $VM_0$ . Therefore,  $\Delta W_0$  in each case was set equal to  $VM_0$  i.e.,  $C = VM_0 - \Delta V$ . Substituting these values into Eq.(3) yields

$$\ln(1 - \Delta V/VM_0) = -kt \quad (4)$$

Plotting the left hand side of Eq.(4) vs.  $t$  yields straight lines (Figure 2.2.10) from which the  $k$  values can be obtained from the slopes of the least squares fits.

The  $k$  values can be used in conjunction with a first order Arrhenius relationship to obtain

$$k = k_0 \exp(-E/RT) \quad (5)$$

where  $E$ ,  $k_0$ ,  $R$  and  $T$  are the apparent activation energy, frequency factor, universal gas constant and reaction temperature, respectively.

Plotting  $\ln k$  vs.  $1/T$  yields straight lines (Figure 2.2.11) from which the values of  $k_0$  and  $E$  can be obtained from respectively, the intercepts and slopes of the least squares fits. Results from this study are given in Table 2.2.7.

While the apparent activation energy values (13.5-24.8 kcal/mole) from this study are higher than those obtained previously in this laboratory (Nsakala, et al., 1985) on coals of various rank (4.7-8.0 kcal/mole), these values are still rather low. These low activation energies are either due to an artifact of the experimental procedure or a physically-

dominated pyrolysis process (i.e., mass and heat transfer). If pyrolysis involved a chemical-bond breakage process, then one would expect activation energies in the neighborhood of 50-60 kcal/mole (Walker, Jr., et. al., 1983).

Comparison to Selected Literature Pyrolysis Kinetic Parameters. Results from the present study are reported along with selected literature data in Table 2.2.8. Activation energies range from less than 10 kcal/mole to more than 25 kcal/mole, with corresponding frequency factors varying over several orders of magnitude. These differences are attributable to differences in coal types and differences in equipment and experimental procedures used. To put these results in perspective, they are plotted in Figure 2.2.12 as variation of activation energy with corresponding frequency factor. It is interesting to note that all the data from this laboratory obtained at different time-intervals fall on a straight line, perhaps indicating some consistency in equipment and experimental methodology used.

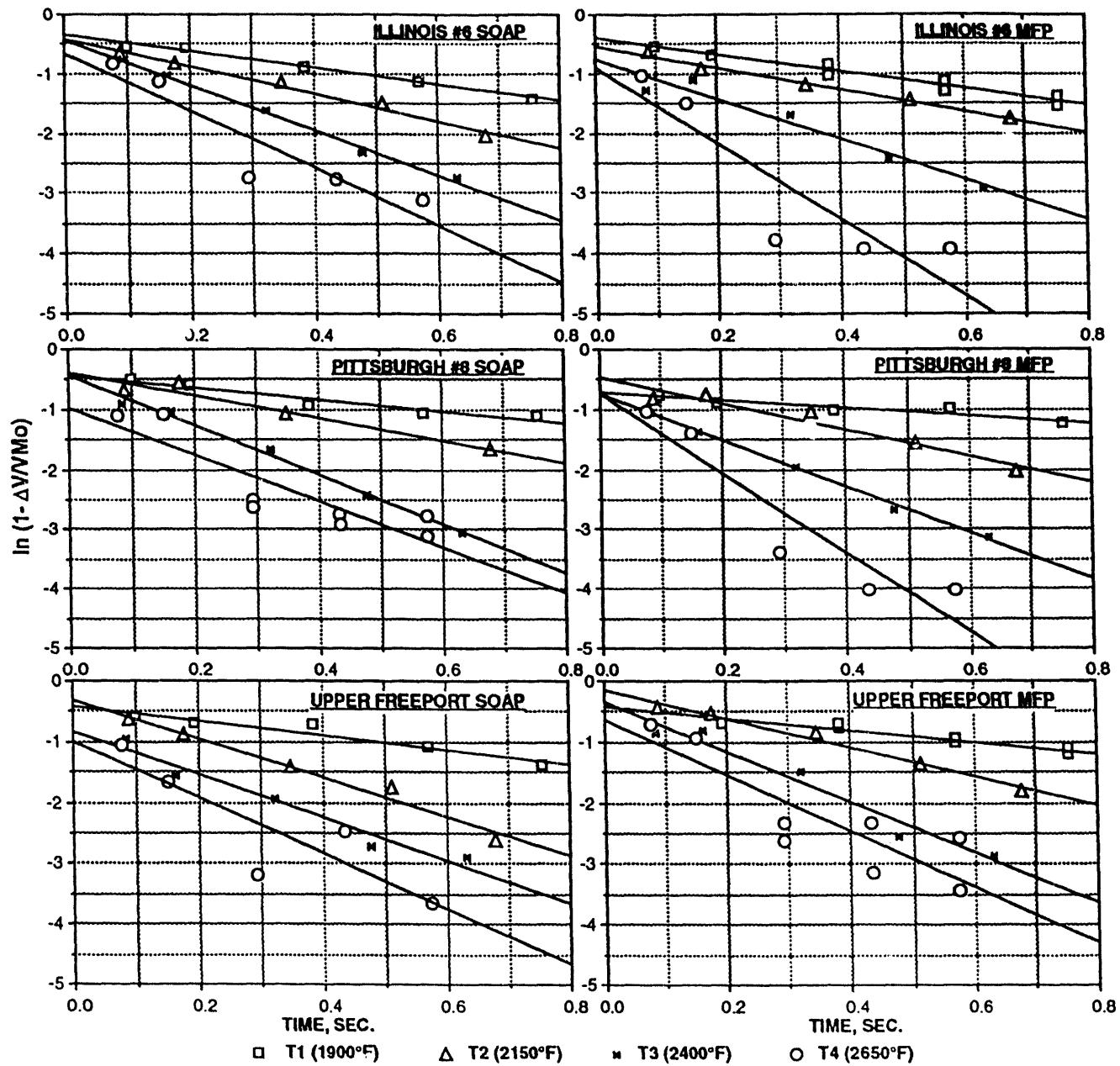


Figure 2.2.10 Variation of  $\ln(1-\Delta V/VM_0)$  with DTFS-1 residence time for pyrolysis of 325x0 mesh BCFs in nitrogen atmosphere at various temperatures

**TABLE 2.2.7**  
**KINETIC DATA FOR PYROLYSIS OF 325 X 0 MESH BCFs**  
**IN NITROGEN ATMOSPHERE AND 1290-1690°K TEMPERATURE RANGE**

FUEL	AVERAGE TEMPERATURE (°K)	KINETIC PARAMETERS			
		k	E	ko	v
ILLINOIS #6	1286	1.424			
	1426	1.793			
	MFP	3.331	15806	592	-0.959
	1691	6.295			
PITTSBURGH #8	1286	0.624			
	1426	2.187			
	MFP	3.855	24830	11554	-0.991
	1691	6.658			
UPPER FREEPORT	1299	0.960			
	1427	2.353			
	MFP	4.116	17848	1114	-0.964
	1692	4.575			
ILLINOIS #6	1286	1.392			
	1426	2.306			
	SOAP	3.751	13511	278	-0.995
	1691	4.764			
PITTSBURGH #8	1292	1.020			
	1426	1.870			
	SOAP	4.107	15606	478	-0.946
	1701	3.881			
UPPLR FREEPORT	1286	1.170			
	1427	3.175			
	SOAP	3.514	13968	328	-0.939
	1692	4.576			

k = Rate Constant, sec<sup>-1</sup>

E = Activation Energy, cal/mole

ko = Frequency Factor, sec<sup>-1</sup>

v = Correlation Coefficient of lnk vs. 1/T

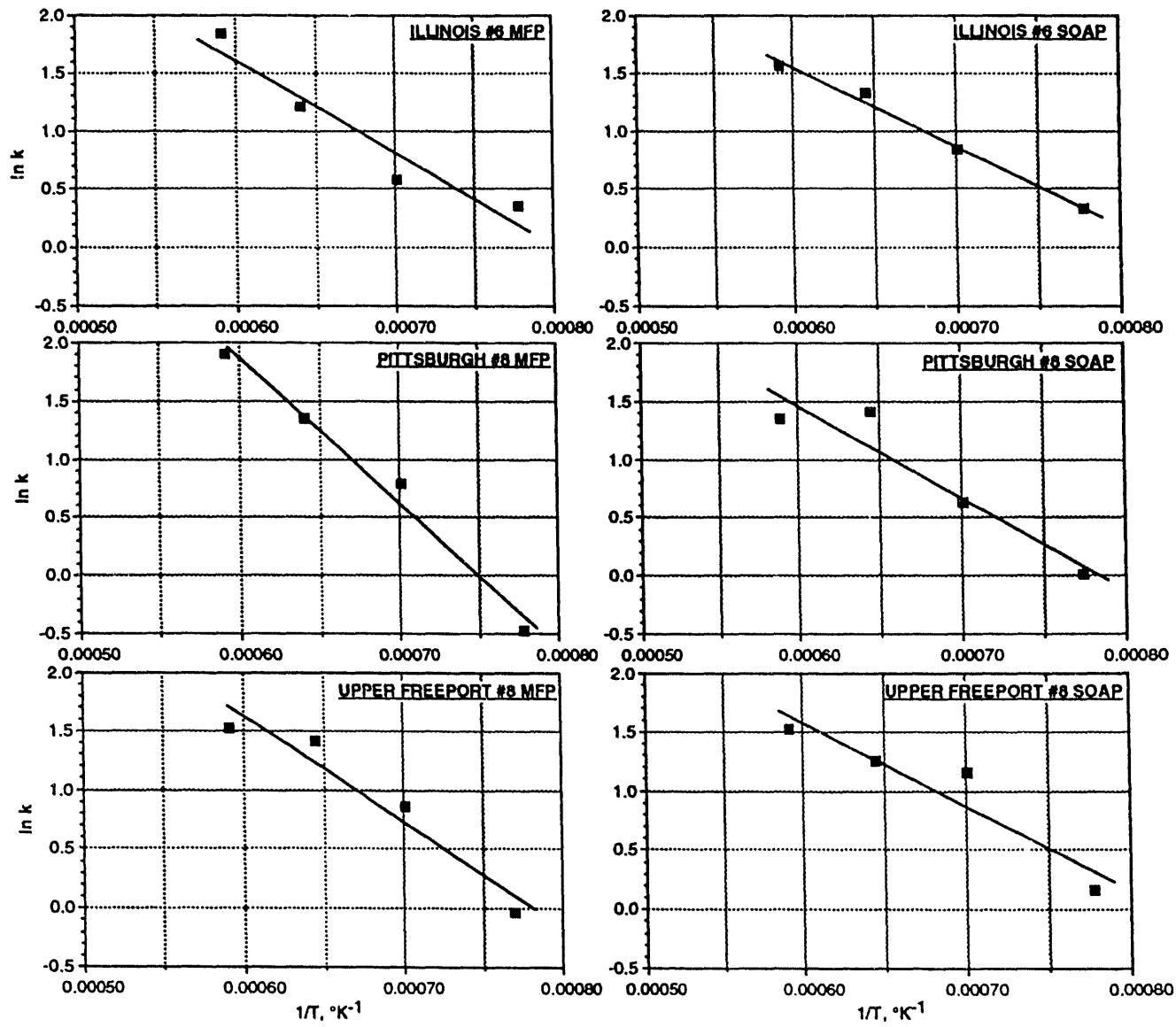


Figure 2.2.11 Arrhenius plots for pyrolysis of various 325x0 mesh BCFs

**Table 2.2.8**  
**COMPARISON OF PYROLYSIS KINETIC RESULTS**  
**FROM THIS STUDY WITH LITERATURE DATA**

Investigators	Coal	Kinetic Parameters	
		E (kcal/mole)	k <sub>0</sub> (1/sec.)
<b><u>This Work</u></b>			
	Illinois #6 MFP	15.8	5.9x10 <sup>^2</sup>
	Illinois #6 SOAP	13.5	2.8x10 <sup>^2</sup>
	Pittsburgh # MFP	24.8	1.2x10 <sup>^4</sup>
	Pittsburgh # SOAP	15.6	4.8x10 <sup>^2</sup>
	Upper Freeport MFP	17.8	1.1x10 <sup>^3</sup>
	Upper Freeport SOAP	14.0	3.3x10 <sup>^2</sup>
<b><u>Selected Literature Data</u></b>			
Stone, et al. (1954)	Pitts. Seam Bituminous	24.4	1.1x10 <sup>^5</sup>
Badzioch and Hawksley (1970)	B NBC 902	17.8	1.1x10 <sup>^5</sup>
	B NBC 601	17.8	3.1x10 <sup>^5</sup>
Shapatina, et al. (1960)	Moscow District Brown Coal	3.8	0.7x10 <sup>^1</sup>
Howard and Essenhigh (1967)	Pitts. Seam Bituminous	27.7	4.9x10 <sup>^4</sup>
Anthony, et al. (1975)	Pitts. Seam Bituminous	13.3	1.8x10 <sup>^3</sup>
Scaroni, et al. (1981)	Texas Lignite	10.7	6.0x10 <sup>^2</sup>
Walker, et al. (1983)	Montana Lignite	13.9	8.1x10 <sup>^3</sup>
Nsakala, et al. (1985)	Texas Lignite	8.0	5.0x10 <sup>^1</sup>
	Montana Subbituminous	4.7	1.4x10 <sup>^1</sup>
	Alabama bituminous coal	7.8	3.3x10 <sup>^1</sup>
	Pennsylvania anthracite	7.8	3.9x10 <sup>^1</sup>

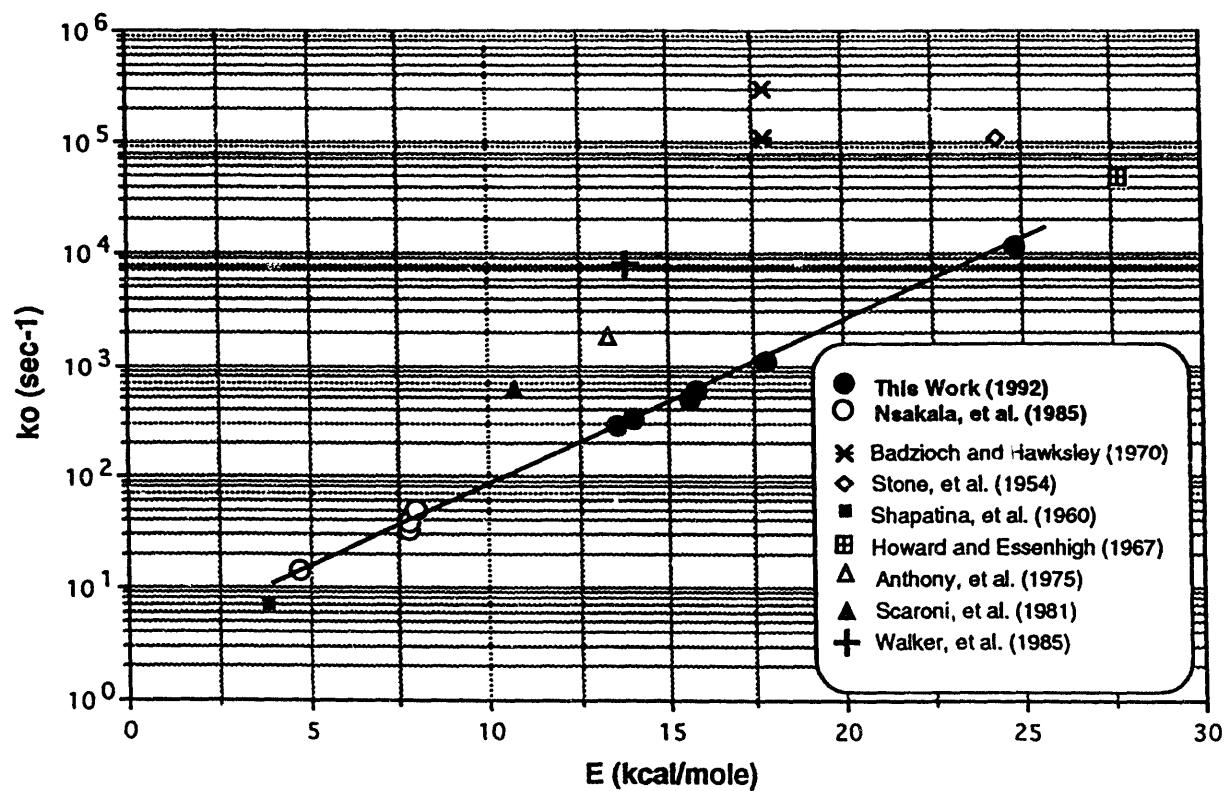


Figure 2.2.12 Variation of apparent activation energy with frequency factor for coal pyrolysis process

### **TASK 3 - PILOT-SCALE TESTING**

The pilot-scale studies were designed to provide key information for the technical and economic assessment of the BCFs for commercial applications. Comprehensive tests were conducted in the CE Fireside Performance Test Facility (FPTF) to evaluate the combustion, furnace slagging, convective pass fouling and fly ash erosion characteristics of the BCFs prepared in both dry (micro-fine) and wet (micro-fine coal-water fuel) forms. Studies were also carried out to evaluate the effect of BCF fly ashes on electrostatic precipitator (ESP) collection performance. Additionally, representative in-flame solids and ash deposit samples collected were analyzed in detail to enhance the understanding of mineral matter transformation and ash deposition and to relate these to fuel mineral distributions and combustion conditions. Also, complementary experiments were carried out in the MIT Combustion Research Facility (CRF) to provide more detailed information on the combustion and emission characteristics of selected BCFs. These experiments focused on application of the coal-water fuel form.

Nine test fuels were evaluated for combustion and performance testing from October, 1989, to June, 1990. These fuels included Illinois No.6, Upper Freeport, Pittsburgh No.8 microbubble flotation products (MFPs), spherical oil agglomeration products (SOAPs), and the MFP parent coals. Those pilot-scale results were reported in three previous quarterly reports: May to June, 1990, October to December, 1990, and January to March, 1991. Results are also included in the papers by Barta, et alia, 1991, and Chow, et alia, 1991, as well as the draft Topical Report issued in June, 1991.

Upper Freeport fresh parent coal was tested in the CE FPTF in October, 1991 for comparison to the previous Upper Freeport feed coal, which had aged for approximately eighteen months, stored in sealed drums. The results were reported in the 11th and 13th quarterly reports.

#### **TASK 4 - SCALE-UP TESTS**

The purpose of the scale-up tests is to verify that the results obtained from tests done at bench- and pilot-scales in Tasks 2 and 3 can be used to provide reasonable estimates of the performance effects when firing BCFs in commercial-scale boilers. Two beneficiated fuels would be fired in either a small utility boiler or a full-scale test furnace.

There were no activities scheduled in this task during this quarter.

#### **TASK 5 - TECHNICAL-ECONOMIC EVALUATIONS**

The results of bench-scale, pilot-scale, and scale-up tests (Tasks 2, 3, and 4) will be used to predict the performance of three commercial boilers. The boilers include: a 560MW coal-designed utility unit; a 600MW oil-designed utility unit; and an 80,000 lb/hr oil designed, shop assembled industrial unit. Eight of the base project BCFs will be used in models of each unit to calculate performance.

Boiler performance guidelines were reviewed to incorporate the BCF test results. The guidelines will also be updated to reflect current theories and correlations.

#### **TASK 6 - TECHNICAL REPORTING**

The Topical Report written in June, 1991 was updated to include all data on the first nine fuels. Results were discussed at a project review meeting in November, and plans were made for future tests.

#### **WORK PLANNED FOR NEXT QUARTER**

- Continue standard bench-scale tests on the new BCFs.
- Prepare for pilot-scale combustion tests and ash deposition tests.
- Procure more BCFs for testing.

## BIBLIOGRAPHY

Barta, L.E., Toqan, M.A., Beer, J.M., Sarofim, A.F. and Hargrove, M.J., "Transformation of Mineral Matter During Combustion of Parent and Beneficiated Upper Freeport Coal," 16th International Conference on Coal & Slurry Technologies, Clearwater, Florida, April 22-25, 1991.

Barta, L.E., G. Vámos, M.A. Toqan, J.D. Teare, J.M. Beér and A.F. Sarofim; "A Statistical Investigation on Particle to Particle Variation of Fly ash Using SEM-AIA-EDAX Technique". Material Research Society, 1989. Fall Meeting, Boston, Paper W1.6.

Barta, L.E., Horváth, F., Beér, M.J., Sarofim, F.A.; Mineral Matter Distribution in Individual Pulverized Coal Particles; Application of the "URN" model. Presented at the "Twenty-third International Symposium on Combustion". Orléan, France July 22-27, 1990.

Barta, L.E. and J.M. Beér; "Distribution Functions of Chemical Compounds and Viscosity of Fly Ash Originated from Monosize Coal Particles in the Case of Total Mineral Coalescence", Internal Report, MIT Cambridge, MA, June, 1990.

Beer, J.M., Proc. Anthracite Conference, Bull. 75, Mineral Industries Experiment Station, The Pennsylvania State University, September, 1961.

Chow, O.K., Hargrove, M.J., and Levasseur, A.A., "The Impact of Beneficiated Coal-Based Fuels on Boiler Performance," 16th International Conference on Coal & Slurry Technologies, Clearwater, Florida, April 22-25, 1991.

Chow, O.K., Lexa, G.F., Levasseur, A.A. and Mehta, A.K. "Combustion Characterization of the Kentucky No. 9 Cleaned Coals," EPRI Final Report CS-4994, February, 1987.

Chow, O. K., Nsakala, N. Y., Hargrove, M. J., and Levasseur, A. L., "Fireside Combustion Performance Evaluation of Beneficiated Coal-Based Fuels," International Joint Power Generation Conference, Atlanta, Georgia, October, 1992.

Durant, J.F., Kwasnik, A.F., Levasseur, A.A. and Baumann, P.D., "Impacts of Cleaning Texas Lignite on Boiler Performance and Economics," EPRI Final Report GS-6517, August 1989.

Feeley, III, T.J., and Hervol, J.D., "Testing of Advanced Physical Coal Cleaning Processes--Current Status," Presented at Fourth Annual Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 28-October 2, 1987.

Field, M.A., Gill, D.W., Morgan, B.B., and Hawksley, P.G.W., "The Surface Reaction Rate of Carbon with Oxygen," Combustion of Pulverised Coal, BCURA, Leatherhead, England, 1967, p. 329.

Goetz, G.J., Nsakala, N., and Patel, R.L., "Combustion and Gasification Kinetics of Chars from Four Commercially Significant Coals of Varying Rank," Proc. International Conference on Coal Science, 1983, p. 571.

Griffith, B.F., Lexa, G.F., Teigen, B.C., Levasseur, A.A. and Mehta, A.K., "Pilot-Scale Combustion Characterization of Two Illinois Coals," EPRI Final Report CS-6009, November 1988.

Hargrove, M.J., et al., "Commercial Applications and Economics of Coal-Water Fuels," Final Report Volume 6, DOE Contract DE-AC-22-82 PC 50271, November, 1989.

Huettenhain, H. and Schaal, A.M., "Advanced Physical Fine Coal Cleaning by Spherical Agglomeration," Final Report for U.S. DOE/PETC under Contract DE-AC-22-87 PC 79867, September 1990.

Huffman, G.P., Huggins, F.E., Dunmyre, G.R., Pignocco, A.J. and Lin, M.C., "Comparative Sensitivity of Various Analytical Techniques to the Low-Temperature Oxidation of Coal," Fuel, 64, 849(1985).

Hurley, J. P., Benson, S. A., Chow, O. K., and Nsakala, N. Y., "The Effects of Coal Beneficiation on Ash Formation and Deposition," 17th International Conference on Coal Utilization and Slurry Technologies, Clearwater, Florida, April, 1992.

Mitchell, R.E., "Experimentally Determined Overall Burning Rates of Coal Chars," Combustion Science and Technology, 53, 165 (1987).

Nsakala, N., Goetz, G.J., Patel, R.L., Lao, T.C., Hickerson, J.D., and Ritz, H.J., "Pyrolysis and Combustion Characterization of Pulverized Coals for Industrial Applications," 189th ACS National Meeting, Miami, Florida, April 28-May 3, 1985. CE Publication TIS-7877.

Nsakala, N., Patel, R.L. and Borio, R.W., "An Advanced Methodology for Prediction of Carbon Loss in Commercial Pulverized Coal-Fired Boilers," 1986 JPGC, Portland, Oregon, October 19-23, 1986. CE Publication TIS-8211.

Nsakala, N. Patel, R. L., and Hargrove, M. J., "Physical, Chemical, and Reactivity Characteristics of Beneficiated Coal-Based Fuels," 15th International Conference on Coal and Slurry Technologies, Clearwater, Florida, April 23-26, 1990.

Nsakala, N. Patel, R. L., Raymond, D. R., Hargrove, M. J., Hurley, J. P., and Benson, S. A., "Effects of Coal Natures and Cleaning Processes on the Physicochemical and Reactivity Characteristics of Beneficiated Coal-Based Products," 16th International Conference on Coal and Slurry Technologies, Clearwater, Florida, April 22-25, 1991.

Raask, E.; Mineral Impurities in Coal Combustion: Behavior, Problems, and Remedial Measures. Hemispheres Publishing Corporation, Washington DC, 1985.

Sarofim, A.D., J.B. Howard, and P.S. Padia, "The physical transformation of mineral matter in pulverized coal under simulated combustion conditions," Combustion Science and Technology, 16, 187-204 (1977).

Schaal, A.M., and Lippsmeyer, B.C., Proof-Of-Concept Results Using the Arcanum/Bechtel Spherical Agglomeration Approach to Clean Ultra-fine Coals," EPRI's 15th Annual Fuel Science Conference, Palo Alto, California, June 19-21, 1990.

**Smouse, S.M., McIlvried, T.S. and Avon, B.M., "Characterization of Advanced Physical Coal-Cleaning Products," 15th International Conference on Coal & Slurry Technologies, Clearwater, Florida, April 24-27, 1989.**

**Straszheim, W.E., "Application of automated image analysis to the study of mineral matter in raw and processed coals," Ph.D. Thesis, Iowa State University (1986).**

**Walker, Jr., P.L., Rusinko, Jr., F., and Austin, L.G., "Gas Reactions of Carbon," Advances in Catalysis, Vol 11, Academic Press, N.Y. and London, 1959, p. 133.**

**Watt, J.D. and F. Fereday; "The Flow Properties of Slags Formed from the Ashes of British Coals: Part 1. Viscosity of Homogeneous Liquid Slags in Relation to Slag Composition". Journal of the Institute of Fuel. March 1969.**

APPENDIX

**COMBUSTION CHARACTERIZATION OF BENEFICIATED  
COAL-BASED FUELS**

Quarterly Technical Progress Report  
for the Period October - December 1992

*Submitted by:*

Tina M. Strobel, Research Associate  
John P. Hurley, Research Supervisor  
Steven A. Benson, Research Supervisor

Energy and Environmental Research Center  
University of North Dakota  
Box 8213, University Station  
Grand Forks, North Dakota 58202

*Submitted to:*

U.S. Department of Energy  
Pittsburgh Energy Technology Center  
626 Cochran Mill Road  
P.O. Box 10940  
Pittsburgh, Pennsylvania 15236

January 1993

Work Performed under Subcontract to Combustion Engineering, Inc.

Contract No. DE-AC22-89PC88654

# COMBUSTION CHARACTERIZATION OF BENEFICIATED COAL-BASED FUELS

## 1.0 INTRODUCTION

The University of North Dakota Energy and Environmental Research Center (EERC) is providing analytical and data interpretation support for the Combustion Characterization of Beneficiated Coal-Based Fuels (BCF) project. Under Task 2, all solid fuels are being analyzed by computer-controlled scanning electron microscopy (CCSEM) to determine the types, size distributions, and degree of affiliation with coal particles for the discrete mineral particles present in each fuel. The CCSEM results of the Illinois No. 6 parent, spherical oil agglomerate process (SOAP), and microbubble flotation process (MFP) fuels were presented in the April 1989 to May 1991 summary report submitted to the Department of Energy (DOE). The same samples were analyzed in December 1992 by CCSEM using three magnifications instead of two, and this quarterly report compares the December 1992 data with the original data.

Three spherical agglomerate (SA) beneficiated fuels, which include the Upper Freeport, Pittsburgh, and Illinois No. 5, were analyzed by CCSEM in December 1992. These data will also be presented. The computer program used to reduce the CCSEM data was also updated to include new phases, which include quartz-pyrite and clay-pyrite classifications. A large percentage of the data that were originally classified as unknowns were adjacent quartz and pyrite or clay and pyrite particles. Adding these two classifications has reduced the amount of unknown data by 5% to 10%.

## 2.0 TASK 2 RESULTS AND DISCUSSION

### 2.1 CCSEM Analyses for Illinois No. 6 Fuels

#### 2.1.1 CCSEM Analyses of Illinois No. 6 Parent Fuel

The cumulative size distribution of the mineral particles in the Illinois No. 6 parent fuel is illustrated in Figure 1. The data were determined by CCSEM analysis of polished coal/wax pellets. Therefore, the data are for mineral particles with cross-sectioned diameters in the range of 1 to 100 microns. The data from the 1991 and 1992 analyses show very similar particle-size distributions, with approximately 90% of the particles in the less-than-22.0-micron size range. Some discrepancy exists between the 1991 and 1992 data in the 1.0- to 4.6-micron particle-size range and may be due to different analytical methods. The 1992 CCSEM analysis used three magnifications instead of two, and the higher magnification may allow for easier grain boundary distinctions. By distinguishing grain boundaries more easily, smaller particles would be segregated into the proper particle-size bin. CCSEM with only two magnifications may not distinguish some grain boundaries and identify two adjacent particles as one single particle. The better ability of the three-magnification routine to distinguish adjacent particles can be seen in the reduction of particles classified as unknown, as shown in Figure 2. This figure shows the relative quantities of the different types of mineral particles detected by CCSEM in the Illinois No. 6 parent fuel. Both 1991 and 1992 analyses contain mainly quartz, kaolinite, K-Al silicates, pyrite, and unknowns. The 1992 analyses contain a lower amount of

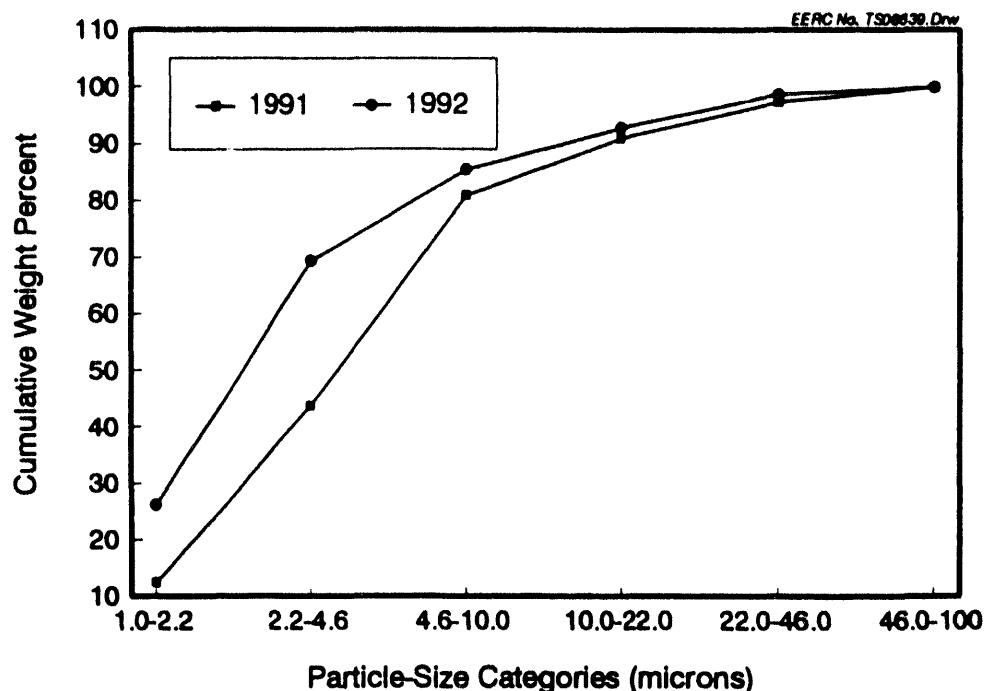


Figure 1. Cumulative size distributions of the inorganic particles with sectioned diameters between 1 and 100 microns in the Illinois No. 6 parent fuel.

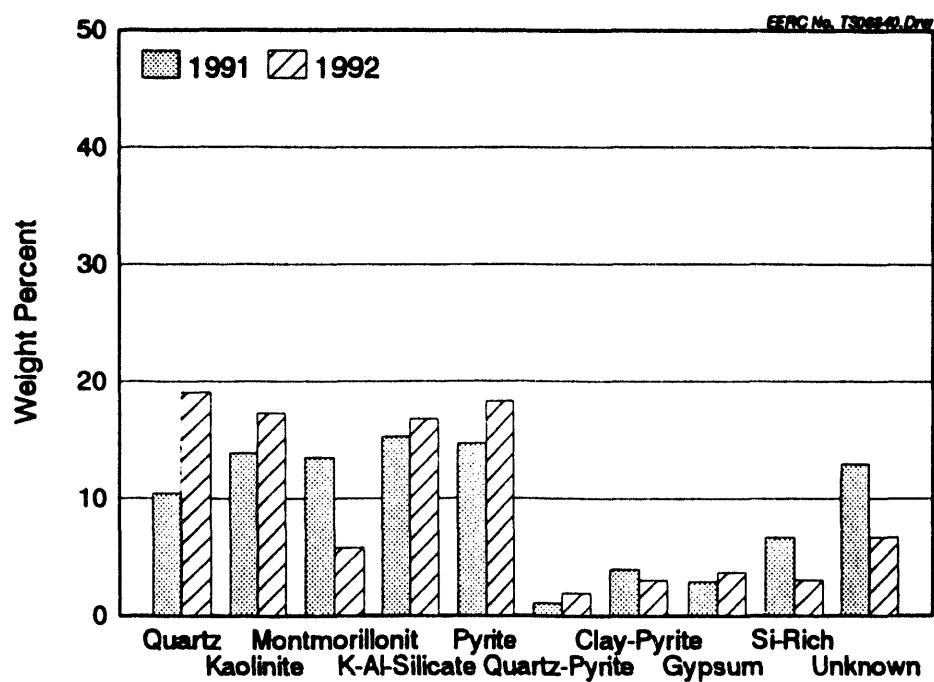


Figure 2. The composition distributions of the inorganic particles with sectioned diameters between 1 and 100 microns in the Illinois No. 6 parent fuel.

montmorillonite and unknowns. The lower percentage of unknowns in the 1992 data can be explained by the ability of the three-magnification technique to distinguish better between adjacent particles. Some of the unknowns in both sets of analyses can be attributed to grain boundary analyses of organic sulfur and quartz or aluminosilicate particles. The difference in montmorillonite content is difficult to explain, although the total amount of aluminosilicate phases (kaolinite + montmorillonite + K-Al silicate) is comparable.

#### 2.1.2 CCSEM Analyses of Illinois No. 6 MFP Fuel

Figures 3 and 4 show the cumulative size distributions and composition distributions of the Illinois No. 6 MFP fuel. The data were determined by CCSEM analysis of fuel particles with sectioned diameters between 1 and 100 microns. Both the 1991 and 1992 analyses follow almost identical curves. Nearly 90% of the fuel particles are less than 10 microns in diameter.

The composition distributions between the two data sets do not match as well as the particle-size distribution data. The main phases present are quartz, kaolinite, K-Al silicates, pyrite, and unknowns. The 1992 analyses show higher percentages of quartz and pyrite. The lower percentage of unknowns in the 1992 MFP data is explained by the better ability of the three-magnification technique to distinguish grain boundaries. Some of the unknowns in both the 1991 and 1992 data were organic sulfur and quartz or aluminosilicate particles, which is a result of the small diameters of the particles in this fuel.

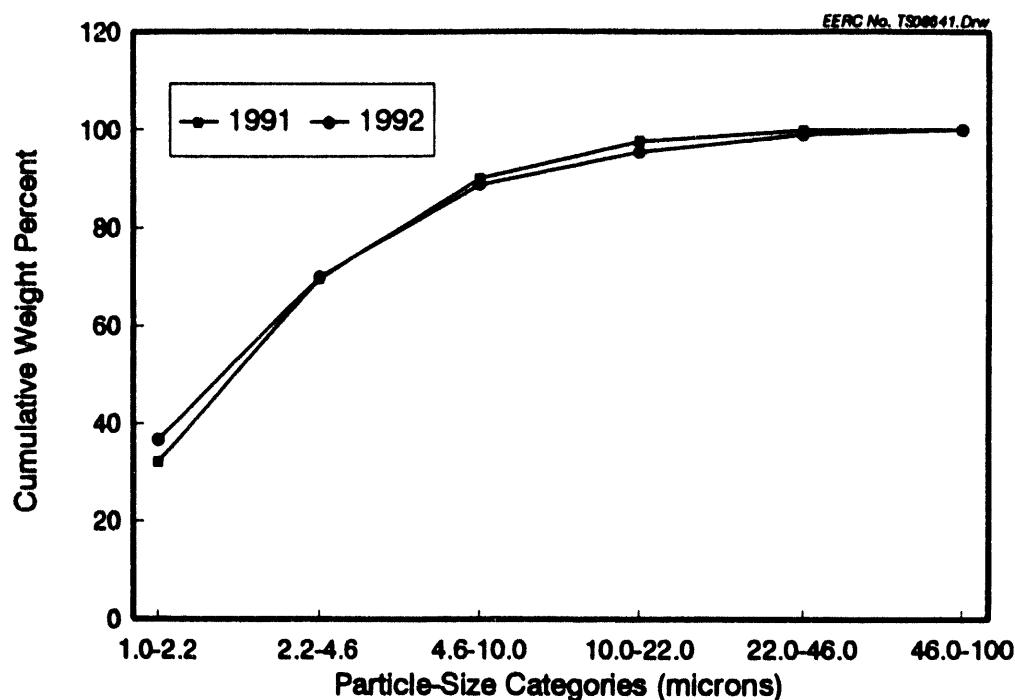


Figure 3. The particle size distributions of the inorganic particles with sectioned diameters between 1 and 100 microns in the Illinois No. 6 MFP fuel.

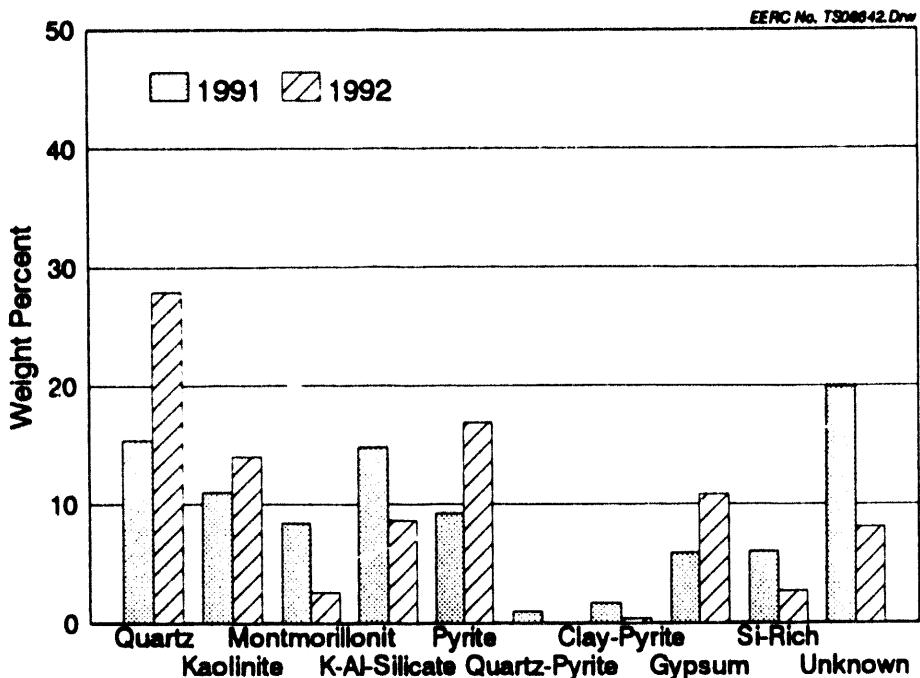


Figure 4. The composition distributions of the inorganic particles with sectioned diameters between 1 and 100 microns in the Illinois No. 6 MFP fuel.

#### 2.1.3 CCSEM Analyses of Illinois No. 6 SOAP Fuel

Figure 5 shows the cumulative size distribution of the 1991 and 1992 CCSEM data from the Illinois No. 6 SOAP fuel. The 1991 and 1992 data are fairly similar, but the new analyses show a higher concentration of particles in the less-than-4.6-micron range than did the 1991 analyses. In the particle-size ranges greater than 4.6 microns, the two data sets show less than 5% difference.

The composition distributions of the Illinois No. 6 SOAP fuel are shown in Figure 6. Although most of the phases show good correlation between the 1991 and the 1992 data sets, some differences occur. The main phases present are quartz, kaolinite, K-Al silicates, pyrite, and unknowns. The new analysis results contain a greater percentage of quartz and pyrite, and the 1991 analyses reveal more montmorillonite and unknowns. The lower amount of unknowns in the 1992 data is again contributed to the three-magnification technique, which is offset by the higher percentages of quartz and pyrite in the 1992 data. The difference in montmorillonite content is puzzling. The raw data were examined and found to contain montmorillonite analytes with organic sulfur. This sample may contain mixtures of small clay grains with interdispersed coal particles, or small coal with interdispersed clay particles. Because the two-magnification CCSEM technique does not easily distinguish grain boundaries, these grain boundary analyses are being classified as montmorillonite and unknowns in the 1991 data.

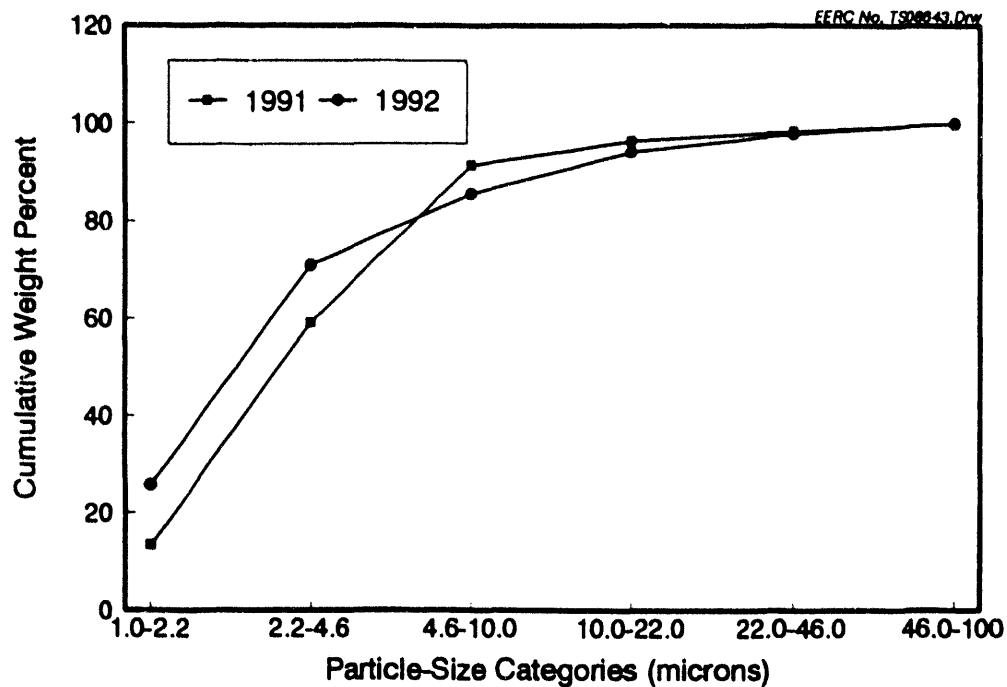


Figure 5. The particle-size distributions of the inorganic particles with sectioned diameters between 1 and 100 microns in the Illinois No. 6 SOAP fuel.

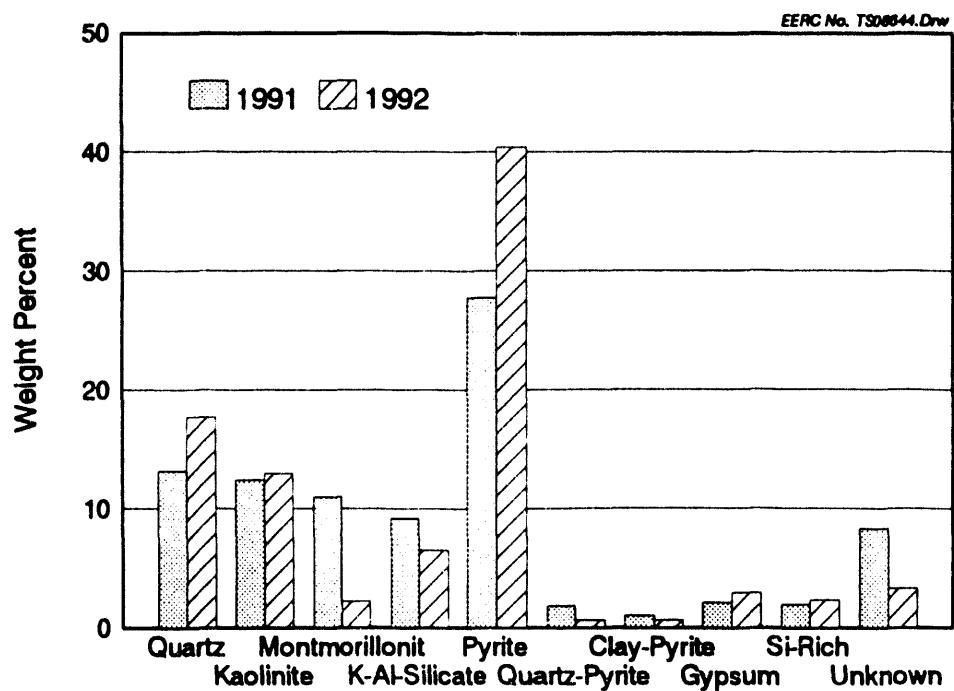


Figure 6. The composition distributions of the inorganic particles with sectioned diameters between 1 and 100 microns in the Illinois No. 6 SOAP fuel.

## 2.2 CCSEM Analyses of Spherical Agglomerate Fuels

The cumulative size distributions of the Upper Freeport, Pittsburgh No. 8, and Illinois No. 5 spherical agglomerate (SA) fuels are presented in Figure 7. All three fuels have very similar size distributions, and approximately 80% of the particles in each sample are less than 22 microns. This cleaning process seems to give a more even particle-size distribution than the other beneficiation processes (SOAP and MFP).

Figure 8 shows the composition distributions for the three SA fuels. The major phases present in all three samples include quartz, kaolinite, K-Al silicates, and pyrite. All of the samples have less than 5% unknown, which is due to the separation of agglomerated grains during beneficiation. The Upper Freeport fuel contains the lowest amount of pyrite and gypsum. The Pittsburgh fuel has high amounts of kaolinite and pyrite, but the lowest amount of K-Al silicates in comparison to the other two fuels. The Illinois No. 5 fuel contains the highest amount of K-Al silicates and the lowest amount of kaolinite of the three fuels.

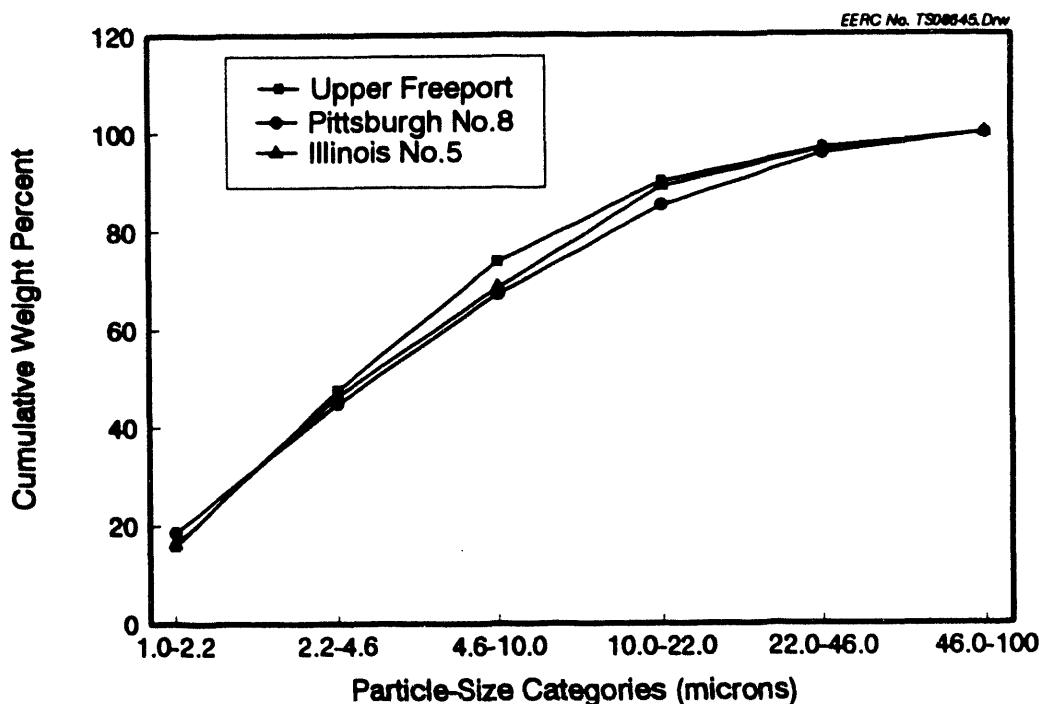


Figure 7. The cumulative size distributions of the inorganic particles with sectioned diameters between 1 and 100 microns in the Upper Freeport, Pittsburgh No. 8, and Illinois No. 5 SA fuels.

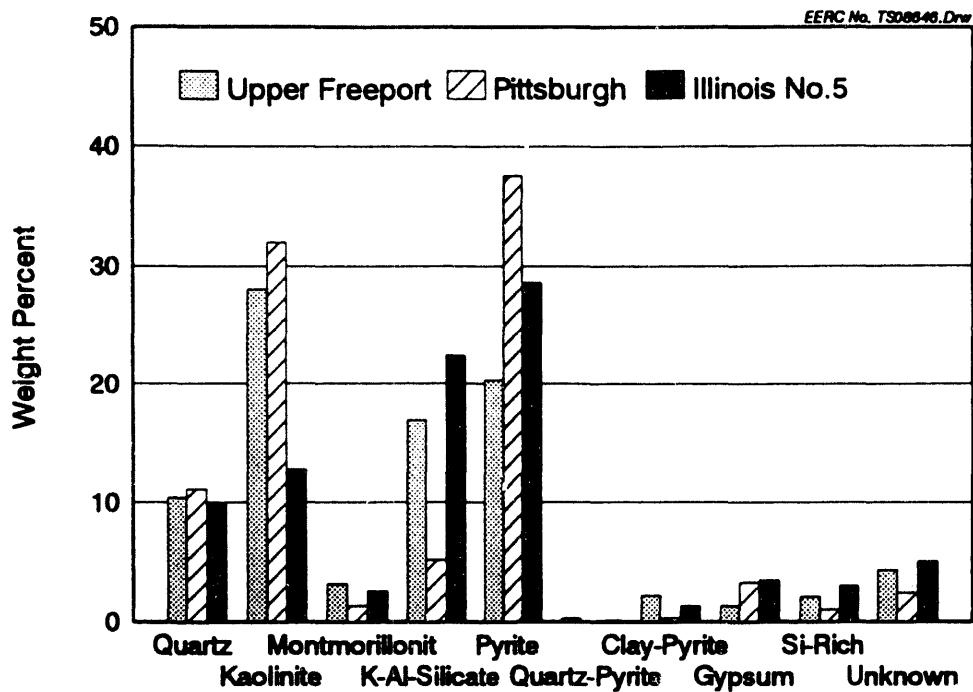


Figure 8. The composition distributions of the inorganic particles with sectioned diameters between 1 and 100 microns in the Upper Freeport, Pittsburgh No. 8, and Illinois No. 5 SA fuels.

### 2.3 CCSEM Data Reduction Program

Some changes were made in the HIRANK CCSEM data reduction program this quarter. The CCSEM results of the 1991 and 1992 Illinois No. 6 parent, spherical oil agglomerate process (SOAP), and microbubble flotation process (MFP) fuels contained high amounts of particles with compositions that did not fall into one of the existing categories. After visual inspection of the raw data, it was concluded that most of the unknown analyses were either: 1) grain boundary analyses of organic sulfur and aluminosilicate particles, 2) grain boundary analyses of quartz and pyrite particles, or 3) grain boundary analyses of aluminosilicate and pyrite particles. To reduce the number of unknowns in these data, the criteria for mineral phases in the HIRANK program were adjusted to account for these analyses.

In the previous version of the HIRANK program, the aluminosilicate phases of kaolinite, montmorillonite, and K-Al-silicate were constrained to have  $\text{Al}_2\text{O}_3 + \text{SiO}_2 \geq 80$  wt%. This criterion did not account for grain boundary analyses with organic sulfur, and therefore was changed to allow for sulfur in the kaolinite, montmorillonite, and K-Al-silicate criteria ( $\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{SO}_3 \geq 80$  wt%, see Table 1). The result of changing the criteria was to reduce the number of unknown analyses, especially in the 1991 Illinois No. 6 parent fuel. The original HIRANK results for this fuel contained over 25% unknown analyses. The results from the new program had only 13% unknowns, which corresponds to a 50% decrease. The 1991 Illinois No. 6 MFP data also showed a 30% reduction in unknowns from the original to the new HIRANK program results. The decrease in unknown particles was counterbalanced by an increase in montmorillonite analyses for both of the Illinois samples mentioned. The 1992 analyses were not as dramatically affected by the criteria changes, probably due to the ability of the three-magnification technique to distinguish more grain boundaries.

Inspection of the raw data also revealed that some unknowns were grain boundary analyses of adjacent quartz-pyrite or quartz-aluminosilicate particles. To account for these unknowns, the two new mineral categories of quartz-pyrite and clay-pyrite were included in the HIRANK program. Adding these two classifications has reduced the amount of unknown data by 5% to 10% in some fuels.

TABLE I

Listing of the Mineral Phase Definitions Used in the HIRANK Program to Determine Mineral Phases from CCSEM Analysis of High-Rank Coals or Ash. Density Factors are also Listed. (revised January 1993)

Phase Name:	Phase Composition:
1. Quartz Density	$Si \geq 80, Al \leq 5$ 2.65
2. Iron Oxide Density	$Fe \geq 80, Si \leq 10, S \leq 5, Mg \leq 5, Al \leq 5$ 5.3
3. Periclase Density	$Mg \geq 80, Ca \leq 5$ 3.61
4. Rutile Density	$Ti + Ba \geq 80, S \leq 5$ 4.9
5. Alumina Density	$Al \geq 80$ 4.0
6. Calcite Density	$Ca \geq 80, S \leq 10, Mg \leq 5, Si \leq 5, P \leq 5, Ti \leq 5, Ba \leq 5, Al \leq 5$ 2.8
7. Dolomite Density	$Mg \geq 5, Ca \geq 10, Ca + Mg \geq 80$ 2.86
8. Ankerite Density	$Ca + Mg + Fe \geq 80, S \leq 15, Mg < Fe, Fe \geq 20, Ca \geq 20$ 3.0
9. Kaolinite Density	$Al + Si + S \geq 80, 0.8 < Si/Al \leq 1.5, Fe \leq 5, K \leq 5, Ca \leq 5, Na \leq 5$ 2.65
10. Montmorillonite Density	$Al + Si + S \geq 80, 1.5 < Si/Al \leq 2.5, Fe \leq 5, K \leq 5, Ca \leq 5, Na \leq 5$ 2.5
11. K-Al-Silicate Density	$K + Al + Si + S \geq 80, Na \leq 5, Ca \leq 5, Fe \leq 5, K \geq 5, Si \geq 20, Al \geq 15$ 2.6
12. Fe-Al-Silicate Density	$Fe + Al + Si \geq 80, Fe \geq 5, Al \geq 15, Si \geq 20, S \leq 5, Ca \leq 5, K \leq 5, Na \leq 5$ 2.8
13. Ca-Al-Silicate Density	$Ca + Al + Si \geq 80, S \leq 5, K \leq 5, Fe \leq 5, Na \leq 5, Ca \geq 5, Al \geq 15, Si \geq 20$ 2.65

continued...

TABLE 1 (continued)

Phase Name:	Phase Composition:
14. Na-Al-Silicate Density	$Na + Al + Si \geq 80, S \leq 5, K \leq 5, Fe \leq 5, Ca \leq 5,$ $Na \geq 5, Al \geq 15, Si \geq 20$ 2.6
15. Aluminosilicate Density	$Si + Al \geq 80, K \leq 5, Ca \leq 5, Fe \leq 5, Na \leq 5,$ $Si \geq 20, Al \geq 20$ 2.65
16. Mixed Silicates Density	$Si + Al + Fe + Ca + K + Na \geq 80, Na \leq 10, Fe \leq 10,$ $Ca \leq 10, K \leq 10, S \leq 5, Si \geq 20, Al \geq 20$ 2.65
17. Fe-Silicate Density	$Fe + Si \geq 80, Fe \geq 10, Na \leq 5, K \leq 5, Ca \leq 5,$ $Al \leq 5, S \leq 5, Si \geq 20$ 4.4
18. Ca-Silicate Density	$Ca + Si \geq 80, Na \leq 5, K \leq 5, Fe \leq 5, Al \leq 5, S \leq 5,$ $Ca \geq 10, Si \geq 20$ 3.09
19. Ca-Aluminate Density	$Ca + Al \geq 80, P \leq 5, S \leq 5, Si \leq 5, Al \geq 15,$ $Ca \geq 20$ 2.8
20. Pyrite Density	$Fe + S \geq 80, Fe \geq 15, Fe/S \leq 0.7, S \geq 40, Ca \leq 10,$ $Ba \leq 10$ 5.0
21. Pyrrhotite Density	$Fe + S \geq 80, Fe \geq 20, S \geq 20, 0.7 < Fe/S \leq 1.5,$ $Ca \leq 10, Ba \leq 5$ 4.6
22. Oxidized Pyrrhotite Density	$Fe + S \geq 80, Fe \geq 40, S \geq 5, Fe/S \geq 1.5, Ca \leq 10,$ $Ba \leq 5$ 4.6
23. Quartz-Pyrite Density	$Al \leq 5, Si \geq 10, S \geq 10, Fe \geq 5, Fe/S \leq 0.9,$ $Si + S + Fe \geq 80, Na \leq 5, K \leq 5, Ca \leq 5$ 3.8
24. Clay-Pyrite Density	$Al \geq 5, Si \geq 10, S \geq 10, Fe \geq 5, Fe/S \leq 0.9,$ $Al + Si + S + Fe \geq 80, 0.6 < Si/Al \leq 2.6, Na \leq 5,$ $K \leq 5, Ca \leq 5$ 3.8
25. Gypsum Density	$Ca + S \geq 80, Ti \leq 10, Ba \leq 10, Si \leq 10, S \geq 20,$ $Ca \geq 20$ 2.5

continued...

TABLE 1 (continued)

<u>Phase Name:</u>	<u>Phase Composition:</u>
26. Barite Density	$Fe \leq 10, Ca \leq 5, S \geq 20, Ba + Ti \geq 20,$ $Ba + S + Ti \geq 80$ 4.5
27. Apatite Density	$P \geq 20, Ca \geq 20, Al \leq 5, S \leq 5, Ca + P \geq 80$ 3.2
28. Ca-Al-P Density	$Al \geq 10, P \geq 10, Ca \geq 10, S \leq 5, Si \leq 5,$ $Al + Ca + P \geq 80$ 2.8
29. K-Fe-Al-Si Density	$K + Fe + Al + Si \geq 80, K \geq 5, Al \geq 15, Si \geq 20,$ $Fe \geq 5, S \leq 5$ 2.8
30. Fe-Al-Si-Rich Density	$Fe + Al + Si \geq 65, Al \geq 10, Si \geq 10, Fe \geq 10$ $Ca \leq 10, S \leq 5$ 2.8
31. Ca-Fe-Al-Si-Rich Density	$Ca + Fe + Al + Si \geq 65, Al \geq 10, Si \geq 10, Ca \geq 10,$ $Fe \geq 10, S \leq 5$
32. KCl Density	$K \geq 30, Cl \geq 30, K + Cl \geq 80$ 1.99
33. Gypsum/Barite Density	$Fe \leq 5, Ca \leq 5, Ba \geq 5, Ti \geq 5, S \geq 20,$ $Ca + Ba + S + Ti \geq 80$ 3.5
34. Gypsum/Al-Silicate Density	$Ca + Al + Si + S \geq 80, Al \geq 5, Si \geq 5, S \geq 5,$ $Ca \geq 5$ 2.6
35. Ca-Si-Rich Density	$Ca + Si \geq 80, Ca \geq 20, Si \geq 20$ 2.6
36. Si-Rich Density	$Si \geq 65$ 2.65
37. Ca-Rich Density	$Ca \geq 65, Al \leq 15$ 2.6
38. Unknown Density	All Other Compositions 2.7

A vertical stack of three abstract black and white shapes. The top shape is a rectangle divided into four quadrants by a horizontal and a vertical line. The middle shape is a trapezoid with a diagonal line from top-left to bottom-right. The bottom shape is a U-shaped cutout from a rectangle.

THE  
W  
H  
I  
C  
H

# DATA

