PYROLYSIS AND COMBUSTION CHARACTERIZATION OF PULVERIZED COALS FOR INDUSTRIAL APPLICATIONS

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ABSTRACT

This paper presents in-depth fundamental information obtained from a two-inch inner diameter laminar flow reactor referred to as the Drop Tube Furnace System (DTFS). This information consists of the following: (1) pyrolysis kinetic characteristics of four coals of various rank (Pennsylvania anthracite, Alabama high volatile bituminous coal, Montana subbituminous coal, and Texas lignite); and (2) combustion kinetic studies of chars produced from the foregoing parent coals. The combustion kinetic information obtained on the high volatile bituminous coal has been used in conjunction with Combustion Engineering's proprietary mathematical model to predict the combustion performance of the pilot scale (500,000 Btu/hr) Controlled Mixing History Furnace (CMHF). Comparison of the predicted data with the experimental results shows a virtually one-to-one scale-up from the DTFS to the CMHF.

INTRODUCTION

The Department of Energy's intent in sponsoring this and other related programs is to foster increased coal usage in the United States. To effectively use coal in existing and new applications requires a more definitive, quantitative understanding of coal properties vs. performance. The objective of this program is to develop the methodologies that most reliably characterize coals from a pyrolysis/combustion standpoint thereby permitting accurate performance predictions to be made. This will in turn allow intelligent use of our coal reserves for a multiplicity of industrial applications with the confidence levels required.

The quantitative fundamental data developed from this study indicate significant differences in coal/char chemical, physical, and reactivity characteristics, which should be useful to those interested in modeling coal combustion and pyrolysis processes. Coal selection is known to be one of the keys governing a successful coal conversion/utilization process. Practical applications of these data involve providing vital information to a designer in the area of carbon burnout and NO_x reduction for a large scale coal utilization scheme.

The primary research tools used in this program were CE's Drop Tube Furnace System (DTFS), a bench scale entrained laminar flow furnace and the Controlled Mixing History Furnace (CMHF), a pilot scale entrained plug flow furnace. Both the DTFS and CMHF by virtue of their ability to resolve combustion time into distance along their respective furnace lengths were used to examine carbon burnout phenomena. In addition, the CMHF by virtue of its staged-combustion capabilities was used to evaluate NO_x emissions and establish conditions conducive to low NO_x. The NO_x results obtained from this program will not be discussed in this paper. They will appear in the forthcoming final DOE report.

EXPERIMENTAL FACILITIES AND PROCEDURES

Drop Tube Furnace System (DTFS)

The DTFS (Figure 1) is comprised of a 1-inch inner diameter horizontal tube gas preheater and a 2-inch inner diameter vertical tube test furnace for providing controlled temperature conditions to study pyrolysis and/or combustion phenomena. This entrained flow reactor is capable of heating reactant gases and reacting particulates to temperatures up to 2650°F (1730°K) and obtaining particle residence times up to about one second to simulate the rapid heating suspension firing conditions encountered in pulverized coal fired boilers. The DTFS testing procedure entails the following: (1) feed the fuel at a precisely known rate through a water-cooled injector into the test furnace reaction zone; (2) allow the fuel and its carrier gas to rapidly mix with a preheated down-flowing secondary gas stream ; (3) allow combustion and/or pyrolysis to occur for a specific time (dictated by the transit distance); (4) quench the reactions by aspirating the products in a water-cooled sampling probe; (5) separate the solids from the gaseous products in a filter medium; and (6) determine on-line NO_x, O_2, CO_2, and CO concentrations in the effluent gas stream. An ash tracer technique (1, 2) is used in conjunction with the proximate analyses of a given feed sample and the chars subsequently obtained from the test furnace to calculate the pyrolysis weight losses and/or combustion efficiencies as a function of selected operational parameters (temperature, residence time, fuel type, etc.).

Controlled Mixing History Furnace (CMHF)

The pilot scale (500,000 Btu/hr) CMHF (Figure 1) is based on the principle of plug flow which resolves time into distance along the length of the furnace. It consists of a refractory-lined 1.5 foot inner diameter cylinder with an overall height of 22.6 ft. A mixture of pulverized fuel and primary air is fired downward into the furnace from a single burner centrally located at the top of the furnace. The furnace consists of four zones--preheat, combustion, water-cooled, and after-burner--proceeding downward from the fuel admission point. By sampling at different ports along the length of the furnace, it is possible to examine the carbon burnout and NO_x formation histories of a fuel. An ash tracer method is also used to determine the solids combustion efficiency as a function of operational parameters. Gaseous products aspirated in a sampling probe are analyzed on-line to determine NO_x, O_2, CO, and CO_2 concentrations.

RESULTS

Analysis of Coals

The coals selected for this study include a ligA from Wilcox seam in Texas, a subB coal from Rosebud seam in Montana, a hvAb coal from Black Creek seam in Alabama, and an anthracite from Buck Mountain seam in Pennsylvania. The proximate and ultimate analyses and higher heating values of these coals (Table 1) are consistent with their ASTM classifications.

Pyrolysis Characteristics of Coals

Size graded (200x400 mesh) coals were pyrolyzed in the DTFS in the presence of nitrogen atmosphere at five different temperatures (1450, 1600, 1900, 2400, and

TABLE 1

SELECTED ANALYSES OF COALS

ANALYSIS	TEXAS (WILCOX) ligA		MONTANA (ROSEBUD) subB		ALABAMA (BLACK CREEK) hvAb		PENN (BUCK MT.) an	
	As Rec'd	DAF	As Rec'd	DAF	As Rec'd	DAF	As Rec'd	DAF
Proximate, Wt. Percent								
Moisture (Total)	21.2	--	23.9	--	3.6	--	5.7	--
Volatile Matter	34.7	53.6	30.7	45.0	37.7	40.3	3.5	4.1
Fixed Carbon	30.0	46.4	37.6	55.0	55.8	59.7	83.3	95.9
Ash	14.1	--	7.8	--	2.9	--	7.5	--
Ultimate, Wt. Percent								
Hydrogen	3.5	5.5	3.6	5.3	4.9	5.3	1.7	1.9
Carbon	45.6	70.5	51.6	75.5	78.5	84.0	82.7	95.3
Sulfur	0.6	0.9	0.7	1.0	0.7	0.7	0.4	0.5
Nitrogen	0.8	1.3	0.9	1.3	1.6	1.7	0.7	0.8
Oxygen (Diff)	14.2	21.8	11.5	16.9	7.8	8.3	1.3	1.5
Ash	14.1	--	7.8	--	2.9	--	7.5	--
Higher Heating Value, Btu/lb	7845	12130	8800	12080	13935	14910	12740	14675

2650°F) and residence times ranging up to 0.9 sec. Results, Figure 2, show that: (1) pyrolysis weight loss depends significantly on temperature and time for each coal; (2) and pyrolysis is virtually complete within 0.2 sec. for the lignite, subbituminous, and high volatile bituminous coals. The lignite and subbituminous coal showed, respectively, 12% and 14% volatile matter enhancements over their proximate ASTM volatile matter yields; the high volatile bituminous coal and anthracite, on the other hand, showed no volatile matter enhancements over ASTM results.

Results in Figure 2 were used to derive the pyrolysis kinetic parameters for each coal. The derivation method used by Nsakala et al. (1), Scaroni et al. (3), and Walker et al. (4) was also used here. That is, briefly:

$$C = Co \exp(-kt) \qquad 1)$$

where Co is the maximum obtainable weight loss referred to as ΔW_∞, and C is the remaining pyrolyzable material weight at time t ($C = \Delta W_\infty - \Delta W$, where ΔW is the pyrolysis weight loss at time t), and k is a pyrolysis rate constant. Plugging these values into and manipulating Equation 1 yields

$$\ln\ (1 - \Delta W/\Delta W_\infty) = -kt \qquad 2)$$

Plotting the left hand side of Equation 2 vs. t yields straight lines (Figure 3) from which the k values can be obtained from the slopes of the least squares fits.

Now, the k values can be used in conjunction with a first order Arrhenius law to obtain

$$k = ko \exp(-E/RT) \qquad 3)$$

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

Plotting ln k vs. 1/T yields straight lines (Figure 4) from which the values of ko and E can be obtained from the intercepts and slopes of the least squares fits. Results from this study are given in Table 2.

TABLE 2

KINETIC DATA FOR PYROLYSIS OF 200X400 MESH COALS IN NITROGEN ATMOSPHERE AND 1450-2650°F(1060-1730°K) TEMPERATURE RANGE

FUEL TYPE	E(cal/mole)	ko(sec^{-1})	γ
Texas LigA	7980	50.8	-0.95
Montana subB	4740	13.5	-0.93
Alabama hvAb	7825	32.5	-0.98
Pennsylvania Anthracite	7755	38.7	-0.79

γ = Correlation Coefficient

The low activation energies (4.7-8.0 kcal/mole) encountered here seem to indicate that a physical, rather than a chemical, control mechanism does control the thermal decomposition process. Various investigators (2, 3, 4, 5) employing dilute-phase reactors similar to the present DTFS have also encountered relatively low activation energies (generally less than 20 kcal/mole) for thermal decomposition of coals of various rank.

Combustion Characteristics of Coal Chars

A commercial grind (~70%-200 mesh) of each coal was pyrolyzed in the DTFS in nitrogen atmosphere at 2650°F. The resultant char was subsequently size graded to obtain a 200x400 mesh size fraction. The proximate and pore structural analyses of each coal char is given in Table 3. It is noteworthy that: (1) all the chars are virtually volatile matter-free; and (2) while the BET surface areas follow the

TABLE 3

PROXIMATE AND PORE STRUCTURAL ANALYSES OF 200X400 MESH DTFS-GENERATED CHARS

QUANTITY	TEXAS ligA	MONTANA subB	ALABAMA hvAb	PENN. an.
Proximate, Wt.%.				
Volatile Matter	2.3(3.5)*	2.3(2.8)*	1.5(1.6)*	1.3(1.4)*
Fixed Carbon (Diff)	64.3	80.3	94.6	92.1
Ash	31.2	14.9	3.9	5.9
$S_{BET}, m^2/g, daf$	191.3	89.9	16.4	2.6
$S_{CO2}, m^2/g, daf$	210.9	162.9	16.3	1.6
$\rho_{Hg}, g/cm^3, daf$	0.79	0.69	0.86	1.62
$\rho_{He}, g/cm^3, daf$	1.71	2.01	1.75	1.86
$V_T, cm^3/g$	0.681	0.952	0.591	0.080
Porosity, %	53.8	65.7	50.9	12.9

*Dry-ash-free-basis

trend ligA > subB > hvAb > anthracite, the total open porosity trend is subB > ligA > hvAb > anthracite.

Each char was burned in the DTFS in 0.03 atm. O_2 (in nitrogen balance) at five temperatures (1600, 1900, 2150, 2400, and 2650°F) and residence times ranging up to 0.85 sec. Results show: (1) a strong temperature and time dependence of combustion efficiencies of the ligA, subB, and hvAb chars; and (2) a relatively weak temperature and time dependence of the anthracite char combustion efficiency.

Results in Figure 5 were used to determine for each char the overall rates of carbon removal per unit external surface area (K) assuming that the reaction proceeds by a shrinking core mechanism. The K values were then used in conjunction with classically calculated corresponding diffusional reaction rate coefficients (K_D) to derive the surface reaction rate coefficients (K_S) according to

$$1/K=1/K_D+1/K_S \qquad 4)$$

First order Arrhenius Equations is then applied to the data as follows

$$K_S=A \exp(-E/RT) \qquad 5)$$

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

Plotting ln K_S vs. 1/T yields straight lines (Figure 6) from which the values of A and E can be obtained from the intercepts and slopes of the least squares fits. This calculation procedure is given in detail by Field (6, 7) and Goetz et al. (8).

Two methods were used in this derivation. The first method used the bulk gas temperatures (T_g). The second method entailed calculating particle surface temperatures (T_s) by a heat balance method (7) as follows

$$H_g = H_c + H_r \qquad 6)$$

Where H_g, H_c, and H_r are, respectively, the rate of heat generation per unit area, the rate of heat loss by conduction, and the rate of heat loss by radiation. Differences between T_s and T_g ranged from 20 to 197°F. These differences are reflected in the reaction kinetic parameters given in Table 4. These results depict the importance of specifying the method used in deriving combustion kinetic parameters.

TABLE 4

SENSITIVITY OF COMBUSTION KINETIC PARAMETERS OF VARIOUS 200X400 MESH CHARS TO THE METHOD OF DERIVATION

	E(CAL/MOLE)		A($g/cm^2 sec. O_2 atm.$)	
FUEL TYPE	METHOD 1	METHOD 2	METHOD 1	METHOD 2
Texas Lignite	21050	20350	57	35.6
Montana subB	26730	25400	593	271
Alabama hvAb	23320	22550	80	50
Pennsylvania Anthracite	17900	17840	4.3	3.7

Method 1: Using measured gas temperature (T_g)
Method 2: Using calculated particle surface temperature (T_s)

DTFS to CMHF Scale Up Studies

The combustion and NO_x characteristics of the Alabama hvAb coal were also determined in the CMHF at 500,000 Btu/hr firing rate. The DTFS-derived kinetic parameters of this coal char were used in conjunction with other coal data and an in-house mathematical model to simulate the CMHF combustion processes under various conditions. This mathematical model is essentially based upon the formulation of Field and co-workers (9), whereby the following differential equation is solved

$$du_j/dt = -S_j q_j \qquad 7)$$

where u_j, S_j, and q_j are, respectively, the weight of a particular residual char fraction at time t per unit initial weight of char, the geometric surface area of each particular fraction per unit weight of char and the rate of carbon removal per unit geometric surface area. Equation 7 assumes that the volatile matter is instantaneously released and burned. As such, the pyrolysis process is not modeled. It is noteworthy that the pyrolysis information presented in this paper can be used in developing coal pyrolysis models for incorporation in overall combustion models.

Results obtained from the present simulation study will be explained in detail in the final DOE report. Figure 7 depicts two cases: (1) a base line (no air staging, 20% excess air, commercial fuel grind); and (2) an optimum NO_x reduction (50% primary stage stoichiometry, 20% excess air, fine grind). A very good agreement exists between theoretical and experimental results, indicating a virtually one-to-one DTFS-to-CMHF scale-up. CE is beginning to use this technique for predicting carbon heat losses in utility and industrial boilers. This technique is therefore of practical uses.

CONCLUSIONS

- The apparent activation energies for coal pyrolyses are so low (4.7-8.0 kcal/mole) that they seem to indicate a physical rather than a chemical control of the pyrolysis process.
- The apparent activation energies for coal char combustion are in the 17.9-26.7 kcal/mole range, indicating a very significant temperature dependence of coal char combustion.
- Pore structure plays an important role during char combustion. The higher the total open porosity, generally, the greater is the char reactivity.
- Combustion performance as predicted from DTFS kinetic data and use of a mathematical model agrees very well with combustion performance as directly measured on the CMHF using the same coal.
- The fundamental data presented here have significant practical value as inputs to computer models to predict carbon heat losses.

ACKNOWLEDGEMENTS

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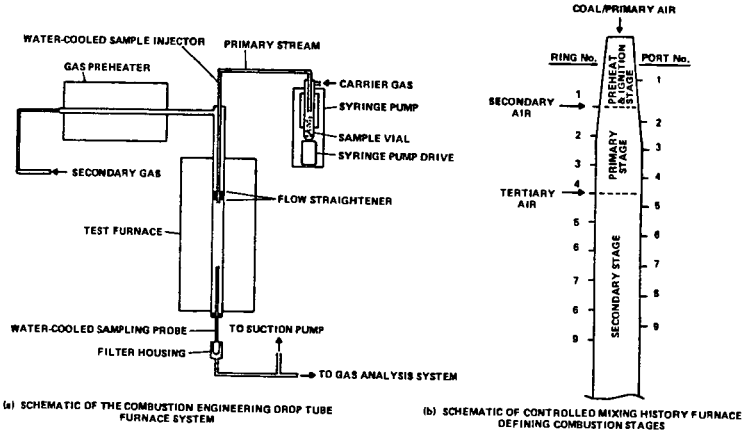

FIGURE 1 PRINCIPAL EXPERIMENTAL EQUIPMENT USED

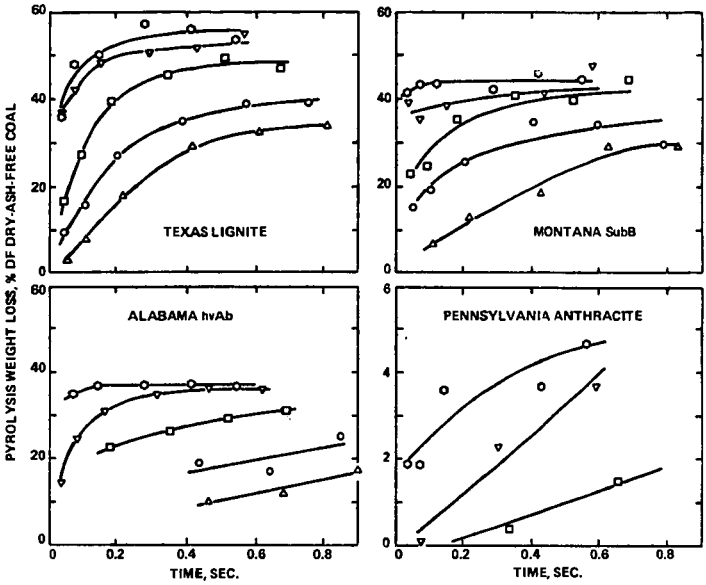

FIGURE 2 DTFS PYROLYSIS WEIGHT LOSSES OF 200 x 400 MESH COALS IN NITROGEN ATMOSPHERE AT VARIOUS TEMPERATURES (△ 1450°F, ○ 1600°F, □ 1900°F, ▽ 2400°F, ◇ 2650°F)

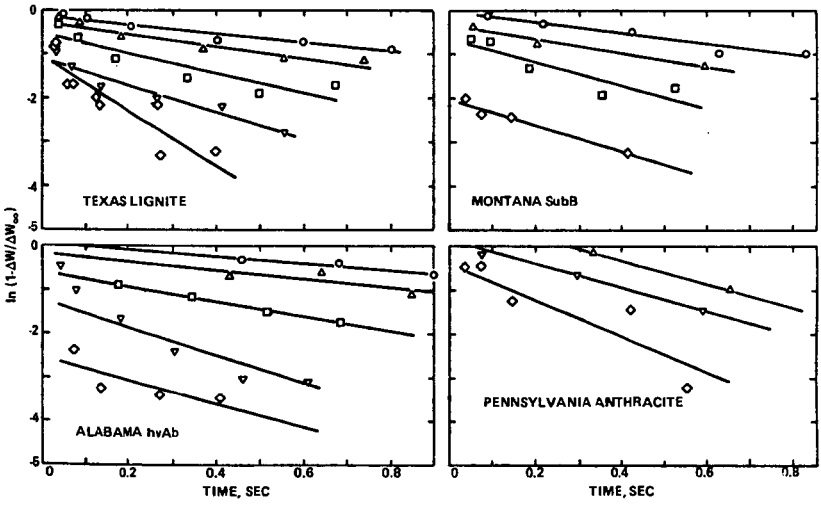

FIGURE 3 VARIATION OF ln (1-ΔW/ΔW$_\infty$) WITH DTFS RESIDENCE TIME FOR PYROLYSIS OF 200 x 400 MESH COALS IN INITROGEN ATMOSPHERE AT VARIOUS TEMPERATURES (○ 1450°F, △ 1600°F, □ 1900°F, ▽ 2000°F, ◇ 2650°F)

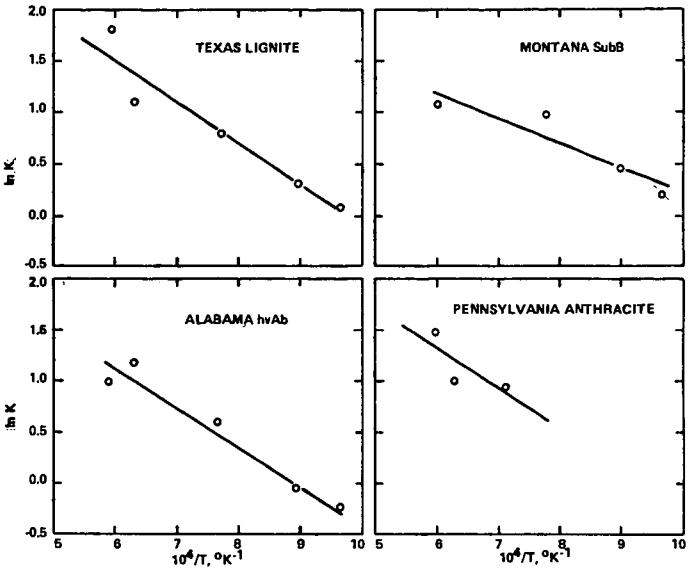

FIGURE 4 ARRHENIUS PLOTS FOR DTFS PYROLYSIS OF VARIOUS 200 x 400 MESH COALS

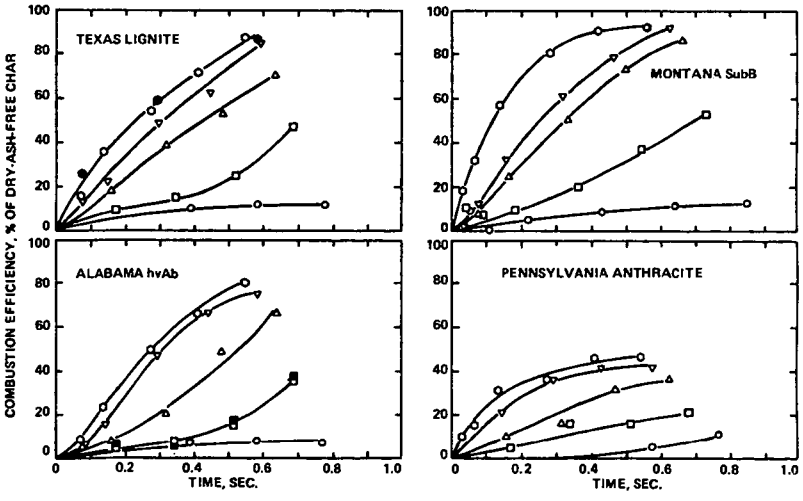

FIGURE 5 DTFS COMBUSTION EFFICIENCIES OF 200 x 400 MESH COAL CHARS IN 3% O_2 / 97% N_2 MEDIUM AT VARIOUS TEMPERATURES (○1600°F,□■1900°F, △ 2150°F, ▽ 2400°F,○●2650°F)

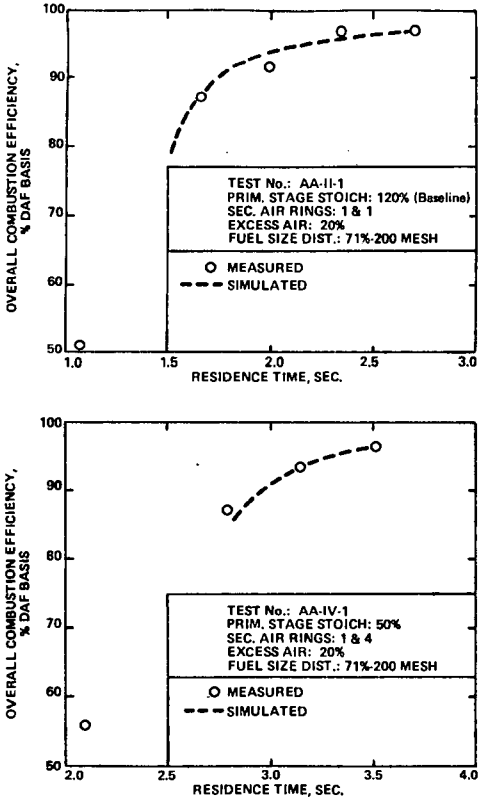

FIGURE 7 SIMULATED CMHF COMBUSTION PERFORMANCE FOR ALABAMA hvAb COAL USING DTFS KINETIC INFORMATION

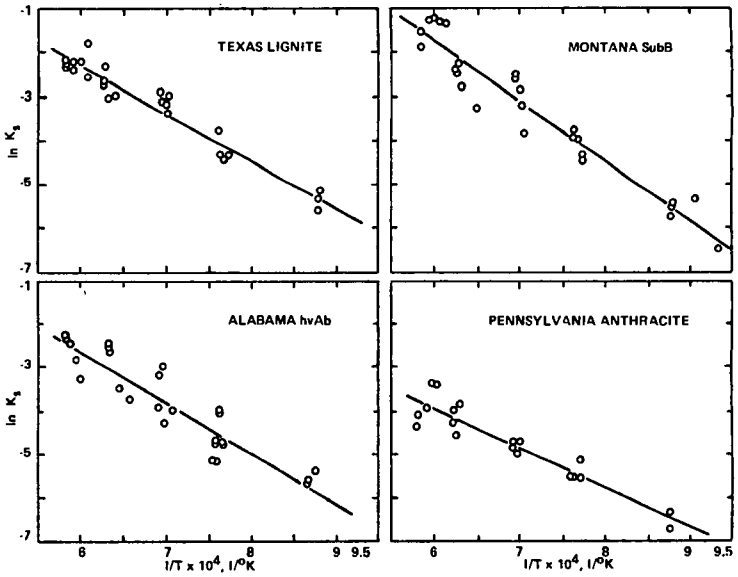

FIGURE 8 ARRHENIUS PLOTS FOR OTFS COMBUSTION OF VARIOUS 200 x 400 MESH COAL CHARS