CHARACTERISTICS OF CHARS PRODUCED BY PYROLYSIS FOLLOWING RAPID HEATING OF PULVERIZED COAL

N. Nsakala, R.H. Essenhigh, and P.L. Walker, Jr.

The Pennsylvania State University, Material Sciences Department, University Park, Pennsylvania 16802.

INTRODUCTION

Due at least partly to the dwindling native supplies of oil and natural gas, major research and development efforts aimed at converting coal into alternative fuels are currently underway in this country. During these various coal conversion processes two main events take place, namely: (i) evolution of the volatiles (pyrolysis) and (ii) gasification of the solid residue.

The understanding of the mechanisms of pyrolysis and gasification of coal is therefore important for achieving optimization of any conversion process. Nevertheless, the complexity of this subject matter is so great that it is always desirable to study pyrolysis separately from gasification. Accordingly, this paper describes experiments in which closely size graded pulverized coal particles were pyrolyzed (in a laminar flow pyrolysis furnace) follwoing a rapid rate of heating. The resulting chars were examined to determine the changes in physical characteristics due to rapid heating.

EXPERIMENTAL

Apparatus The apparatus built for studying pyrolysis following rapid heating of pulverized coal is, in principle, similar to that of Badzioch and Hawksley (1). It was specifically designed to accomplish the following major functions in the given order: (i) feed coal particles into the pyrolysis furnace at a known rate, (ii) raise the temperature of the particles as rapidly as possible (i.e. at a rate approaching 10^4 $^oC/sec$) to the predetermined temperature (i.e. that of the pyrolysis medium), (iii) allow the particles to be pyrolyzed at this temperature for a specific time, (iv) rapidly cool the products to suppress further pyrolysis reactions, and (v) separate solid (i.e. char) from the gaseous products.

The major components of this apparatus (Figure 1) are: a pyrolysis furnace, a gas preheat furnace, a fuel supply system, and a cyclone. All these components have been described in detail elsewhere (2). Following is a summary on the pyrolysis and gas preheat furnaces. The pyrolysis furnace consists of two concentric McDanel MV 30 mullite tubes. The inner, reaction tube is 5.08 cm id, 5.72 cm od, and 58.42 cm long; the outer, "winding" tube is 6.35 cm id, 6.985 cm od, and 50.8 cm long. The winding tube carries two different sizes of Kanthal A-1 heating elements with spacing of about 1.5 windings per centimeter over a total length of 45.72 cm. Six shunt taps were connected to the electrical circuit of the furnace to provide control over the shape of the gas temperature profile in the reaction zone. The space between the winding tube and the furnace housing (which was made of stainless steel sheet), was filled with fibrefrax insulation. The gas preheat furnace (or preheater) also consists of a McDanel MV 30 mullite tube of 1.905 cm id, 2.54 cm od, and 53.43 cm long. Silicon carbide (SiC) bars were used as the heating elements. The preheater was insulated as specified for the pyrolysis furnace. The wall temperatures of the furnace and preheater tubes were measured with chromel/alumel thermocouple beads placed along the tubes. The pyrolysis gas temperature profile in the reaction zone was measured with a small suction pyrometer also using a chromel/alumel thermocouple bead. The temperatures of the furnace and preheater tubes were each controlled by a TEM PRESS temperature controller.

Procedure With the temperature controllers of the pyrolysis and gas preheat furnaces

set at 955 and 965 °C, respectively, and at the total nitrogen gas (pyrolysis medium) flow rate selected, the temperature of nitrogen gas in the reaction zone was 808 °C. An appropriate arrangement of the shunts across the shunt taps rendered this nitrogen gas temperature profile reasonably flat (2). The gas flow in the pyrolysis furnace was laminar with a Reynolds number of 438. Laminar flow helps to keep the pyrolyzing coal particles in a narrow stream down the furnace axis.

Coal from the hopper (Fig. 1) was carried into the pyrolysis furnace through a water-cooled, and insulated feeder probe by a small flow of the primary nitrogen gas stream. This feeder was chosen such that its cold velocity was approximately isokinetic with the hot secondary stream; this has been found to disturb the particle stream the least (1). In the furnace,the particles were collected by an adjustable water-cooled, insulated probe. Adjustment of the probe altered the residence time in the furnace.

The coal particles in the furnace were in a dilute suspension (gas to solid ratio was about 80 to 1) and consequently were heated to the gas temperature at a rate of about 8000 °C/sec. The particles were allowed to pyrolyze at the reaction temperature for a specific time, determined by the collection probe position. To avoid disturbing the flow of gas in the pyrolysis furnace, the suction rate used for aspirating the solid and gasious products into this probe was kept essentially isokinetic with the flow stream in the furnace. Solid and gaseous products were separated in a small cyclone. The following conditions were kept constant throughout the investigation: (i) coal feed rate ≈ 0.5 g/min, (ii) total nitrogen gas flow rate into the pyrolysis furnace = 31.72 ℓ/min [29.74 ℓ/min from the secondary stream and 1.98 ℓ/min from the primary stream], (iii) gas suction rate into the char collector probe = 16.99 ℓ/min, (iv) final pyrolysis temperature ≈ 808 °C, and (v) pressure = normal atmospheric. The pyrolysis of coal particles was determined as a function of the mean particle size by weight (50 - 181 μm), isothermal pyrolysis time (0.018 - 1.025 seconds), and parent coal (three lignites, Table 1).

RESULTS

Weight Loss Coal particles flowing downwards in the pyrolysis furnace went through the heating, isothermal, and cooling periods. Based on the particle cooling rate of 2.72×10^4 °C/sec in the char collection probe, it was concluded that pyrolysis during the cooling period was neglible compared to that occurring at the maximum temperature (2). Experimental results also showed that pyrolysis during the rapid heating period (the duration of which was about 0.095 sec for all the particle sizes studied) was negligible compared to that occurring at the maximum temperature (2). On the basis of these results it was concluded that pyrolysis in the laminar flow furnace occurred under essentially isothermal conditions.

Under the experimental conditions given above, the total residence time of nitrogen gas in the reaction zone of 30.48 cm in length was 0.3 second. Small coal particles were assumed to travel at the same velocity as the gas, implying therefore that their total residence time in the reaction zone was also 0.3 second. Since no appreciable pyrolysis occurred during the rapid heating period, the maximum isothermal pyrolysis time (τ_{iso}) could be obtained from the difference between the total residence time and heating time in the reaction zone, i.e. $\tau_{iso} = 0.3 - 0.095 = 0.205$ second. Assuming that the temperature gradient between the center and the surface of coal particles was negligible, the heating rate of these particles was estimated, on the assumption of linear rise, to be 8000 °C/sec (2).

Due to the geometric configuration of the apparatus (Fig. 1) appreciable amounts of solids missed the char collection probe, rendering a direct materail balance unreliable. Therefore, weight loss (i.e. volatile yield) was determined using ash as a tracer. For each lignite studied, weight loss was expressed as function of mean particle size by weight and isothermal pyrolysis time. Some samples of one lignite (PSOC-246) were recycled into the pyrolysis furnace one or more times giving

a maximum cumulative isothermal pyrolysis time of 1.025 seconds. A subsidiary experiment showed that recycling the samples into the furnace had no measurable effect on the kinetics of the pyrolysis. A similar result was obtained by Anthony et al. (3).

Typical results on weight loss are presented in Figures 2 and 3. The solid/dashed curves in these figures are generated by the empirical Badzioch and Hawksley Equation, using the physical kinetic constants given in Table 2:

$$\Delta W = VM_o \cdot Q \cdot (1 - C)[1 - \exp(-k\tau_{iso})] \qquad 1)$$

where ΔW is the weight loss expressed as a percentage of the original dry-ash-free coal, VM_o is the proximate volatile matter of coal on dry-ash-free basis, Q is the so-called Q-factor, C is the Badzioch and Hawksley empirical constant, k is the reaction rate constant, and τ_{iso} is as defined above.

The results in Figures 2 and 3 show that: (i) weight loss depends on the particle size and pyrolysis time, smaller sizes and longer times giving greater weight loss, (ii) the agreement between the experimental and calculated weight losses is good for times shorter than about 0.2 second, but the disparity becomes great thereafter, and (iii) the extent of weight loss for the two lignites (PSOC-90 and PSOC-246) is comparable; this is perhaps due to the fact that these lignites are quite similar as far as chemical composition goes (Table 1). PSOC-140 exhibited a behavior similar to that of PSOC-90 and PSOC-246, and hence is omitted here.

Characteristics of Coals and Chars The following physical characteristics of both the original coals and the subsequent chars were determined as follows: (i) nitrogen and carbon dioxide specific surface areas calculated from the BET and Dubinin-Polanyi equations (4, 5), using the adsorption data at 77 and 298 ^{o}K, respectively; (ii) apparent and true densities obtained from mercury and helium displacements, assuming that samples were properly degassed (6); and (iii) total open pore volumes and porosities, calculated from mercury and helium densities.

For each lignite studied, the changes in the structural parameters were determined as a function of the mean particle size by weight and isothermal pyrolysis time. Typical results are given in Figures 4 and 5. The figures show that: (i) the specific surface areas increase with increasing pyrolysis time, the increase becoming more appreciable after times greater than about 0.2 second, (ii) the helium density gradually increases with increasing pyrolysis time, whereas the mercury density decreases with time, rapidly at first, then more slowly later; both densities tend to level off after about 0.6 second, and (iii) the total open pore volumes and porosities, which were calculated from the density data, rapidly increase with increasing pyrolysis time, tending to level off after about 0.6 second; this last result is given elsewhere (2).

Correlation Between Weight Loss and Some Physical Structural Parameters The release of volatile matter during pyrolysis results in a development in the internal porosity of the initial material. This is a direct result of one or a combination of the following: (i) opening of previously closed pores, (ii) opening of new pores, and (iii) enlargement of existing and/or newly developed pores. The development of the internal porosity can be followed by measuring the changes in the physical structural parameters given above. This type of information is important because the nature of pore structure of a particular coal determines to a large degree the extent of its reactivity during a given coal conversion process. The results given in Figures 6 and 7 show the development of the pore structure of PSOC-90 and PSOC-246 as a direct result of volatile matter release.

DISCUSSION

Experimental results showing negligible pyrolysis during the rapid heating period are supported by calculations based on first order non-isothermal kinetics.

Details on these calculations are given elsewhere (2). Briefly, assume that the rate of gas (i.e. volatiles) release during coal pyrolysis is (7)

$$dV/dt = k(V_o - V) \qquad 2)$$

where V_o is the volume of gas liberated at infinite time, V is the volume of gas liberated at time t, and $k = k_o \exp(-E/RT)$ where k_o is the frequency factor, E is the activation energy, R is the gas constant, and T is the temperature. Equation 2 was used to estimate the variation of fractional weight loss of volatiles (V/V_o) with time.

The values of k were determined experimentally (2) and that of k_o was estimated to be of the order of 10^{13} sec^{-1} (8). The relation $k = k_o \exp(-E/RT)$ was then used to estimate the values of activation energies (E). For example for k = 2.6 sec^{-1} and T = 1081 ^oK (Table 2), E was found to be $\sim$ 63 kcal/mole. The results from these calculations are given in Figure 8. It is clear from Figure 8 that the fractional weight loss of volatiles during the heating period is negligibly small (< 2%) for all values of E > 55 kcal/mole. If one accepts the value of 10^{13} sec^{-1} for k_o which, in this particular case, gives a value of 63 kcal/mole for E, then the results in Figure 8 are consistent with the experimental finding.

While Badzioch and Hawksley's empirical Equation 1 correlates fairly well with the experimental data at short isothermal pyrolysis times (Figures 2 and 3), it should be treated with some reserve. For example their assumption that C remains a positive constant value at infinite time for weakly swelling coals is contrary to kinetic expectations. It can be shown using the two-component hypothesis that C approaches zero at infinite time (2). Badzioch and Hawksley's value of 0.14 for C was nevetheless used in this investigation (2) since it gave results that closely approximated the expimental results at short times.

CONCLUSIONS

This study gives an insight into the pyrolysis behavior of pulverized coal following a rapid rate of heating in a laminar flow furnace. It is also helpful for the understanding of the reactivities of particular coals with common gasifying gases (e.g. steam, air, oxygen, carbon dioxide, hydrogen). For example, the results show that the change in the specific surface areas becomes appreciable only at total residence times greater than 0.3 second (i.e. at pyrolysis times greater that 0.2 second) at $\sim$ 808 ^oC. This type of information should be helpful in assessing the suitability of particular coals for gasification and/or determining the utilization processes for which they are most suitable.

ACKNOWLEDGEMENTS

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Table 1

Chemical Analyses of Coals

Coal Identification			Chemical Analysis (in weight percent)					
Code No.	Origin or Source Area	ASTM Rank Range	Proximate Analysis+	(dry)	(daf)*	Ultimate Analysis**	(dry)	(daf)*
PSOC-140	Lignite Seam; Darco Mine, Texas	Lignite	Volatile Matter	46.0	50.4	C	65.0	71.7
			Fixed Carbon	45.3	49.6	H	4.7	5.2
			Ash	8.7	-	N	1.1	1.3
						S	0.7	0.7
						O	19.1	21.1
						Ash	9.4	-
PSOC-90	Lower Lignite Seam; Savage Mine, Montana	Lignite	Volatile Matter	39.9	43.5	C	64.8	71.6
			Fixed Carbon	51.7	56.5	H	4.4	4.9
			Ash	8.4	-	N	0.7	0.8
						S	0.3	0.3
						O	20.3	22.4
						Ash	9.5	-
PSOC-246	Coteau Seam; Glen Harold Mine, North Dakota	Lignite	Volatile Matter	43.7	47.5	C	64.1	71.0
			Fixed Carbon	48.3	52.5	H	4.4	4.9
			Ash	8.0	-	N	1.4	1.6
						S	0.6	0.6
						O	19.8	21.9
						Ash	9.7	-

* daf = dry-ash-free; ** Data obtained from the Penn State University Coal Data Base; + Proximate analysis for size graded materials (200x325 mesh for PSOC-140, 200x270 mesh for PSOC-90 and PSOC-246).

Table 2

Reaction Rate Constants for Pyrolysis of Coal

Constant	PSOC-140 200x325 mesh $\bar{x}$ = 50 μm*	PSOC-90 200x270 mesh $\bar{x}$ = 58 μm*	PSOC-246 200x270 mesh $\bar{x}$ = 64 μm*
T_f (°C)	770	808	808
Q	1.9	2.1	1.8
k (sec^{-1})	3.1	2.2	2.6

* $\bar{x}$ = mean particle size by weight

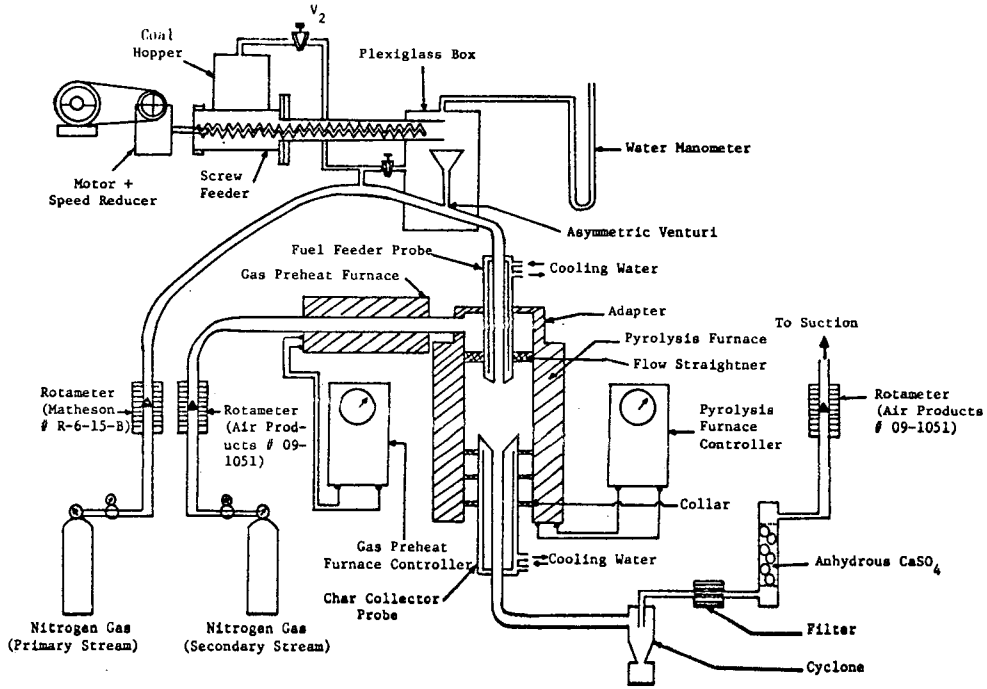

Fig. 1 - Experimental Equipment For Pyrolysis Following Rapid Heating of Pulverized Coal

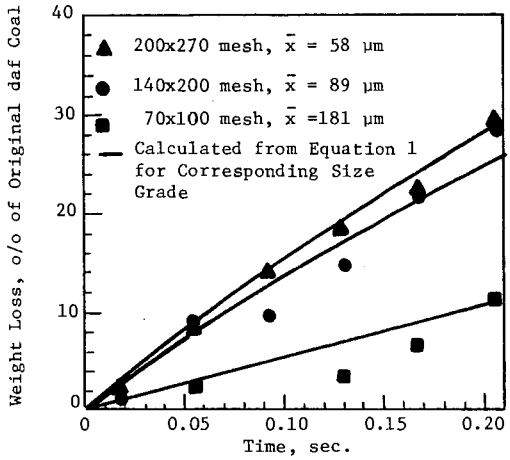

Fig. 2 - Variation of Weight Loss With Isothermal Pyrolysis Time For PSOC-90

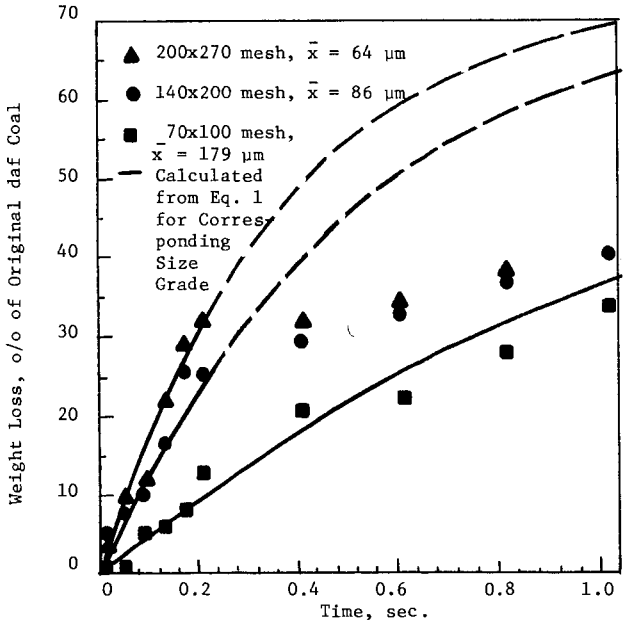

Fig. 3 - Variation of Weight Loss with Isothermal Pyrolysis Time for PSOC-246

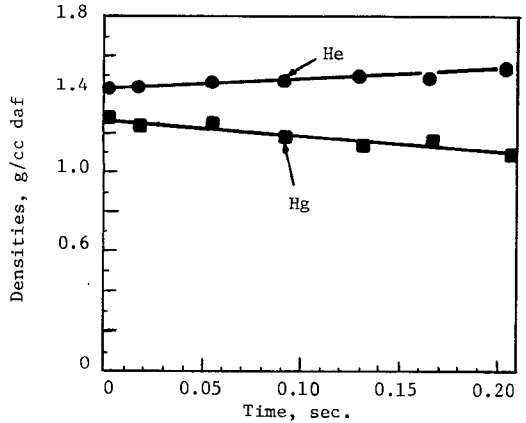

Fig. 4(a) - Variation of Hg and He Densities With Isothermal Pyrolysis Time For PSOC-90

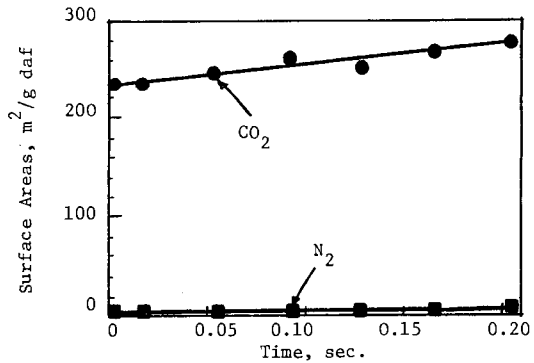

Fig. 4(b) - Variation of N_2 and CO_2 Specific Surface Areas With Isothermal Pyrolysis Time For PSOC-90

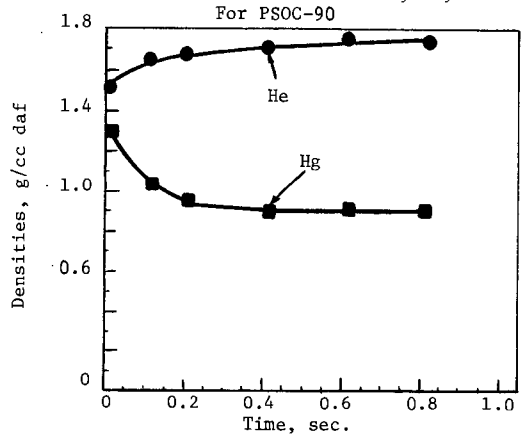

Fig. 5(a) - Variation of Hg and He Densities With Isothermal Pyrolysis Time For PSOC-246

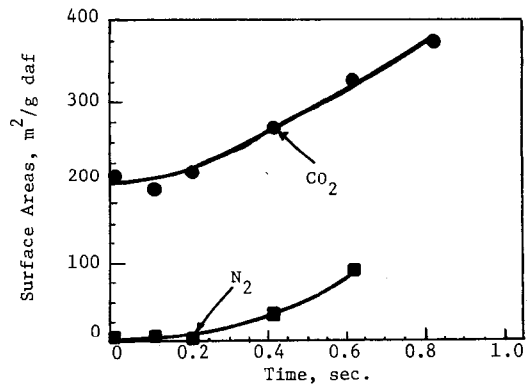

Fig. 5(b) - Variation of N_2 and CO_2 Specific Surface Areas For PSOC-246

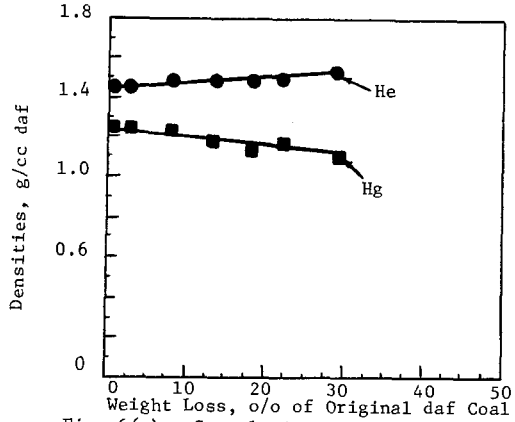

Fig. 6(a) - Correlation Between Weight Loss and Densities for PSOC-90

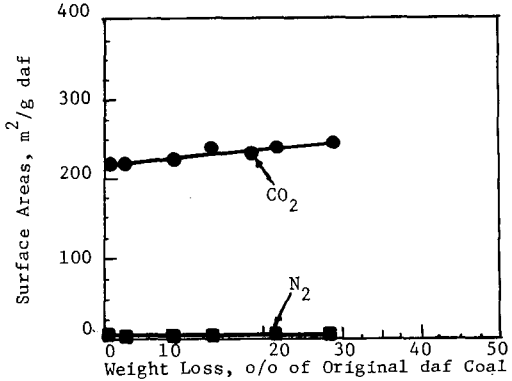

Fig. 6(b) - Correlation Between Weight Loss and Specific Surface Areas for PSOC-90

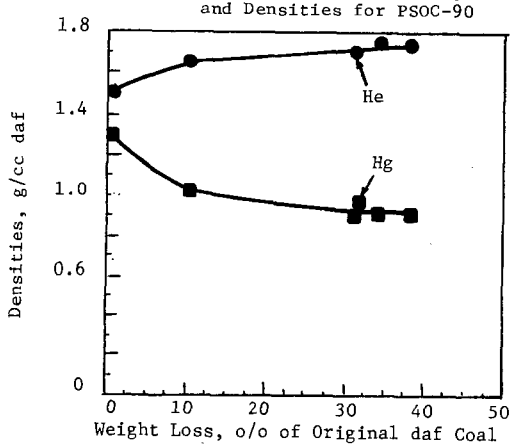

Fig. 7(a) - Correlation Between Weight Loss and Densities for PSOC-246

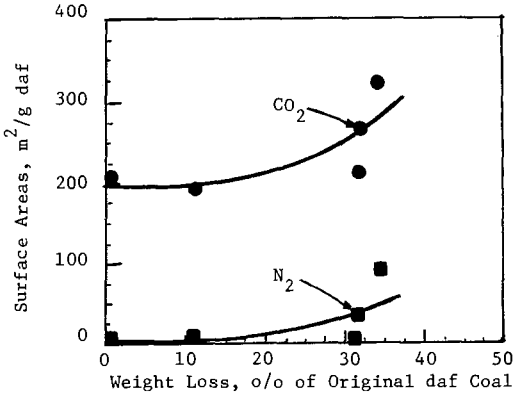

Fig. 7(b) - Correlation Between Weight Loss and Specific Surface Areas for PSOC-246

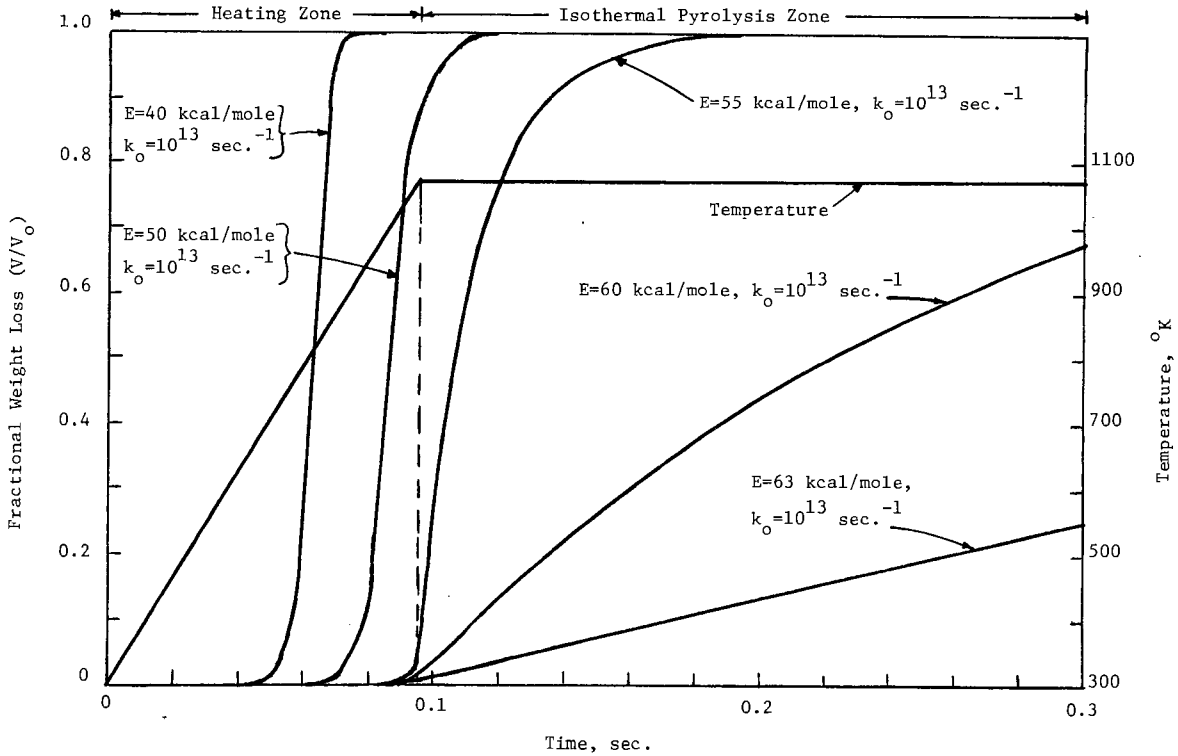

Fig. 8 - Variation of Fractional Weight Loss (V/V_o) of Volatiles With Time
[Calculated From Equations (6.33) & (6.36) of Ref. 2]