

THE COMBINED INFLUENCE OF CHEMICAL AND PHYSICAL FACTORS UPON
COAL PARTICLE TEMPERATURE PROFILES DURING RAPID HEATING PYROLYSIS

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INTRODUCTION

Wide variation in reported kinetic parameters for the pyrolytic decomposition of coal particles in varying experimental conditions causes considerable speculation as to whether coal particle behaviour is capable of generalization. Taking into account the precision and sensitivity of the experimental work performed, with respect to weight loss, the temptation is to attribute the differences in kinetic parameters to the chemical and physical nature of coal itself. The complexity of coal structure is then said to impart to coal a chameleon-like behaviour.

Assuming first order mechanisms for the decomposition of coal, some results indicate pyrolytic decomposition with a singular value for the activation energy and frequency factor, whereas others display behaviour corresponding to distributions of kinetic parameters (1,2). With varying results, apparently related to the unique apparatus and design used in each study, the question naturally arises as to whether sufficient attention is being given to transport processes involved in pyrolytic decomposition.

In particular, it might be asked as to what combination of chemical and physical parameters could influence the internal temperature profile of the coal particles such that the temperature can not be said to be identical to that of the external driving system during the time of initial pyrolysis? In other words, can the initial pyrolytic reactions themselves significantly influence the temperature profile of the particle, and if so, what combination of physical and chemical parameters would be needed to produce or maintain a significant temperature gradient within the particle during initial pyrolysis? If a combination of such capability exists, and the range of parameter values lies within those employed in decomposition studies, then results from studies dealing with coupled transport and reaction principles may aid in the understanding of observed pyrolytic behavior.

PHYSICAL MODEL USED AS THE BASIS OF NUMERICAL CALCULATIONS

In order to numerically determine the effect of chemical and physical parameters upon particle temperature profiles during pyrolysis, a basic composition model of coal itself needs to be postulated. It is desirable to make the model as straightforward and general as possible in order to more clearly ascertain the effects of systematic parametric changes upon results. Keeping the model initially general also allows maximum freedom in refining the model to take into account additional processes which may change the form of the original transport equation.

The basic model proposed here for calculation purposes views coal as consisting of two "fractions." - a pyrolytic fraction and an inert fraction. The "pyrolytic" fraction is taken to mean the thermally active or responsive material present in the coal matrix. The response is assumed to take the form of a first order expression of the Arrhenius type. The pyrolytic fraction exists uniformly throughout the particle. "Inert" is taken to mean the part of the coal matrix which is not subject to thermal decomposition but only to simple heat absorption. Although proposed here for the sake of clarity in calculations, hypotheses of the two-part type are certainly not novices in coal structure studies. Note that "two fraction" here is taken to refer to the inert and pyrolytic parts of the coal matrix to distinguish from similar terms used elsewhere which refer to the thermally responsive material alone (3).

NUMERICAL FORMULATION AND SOLUTION TECHNIQUES

A heat balance for concentric shells within spherical, isotropic particles takes the following form when consideration is given for possible heat absorption by pyrolytic reactions:

$$\dot{q}_{in} - \dot{q}_{out} = \dot{q}_m + \dot{q}_p \quad 1)$$

where m refers to the absorption by unreacting solid matrix and p refers to heat absorption due to the pyrolysis process. The balance leads to the unsteady-state partial differential equation for conductive heat transport of the form:

$$\frac{\partial T}{\partial t} = \left(\frac{k}{\rho C_p}\right) \left[\frac{\partial^2 T}{\partial r^2} + \left(\frac{2}{r}\right) \frac{\partial T}{\partial r} \right] - \beta (\text{Pyrolysis Reaction Rate}) \quad 2)$$

where, k = thermal conductivity, cal/cm-sec-°K

ρ = solid matrix density, g/cc

C_p = solid matrix heat capacity, cal/g-°K

β = $\frac{\text{heat of reaction, cal/g of } P(s)}{k \cdot C_p}$

As noted above, the initial global pyrolytic process is assumed to follow a first order Arrhenius type of expression and, consequently, has the form:

$$\frac{d(P(s))}{dt} = k \cdot P(s) \quad 3)$$

where, $P(s)$ is in g/cc, density of pyrolytic material,

$k = k_0 \times \exp(-E_{act}/R_x T)$

with k_0 in sec⁻¹,

E_{act} in cal/"mole",

$R = 1.99 \frac{\text{cal}}{\text{mole}} \cdot \text{°K}^{-1}$,
 T in °K.

One of several boundary conditions could be chosen for the numerical process:

$$T_{r_o} = T_e = C, C \text{ a constant in } ^\circ K; \quad 4)$$

$$\frac{dT}{dt} r_o = m, m \text{ a linear heating rate in } ^\circ K/\text{sec}; \quad 5)$$

$$\frac{dT}{dt} r_o = H(T_e - T_s), H \text{ a postulated, combined heat transfer coefficient}; \quad 6)$$

$$\frac{dQ}{dt} r_o = F, F \text{ a constant heat flux in } \text{cal}/\text{cm}^2\text{-sec} \quad 7)$$

where "ro" refers to particle surface and "e" refers to the external, driving environment.

The results shown in this study are obtained using the first type of boundary condition noted above. Results for the other type of boundary conditions are to be compared in a subsequent study.

Initial conditions within the particle need also to be specified before the calculation process begins. In this case the initial temperature distribution is assumed to be flat, and at 298°K. A uniform concentration of pyrolytic material, such as 40% of total particle mass and expressed in g/cc, is postulated and assumed to be present uniformly throughout the particle.

Since the reaction rate term of the transport equation contains the temperature variable in an exponential manner, no analytical solution exists and recourse to numerical methods is appropriate. Results were obtained using both explicit and implicit finite difference schemes. Displayed results are from an implicit Crank-Nicholson scheme with iterative solution of the node equations obtained at each time step. Inclusion of a floating time step, whose value is decreased at large heat flux conditions, aids in reducing time required to reach the predetermined tolerance in the iterative process. Integration of the transport equation is accompanied by integration of the first order equation describing the decay of condensed pyrolytic material within the particle matrix.

RESULTS AND DISCUSSION

Given the computational model and scheme above, it remains to determine what parametric value sets, for a given particle size, lead to chemical control of particle decomposition and what value sets lead to heat transport control. Or, given a set of kinetic parameters and reaction conditions, can a change in particle size lead to a transition from chemical control to heat transport control of the initial pyrolytic process?

In chemical control, the process is pictured as taking place uniformly throughout the particle and at, or very near, the stated external driving temperature. In heat transport control, the pyrolytic process is viewed as taking place in a relatively thin-shell, reaction zone. The reaction zone shrinks toward the particle center as the pyrolytic process depletes the concentration of pyrolytic material. Both types of process have been postulated to explain behaviour of coal particles (1,4). Experimental conditions and particle sizes varied considerably, however, and the results shown below indicate that such extreme variation in behaviour is indeed plausible, even for the same coal type.

Ideally the shrinking core process can be described by means of the following limit definitions:

$$\lim_{\Delta r \rightarrow 0} \left[\frac{(P(s))_r - (P(s))_{r + \Delta r}}{\Delta r} \right] = \infty, \text{ and } \lim_{\Delta r \rightarrow 0} \left[\frac{(T_{r + \Delta r}) - T_r}{\Delta r} \right] = \infty \quad (8,9)$$

at the reaction front, corresponding to infinite gradients for the remaining solid pyrolytic material and the temperature of the solid matrix. The isothermal-volumetric, chemical control case might be described by:

$$\lim_{\Delta r \rightarrow 0} \left[\frac{(P(s))_r - (P(s))_{r + \Delta r}}{\Delta r} \right] = 0, \text{ and } \lim_{\Delta r \rightarrow 0} \left[\frac{(T_{r + \Delta r}) - (T_r)}{\Delta r} \right] = 0 \quad (10,11)$$

corresponding to flat concentration and temperature gradients within the particle during the pyrolytic process.

In practice, one must decide in advance upon some finite gradient values which approximate the ideals. It would seem desirable to specify operational gradients for the classification of decomposition type in terms of P_o , concentration of original pyrolytic material present, and r_o , particle radius. In the case of heat transfer control, working gradient indices could be specified as follows:

$$\text{Let, } \Delta(P(s)) = (P(s))_r - (P(s))_{r + \Delta r} = (0.5) P_o$$

within a radial displacement, Δr , of $0.2r_o$. This would give a concentration gradient at the reaction front of $\frac{0.5P_o}{0.2r_o}$, or $\frac{2.5P_o}{r_o}$. An analogous, operational

gradient index could be derived for the temperature denoting heat transfer control. Similar indices can also be formulated for the chemical control case, but in this case radial displacement would be taken as $1.0r_o$. As a result a working table might have the form:

	Heat Transport Control	Chemical Control
Concentration Gradient	$\geq 2.5 \frac{P_o}{r_o}$	$\leq 0.1 \frac{P_o}{r_o}$
Temperature Gradient	$\geq \frac{500^\circ\text{K}}{r_o}$	$\leq \frac{10^\circ\text{K}}{r_o}$

In figures 1, 2, and 3 below are shown the results of the numerical calculations for two different particle sizes held under the same surface boundary conditions and made to decompose by the same set of chemical parameters. Clearly, the 500 μm particle approximates the transport control ideal during the major part of the initial pyrolytic process whereas the 25 μm particle approximates the chemical control limit. Examination of the figures indicate, that, in the case of heat transport control, the reaction process is taking place across a temperature

range significantly different from the stated driving temperature. Figure 4 shows the temperature-time history of the center of the 500 μ m particle. It can be seen that the endothermicity of the pyrolytic process introduces an appreciable time lag in the particle's response to the driving temperature.

Calculations performed with variation of allowed chemical and physical parameters for the same particle size indicate there is a wide range of experimental conditions in which the initial pyrolytic process is non-isothermal and non-uniform within the particle, depending upon the parameters chosen for the thermal decomposition process. These results are being examined more closely in conjunction with various boundary conditions.

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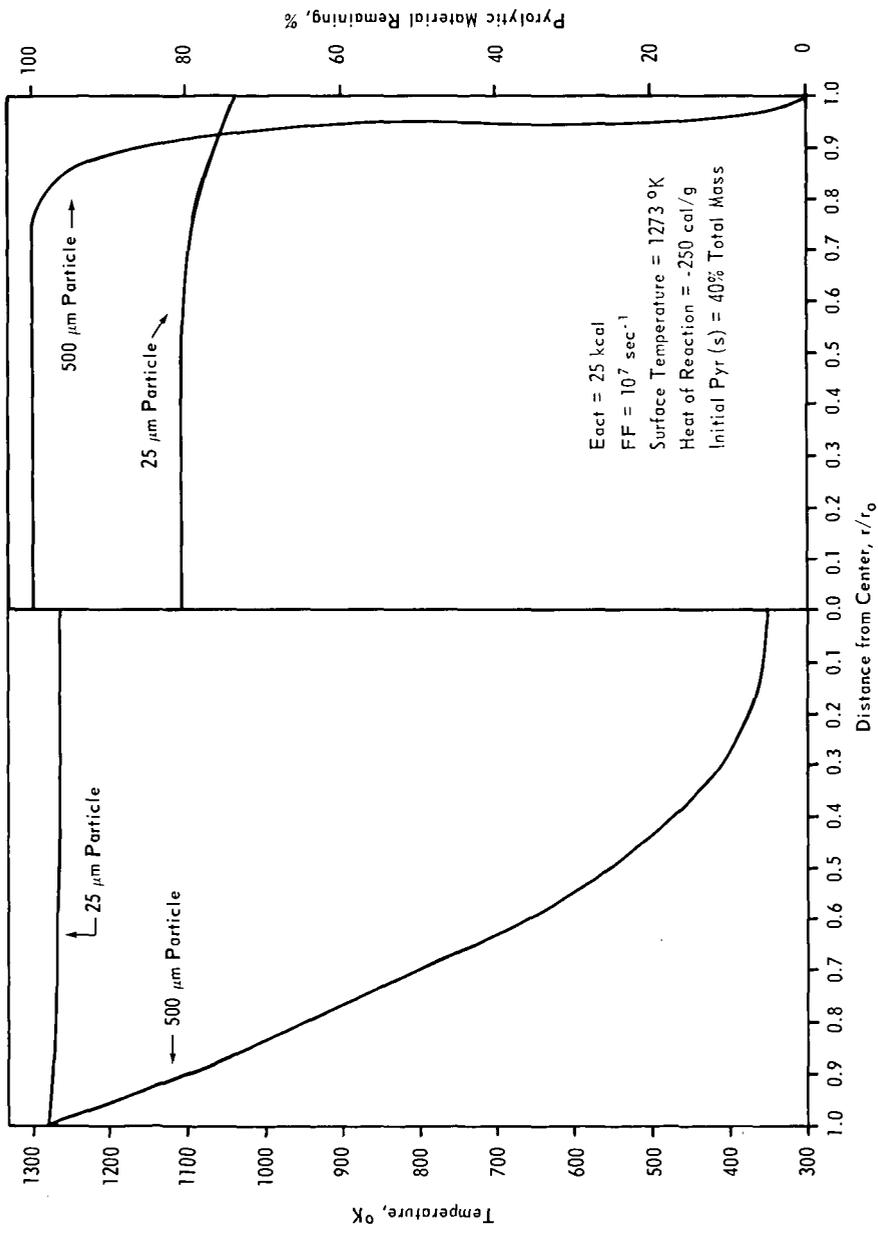


Figure 1. TEMPERATURE AND PYROLYTIC MATERIAL PROFILES AT 25% REACTION COMPLETION

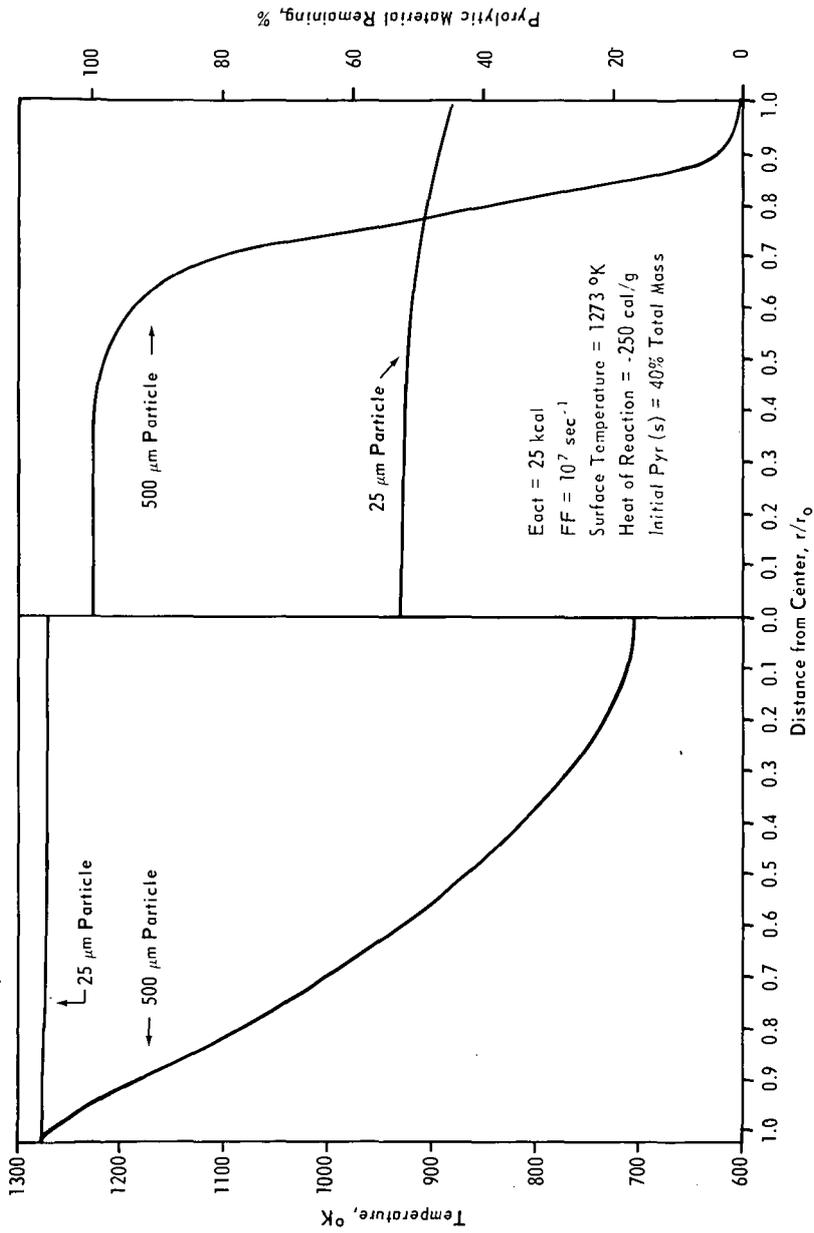


Figure 2. TEMPERATURE AND PYROLYTIC MATERIAL PROFILES AT 50% REACTION COMPLETION

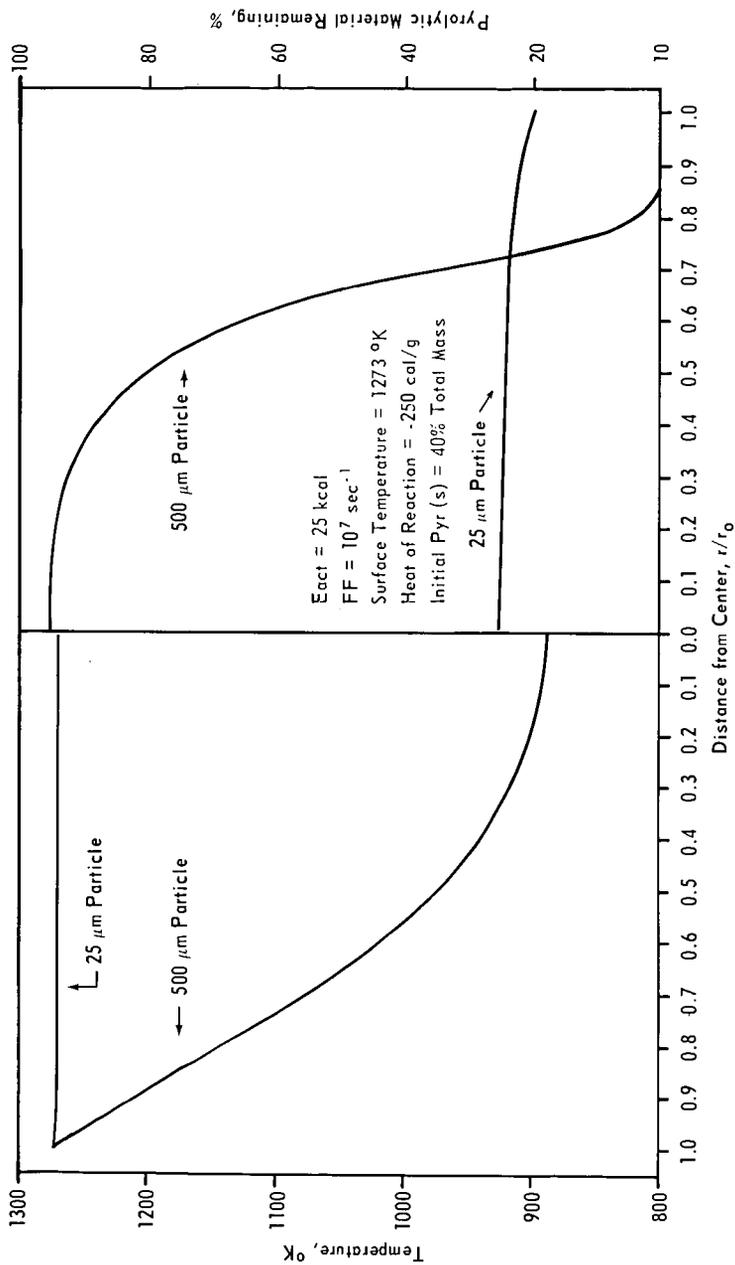


Figure 3. TEMPERATURE AND REMAINING PYROLYTIC MATERIAL PROFILES AT 75% REACTION COMPLETION

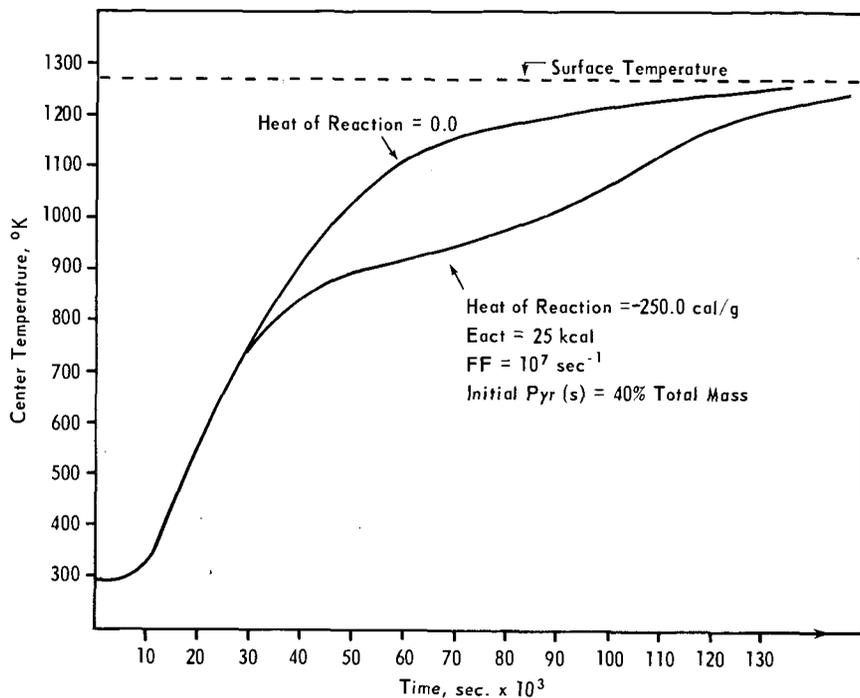


Figure 4. TEMPERATURE RESPONSE OF PARTICLE CENTER (500 μm PARTICLE)