

DIFFUSIONAL CONTRIBUTIONS TO VOLATILE RELEASE IN PYROLYZING COAL PARTICLES

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SUMMARY

Unsteady state calculations of pyrolyzing coal particles under slow and rapid heating have been compared with experimental data for particles in the size range 20 microns to 4 mm; and the comparison has shown, contrary to common assumption, that the diffusional escape is an important factor in determining the pyrolysis times for all particle sizes. Pyrolysis times for particles greater than 500 microns range from 0.1 to 10 sec; and for particles less than 100 microns range from 0.05 to 0.5 sec with an unexpected overlap in times. This overlap is accounted for by assuming that the diffusion coefficients for the escaping volatiles are about 100 times greater (order of 10^{-5} cm²/sec) for the larger particles than for the smaller particles (order of 10^{-8} cm²/sec). This result raises the questions regarding purely kinetic interpretations of pyrolysis rate data for small particles.

1. INTRODUCTION

In this paper we present comparison between calculated and experimental values of pyrolysis times in the particle size range 20 microns to 4 millimeter. The experimental data were taken from the literature [1-17]. The calculations are based on an unsteady state heat transfer model, with escape of volatiles after chemical release inside the particle controlled, we assume, by diffusional or convective escape. The model and a number of other results, notably temperature-time distribution through a particle and profiles of pyrolysis release rates, have been described earlier [18,19]. In this paper, we summarize the elements of the model, the equations and computational procedures; focus here is on the contribution of the diffusional escape.

In past evaluation of pyrolysis studies, it has generally been concluded that escape of pyrolysis products from particles below about 100 microns is so fast as to be effectively "instantaneous". This conclusion, however, is not in fact supported by values of pyrolysis times in the larger data base now available; and, as we shall show in this paper, we have only been able to obtain good agreement between the experimental values and our predictions for the times, and their variations with diameter, when a significant diffusional escape factor is included in the calculations, even for particles as small as 20 microns. This result clearly raises questions regarding the purely kinetic interpretations of pyrolysis rate data for small particles presented in the past.

2. EXPERIMENTAL DATA BASE

A data base consisting of total pyrolysis times under different conditions from the literature was compiled for comparison with our predicted values of times and their variation with particle size. The experimental methods used included (mostly) Drop-tube and or Heated-grid experiments, carried out in inert atmospheres; and from experiments performed in the presence of oxidizing atmospheres (mostly flame experiments). A summary of the data along with the investigators and the nature of experimentation is given in Tables 1 and 2 and in Figure 1.

In the majority of the measurements on captive particles [1] (650 values) coal particles were cemented to silica fibers and burnt between two electrically heated, flat spiral coils. The burning times of the volatiles were determined using a PE

cell, and these times were assumed to be equal to the pyrolysis times. The experiment was carried out for 10 different coals with particle sizes in each case ranging from about 700 microns to 4 millimeters. For each coal type, the pyrolysis time and the particle size could be related by the expression

$$t_v = K_v d^n \quad (1)$$

The values of K_v and n are listed in Table 2; it can be seen that the values of K_v are about 100 c.g.s units, and the index n is about 2. A similar result was obtained by Kallend and Nettleton [2] in a similar experiment, but with the particles mounted on thermocouples. Figure 1 shows that the results of the two experiments are in close agreement. Other data are for particles smaller than 200 microns and have been taken mostly from some of the Drop-tube, Heated-grid, and flame experiments. The pyrolysis times in these cases have been defined as the time period between the 1% and 99% loss by weight of the ultimate yield of Volatile Matter. The data collected are for heating rates ranging from 10^3 to 10^5 deg.K/sec.

Figure 1 shows an unexpected overlap in the pyrolysis times between the larger particles below 100 microns, and the smaller of the captive particles above 700 microns. A continuous curve from a single equation passing approximately through all data sets would be a dog-leg, which is unexpected. Also unexpected is the apparently strong dependence of pyrolysis times on diameter below 100 microns, contrary to the common belief. It is these two aspects of behavior, in particular, that we are addressing in this paper.

3. PHYSICAL MODEL

The model is that of a particle plunged into an enclosure whose temperature is rising. Heat transfer can be jointly by conduction (convection) and by radiation. The calculations show that, in the case of the captive particles, radiation only dominated over conduction for particles greater than 2 millimeters. The behavior is an unsteady state so that temperature non-uniformities can exist through the particles, resulting in variable rates of pyrolysis at different points. Escape of the products is treated phenomenologically as a diffusional process, either actual, and dependent on concentration differences, or effective, where the actual driving force may be pressure differences. One objective here is to establish the actual or apparent diffusion coefficients required to account for the experimental results as targets for further mechanistic analysis using approximate pore and pore-tree models.

4. MATHEMATICAL MODEL

4.1 Governing Equations:

Heat Transfer: For a particle in a thermal enclosure, the dimensionless equations for heat transfer inside and outside the particle, describing the change in temperature, θ , as a function of radial distance, η , and time, τ , is

$$R_c \partial \theta / \partial \tau = (1/\eta^2) \partial [\eta^2 \partial \theta / \partial \eta] / \partial \eta - C \exp(-1/\theta) \delta \quad (2)$$

where the dimensionless groups are defined as

$$\theta = RT/E \quad (3)$$

$$\tau = (\alpha_p / r_o^2) t ; \quad \eta = (r/r_o) \quad (4)$$

$$R_c = 1 \text{ for } \eta < 1; R_c = \alpha_p / \alpha_a \text{ for } \eta > 1.$$

and $\delta = 1$ for $\eta < 1$; $\delta = 0$ for $\eta > 1$

The quantity C is

$$C = \sigma k_o r_o^2 \Delta H (V_o - V) / \lambda_p \quad (5)$$

The initial conditions are (for $\tau = 0$):

for $0 < \eta < 1$, $\theta = 1$ and for $1 < \eta < \infty$, $\theta = \theta_o$
and the boundary conditions are

$$[\partial \theta / \partial \eta]_{\eta=0} = 0 ; [\theta]_{\eta=\infty} = 0 \quad (6)$$

At the particle surface, the temperatures of the particle and the gas are equal, and the heat flux to the particle is the sum of heat flux from the gas and the net radiative heat flux from the enclosure. This shows that the radiation appears as a boundary condition at the particle surface.

Pyrolysis is assumed to be a first-order, one-step reaction; and the heat absorbed in pyrolysis is

$$h = \sigma k_o \exp(-E/RT) (\Delta H) (V_o - V) \quad (7)$$

Mass Transfer: The governing equations for the diffusion of volatiles through the coal matrix are of the same form as the heat transfer equations and can be written as

$$\partial m / \partial t = (1/r^2) \partial (r^2 D_i \partial m / \partial r) / \partial r + \delta m_g \quad (8)$$

where

$$m_g = \sigma k_o \exp(-E/RT) (V_o - V) \quad (9)$$

and

$\delta = 1$, $D_i = D_p$ for $r < r_o$; $\delta = 0$, $D_i = D_a$ for $r > r_o$.
The boundary conditions are

$$\begin{aligned} [\partial m / \partial r]_{r=0} &= 0 \\ [D_i \partial m / \partial r]_{r=r_o} &= [D_a \partial m / \partial r]_{r=r_o} \text{ and } m_{\text{part}} = m_{\text{air}} \\ \partial m / \partial r &= 0 \text{ at } r = \infty. \end{aligned} \quad (10)$$

Mass Loss: At any instant of time, the flow rate of volatiles out of the particle surface is

$$m_t = 4\pi r_o^2 D_p [\partial m / \partial r]_{r=r_o} \quad (11)$$

and the total mass loss over a period t is given by

$$M_t = \int_0^t m_t dt \quad (12)$$

4.2 Solution Procedures Eqn.(2) is transformed into appropriate difference forms for solution using a Central difference approximation on the spatial coordinate, and a backward difference approximation on the time co-ordinate. Equations 2 and 8 can be written in the common dimensionless, difference form

$$\begin{aligned} -\eta_{i-1/2}^2 \theta_{i-1}^{n+1} / \Delta \eta^2 + [R_c \eta_i^2 / \Delta \tau + (\eta_{i+1/2}^2 + \eta_{i-1/2}^2) / \Delta \eta^2] \theta_i^{n+1} - \\ \eta_{i+1/2}^2 \theta_{i+1}^{n+1} / \Delta \eta^2 = \delta C \eta_i^2 \exp(-1/\theta_i^n) + \eta_{i,c}^2 R_c \theta_i^n / \Delta \tau \end{aligned} \quad (13)$$

The relevant difference equations were then solved numerically using a fully implicit backward-difference scheme and iterating at each time step for the non-linear terms.

5. RESULTS

5.1 Pyrolysis Times: Instantaneous Escape of Volatile Matter: The results of earlier attempts to predict pyrolysis times and their variation with particle size with only chemical kinetics in the model and diffusional escape omitted, are presented in Fig. 2, with the experimental data of Fig. 1 included for comparison. These results are obtained by selecting $D_1 = \infty$.

It can be seen in Figure 2 that the predicted curve is sigmoid shaped -- largely under-predicting times for large particles (greater than 2000 microns) and over-predicting times for small particles. The shape of the curve also indicates that pyrolysis times are insensitive to the variation of particle size in the small size range. The predictions are good for a small intermediate range (1000 microns to 2000 microns) but this agreement would now appear to be fortuitous. Increasing the kinetic rate by decreasing the activation energy from 30 kcal/mole to 25 kcal/mole did not improve the predictions. Though the pyrolysis times were reduced, the calculations still over-predicted times for small particles and under-predicted for large particles.

Examination of the calculated temperatures of the small particles during pyrolysis showed that the particles would heat up to a final temperature of about 950 K without significant pyrolysis, and that they then pyrolyzed at constant temperature; it was also found that the temperature gradients within the small particles (less than 500 microns) were insignificant. At constant temperature, pyrolysis is a volumetric process; the pyrolysis time then depends on the temperatures of the particles, and is independent of the particle size. The final temperatures attained by the small particles were about the same. This is the source of the flattening of the predicted curve in the small particle range. Although this supports the common belief that pyrolysis being independent of particle size below 100 microns, it is clearly contrary to the facts. It also emphasizes the inadequacies of the assumptions, and the need to re-examine them (following).

The under-prediction of pyrolysis times for large particles indicated by Fig. 2 suggests that escape time is important for such particles. When this assumption was incorporated in the model equations, it was then found to be applicable to all particle sizes.

5.2 Pyrolysis Times: Diffusion of Pyrolysis Products: With diffusional escape included in the model, the results illustrated in Fig. 3 were obtained. Figure 3 shows 3 diffusional escape times, using diffusion coefficients of 10^{-3} , 10^{-4} , 10^{-5} cm²/sec. To obtain the lines shown, an adjustment to the velocity constant coefficients was necessary; otherwise, the calculated times were high by one or two orders of magnitude. The fit was obtained by reducing the activation energy from 30 to 12 kcal/mole. This is substantially below the values quoted for individual reactions in a multiple pyrolysis model, but it is of the typical magnitude found by fitting a single step to multiple reactions [3].

The fit then shows that the separate trends of the large and the small diameters can be accounted for by attributing the major differences to the different diffusion rates. Second order variations, to the extent that these can be identified, can be attributed to differences in the actual kinetics.

6. DISCUSSION

The principal problem then remaining is to account for the very different diffusion coefficients (by two orders of magnitude) between the "large" and the "small" particles. It is not a matter of oxidizing or non-oxidizing ambient atmospheres since the small particle group include some values obtained in flames. Two possible explanations can be advanced. One factor that can be significant is the extent of swelling. It is now generally agreed that (small) particles heating rapidly swell only marginally or not at all [19]. With the large particles, swelling was very evident -- with the exception of the anthracite -- with measured swelling

factors average 1.5 for all the coals (except for the anthracite) [20]. This explanation, however, does not account for the behavior of the non-swelling anthracite whose large-particle pyrolysis times do not differ significantly from those of the bituminous coal.

If swelling is not responsible for the differences we must postulate, it would seem, some unidentified differences in the mechanical properties of the coals that are solely particle size dependent, and which include anthracite. One such property could be microcracks in all particles greater than about 100 microns so that the VM escape rate in smaller particles can be diffusion-dominated, generating the left-hand data set of Fig. 3. If the VM escape through the microcracks of larger particles was then instantaneous, all pyrolysis times of particles about 100 microns would level off at about 0.5 sec., and the line would become horizontal in the right-hand segment of the graph. If escape through the microcracks is not instantaneous, and is governed by some form of diffusion mechanism, the line to the right would then rise with particle size, as it does in fact.

The same qualitative result is obtained if we assume, alternatively, an array of microcracks at all particle sizes, and with microcrack size diminishing with particle size.

This is all hypothetical at this time but it does indicate the line of thinking that would appear to be necessary at this time to account for the observed results.

7. CONCLUSIONS

1. The experimental data on the variation of pyrolysis times with diameter clearly show influence of particle size over the size range 20 to 4000 microns.
2. The dependence of pyrolysis times on diameter is interpreted at this time as being due to the influence of (diffusional) escape in the pyrolysis mechanism. This is in agreement with conventional views of pyrolysis greater than 100 microns; but it contrary to those views for particles less than 100 microns.
3. A single line or band drawn (empirically) through all the data has a sigmoid (dog-leg) shape that cannot at this time be accounted for, theoretically, by any model that excludes diameter-dependent parameter coefficients.
4. The two extreme segments of the sigmoid curve can be predicted by arbitrarily assuming that values of a diffusion coefficient governing VM escape differ by two orders of magnitude.
5. Mechanistic reasons for any such difference in diffusion coefficients are not clear at this time. Some factors, such as the influence of the composition of the ambient atmosphere (oxidizing or non-oxidizing) can apparently be ruled out. A tentative explanation in terms of microcracks is suggested but this needs to be tested by approximate analytical developments and physical examinations.

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NOMENCLATURE

D	: diffusion coeff. in air (cm^2/s)	D	: diff. coeff. in particle (cm^2/s)
E_a	: activation energy (kcal/mole)	k^p	: rate constant (s^{-1})
k	: preexponential factor (s^{-1})	m	: mass conc. of VM (g/cc)
m_{O_2}	: volatile generation rate ($\text{g}/\text{cm}^3\text{s}$)	q_r	: radiative heat flux ($\text{cal}/\text{cm}^2\text{s}$)

r	: radial distance (cm)	r	: radius of a particle (cm)
R	: gas constant (cal/mole deg.K)	t°	: time (s)
T	: Temperature (deg.K)		
T	: Initial Temperature (deg.K)	V	: volatile yield (%)
V°	: ultimate volatile yield (%)	α	: thermal diffusivity in air
α°	: thermal diffusivity in particle	ΔH°	: heat of reaction (cal/gram)
r°	: dimensionless radial distance	λ_a	: thermal conductivity of air
λ	: thermal conductivity of coal	σ^a	: density of air (gram/cc)
σ°	: density of coal (gram/cc)	τ^a	: dimensionless time
θ°	: dimensionless temperature		

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**Table 1: Pyrolysis Times from Drop-tube (DT)
Heated -grid (HG), and Flame (F) Experiments.**

Investigators	Particle Size (microns)	Heating Rate (deg.K/sec)	Pyrolysis Time (sec)	
Anthony [3]	53-83	10^4	0.1	HG
		3×10^3	0.3	
Nsakala [9]	64	9×10^3	0.2	DT
Niksa [8]	125	10^4	0.5	HG
Kobayashi [6]	37-44	$> 10^4$	0.1	DT
Howard [5]	< 200	10^4	0.2	F
Smoot [13]	21	10^4	0.05	F
Thring [15]	< 100	-	0.1	F
Ubhayakar [16]	< 74	$> 10^5$	0.011	DT
Seeker [12]	80	10^5	0.08	Shock Tube
Peter [10]	1200	200	3.5	-
Desypris [4]	126	-	0.5	HG
	44	-	0.5	
Maloney [7]	62	-	0.17	DT
Solomon [14]	53-74	10^4	0.064	DT
	44-74	3×10^4	0.02	
	44-74	4×10^4	0.023	

Table 2: Values of the volatile combustion constants (K_v and n).

(Source: Ref. 1)

(The errors in K_v are between 2 and 5% , the errors given against n are in percentage.)

COAL	VM% (d.a.f)	K_v (c.g.s units)	n
1. Starllyd	9.9	44.6	$1.82 \pm 4.13\%$
2. Five ft.	14.9	80.0	$2.32 \pm 4.37\%$
3. Two ft. Nine	28.8	120.0	$2.63 \pm 3.33\%$
4. Red Vein	23.3	86.6	$2.19 \pm 4.22\%$
5. Garw	30.6	96.8	$2.06 \pm 2.14\%$
6. Silkstone	41.5	91.6	$2.19 \pm 3.86\%$
7. Winter	39.3	93.6	$2.24 \pm 3.18\%$
8. Cowpen	40.2	91.4	$2.15 \pm 3.28\%$
9. High Hazel	40.7	134.0	$2.28 \pm 2.79\%$
10. Lorraine	40.2	98.9	$2.14 \pm 2.55\%$

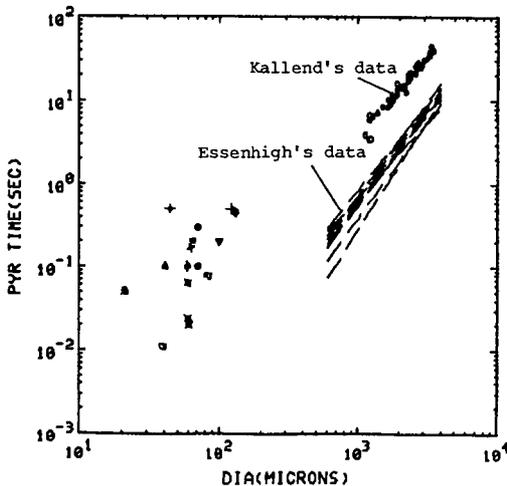


Figure 1. Experimental values of variation of total pyrolysis times with particle size. Values are listed in Tables 1 and 2.

- Anthony. ■ Nsakala. ◆ Niksa. ▼ Howard. ▲ Kobayashi. * Smoot.
- ◆ Thring. ▣ Solomon. * Maloney. + Desypris. ○ Ubhayakar.
- Peters. ▼ Seeker.

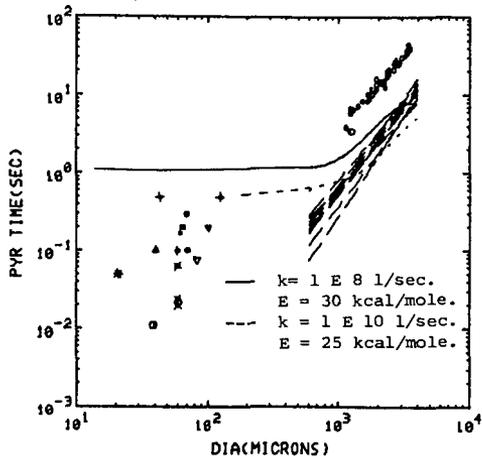


Figure 2. Comparison of the calculated and experimental variation of pyrolysis times with particle size. The calculations do not include the diffusional escape of VM.

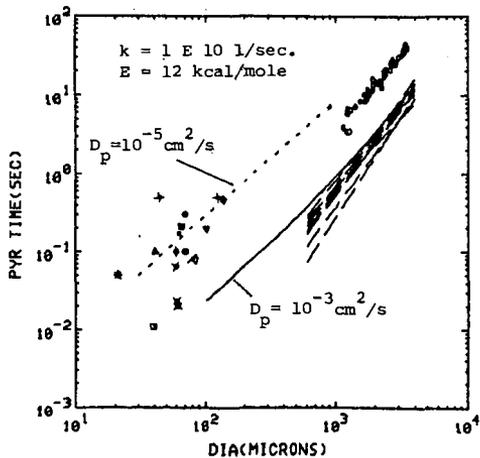


Figure 3. Comparison of calculated and experimental variation of pyrolysis times with particle size. The calculations include the diffusional escape of VM.