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Internal mass transfer considerations during the pyrolysis of an isolated spherical softening coal particle

YUSUF SEZEN
Mechanical Engineering Department, University of Anatolia, Eskisehir, Turkey

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INTRODUCTION

RAPID rate devolatilization is of importance in many of the coal processes in industry. A common technique which is usually called the 'heated wire mesh' technique for pyrolysis studies involves electrically heating a wire mesh containing coal particles at high heating rates. Such a system can be found described elsewhere [1]. Usually, a monolayer of approximately 5–10 mg of finely ground and sieved coal is sandwiched in a folded strip of stainless steel screen suspended horizontally between relatively massive brass electrodes. The mesh is rapidly heated to a desired temperature, held there for a desired time, and rapidly cooled by radiation and convection where the circuit is broken. The heating element and electrodes are enclosed in a vessel which is capable of operating under vacuum or at pressures up to 10 MPa. The external heating unit is comprised of two circuits, the first for rapid heating (in excess of 10 000°C s^{-1}) and the second for maintaining the final temperature about 400–1100°C. The actual time–temperature history of each run is normally recorded by a fast response thermocouple placed with the coal particles between the folds of the screen.

It is apparent that mass transfer limitations can play a significant role in determining the yields of heavy tars during the pyrolysis of coals. The evaporation processes are a key to determining yields of tar so that any model must consider such processes. There are a number of models in the literature, generally classified as softening and non-softening coal models. The interest here is in softening coals so that the models mostly pertain to this category of coals, i.e. softening bituminous coals. Some of the important coal pyrolysis models have been discussed extensively in a recent review [2].

Most of the models in the coal pyrolysis field neglect the importance of mass transfer limitations, while some that take account of mass transfer limitations do so with a pore diffusion model which is inappropriate for softening coals. For this reason, there is a need to develop a new model that includes mass transfer limitations along with diffusional transport of individual species within the coal particle.

The present study develops a semi-analytical model for an isolated coal particle in an inert atmosphere such as helium gas with attention directed at mechanisms of chemical reaction and diffusion. The results from the model and experiments have been compared, and agreement has been found to be excellent.

SOFTENING COAL PYROLYSIS MODEL

The focus is on the problem of pyrolysis of softening bituminous coal particles which are undergoing a devolatilization process and exhibit liquid-like behaviour at elevated temperatures. It can generally be said that these systems have a multicomponent liquid character which is well established experimentally. The model to be reviewed below for coal pyrolysis has some qualitative features. First, it is assumed that thermodynamic equilibrium is always maintained at the coal particle surface. The model at hand is concerned with heavy species, the rate of evaporation of which is so low that heat transfer is not limiting.

Second, some additional formation of evaporable species may occur through reactions that break down the original large molecules to smaller, more volatile species. These degradation fragments are termed 'metaplast'. Once metaplast evaporates from the surface of the coal, it is termed 'tar'. There is no chemical distinction between metaplast and tar, the only distinction is where the material is found, if in the particle metaplast or outside of it, i.e. tar.

Third, the breakdown into lighter species may participate in chemical reactions that form higher molecular weight species. These newly formed higher molecular weight species may be potentially evaporable if they are still of low enough molecular weight, or they may be completely nonvolatile. In the latter case, the product of these reactions of smaller species is 'char'. Char is generally a highly carbonaceous solid which is incapable of undergoing further reactions to release metaplast or tars.

Finally, there is a small amount of material which is released by pyrolysis which may be viewed as consisting of 'fixed' gases, e.g. H_2O, CH_4, H_2, CO_2, etc. These are so far above their boiling points that it makes no sense to count them as part of the metaplast or evaporable fraction within the coal particle. They are treated as instantaneously released from the particle, at the time of their formation. They may amount to 15% by mass of a coal particle. The sum of tar plus fixed gases is what is referred to as 'volatiles'.

The above features are incorporated into the following schematic representation of the model:

Fixed gases
↗
Coal→Metaplast→Diffusion to surface→Tar (Evaporation)
↘
Unreactive
portion of coal→Char (Recombination reactions)

Scheme 1.

MODEL FORMULATION

The transient evaporation of a single isolated multicomponent liquid coal melt into an infinite stagnant gas is considered. The following assumptions have been made.

(1) A spherical liquid-like coal particle of initial radius R_0.

(2) A quiescent liquid phase, i.e. no circulation within the particle. All condensed phase transport is by diffusion, characterized by a diffusivity, D_l, equal for all species.

(3) Ideal solution behaviour within the particle, that is, Raoult's law applies at the liquid–vapour interface for any species i:

$$P_i^0 x_{ia} = P_t y_{ia}. \qquad (1)$$

(4) Thermal diffusion within the particle is rapid so that the particle may be viewed as spatially isothermal.

(5) The particle tracks the gas temperature.

(6) The density of the condensed phase is unchanged by reaction or evaporation loss of components.

NOMENCLATURE

a	instantaneous coal particle radius [μm]
b_h	heating rate [K s^{-1}]
C_l	molar concentration of liquid phase [kmol m^{-3}]
C_v	molar concentration of vapour phase [kmol m^{-3}]
d_0	initial coal particle diameter [μm]
D_l	liquid phase diffusivity [m^2 s^{-1}]
D_v	vapour phase diffusivity [m^2 s^{-1}]
E_0	mean activation energy of the distribution [kJ mol^{-1}]
E_d	destruction activation energy [kJ mol^{-1}]
k_{d0}	pre-exponential in destruction rate constant [s^{-1}]
k_0	pre-exponential factor [s^{-1}]
k_p	production rate constant [s^{-1}]
k_{p0}	pre-exponential in production rate constant [s^{-1}]
m_t	total mass flux of evaporative species [kg m^{-2} s^{-1}]
M_i	molecular weight of species i [kg kmol^{-1}]
n	number of evaporative species
N_i	molar flux of species i [kmol m^{-2} s^{-1}]
P_i	vapour pressure of species i [MPa]
P_t	total pressure in the system [MPa]
r	radial position from the centre of the particle [μm]
R	universal gas constant [J mol^{-1} K^{-1}]
R_0	initial coal particle radius [μm]

t	time [s]
T	temperature [K]
T_p	peak temperature attained during pyrolysis [K]
x_i	mole fraction of species i in the liquid phase
y_i	mole fraction of species i in the vapour phase.

Greek symbols

α_i	mass fraction of metaplast species i at infinite time
ρ	liquid phase density [kg m^{-3}]
σ	standard deviation of activation energy distribution [kJ mol^{-1}]
ϕ_i	net volumetric production rate of species i [kg m^{-3} s^{-1}]
ω_i	mass fraction of species i in liquid phase.

Subscripts

a	at the coal particle surface
i	species i
l	liquid phase
v	vapour phase
0	time zero.

Superscript

0	at the coal particle surface.

(7) The particle is far from its boiling point such that for all species $y_{ia} \ll 1$.

(8) Vapour phase transport is governed by ordinary diffusion, and all vapour species have equal diffusivities, D_v.

(9) Bubble nucleation within the particle is not allowed.

Figure 1 shows one isolated coal particle which is exposed to infinite stagnant inert gas, e.g. helium. There are 'n' species within the particle. Species '$n+1$' is an inert gas surrounding the particle. The vapour phase formulation is actually similar to the one introduced for multicomponent droplets [3]. In the absence of sources or sinks of species in the vapour phase, the species continuity equation may be written as

$$r^2 N_i = a^2 N_{ia} \tag{2}$$

which is subject to the boundary conditions

$$\left.\begin{aligned} y_i &= 0, \quad i = 1,2,\dots,n \\ y_{n+1} &= 1 \end{aligned}\right\} \quad \text{as} \quad r \to \infty \tag{3}$$

and

$$y_{ia} = x_{ia}\frac{P_i^0}{P_t} \quad \text{at} \quad r = a \tag{4}$$

except for the inert gas, for which

$$y_{n+1} = 1 - \sum_{i=1}^{n} y_{ia} \quad \text{at} \quad r = a. \tag{5}$$

Since the flux of inert gas at the coal particle surface is zero, the flux of species i, N_{ia}, at the surface is

$$N_{ia} = -\frac{C_v D_v}{a} y_{ia} \frac{u \ln u}{u-1} \tag{6}$$

where

$$u = \left(1 - \sum_{i=1}^{n} y_{ia}\right)^{-1}. \tag{7}$$

Since the present analysis is concerned only with 'slow' evaporation of heavy species, it is reasonable to assume

$$\sum_{i=1}^{n} y_{ia} \ll 1.$$

Now it is possible to simplify equation (6) as

$$N_{ia} = \frac{C_v D_v}{a(t)} y_{ia}. \tag{8}$$

The advantage of such a simplification is, naturally, that it decouples the vapour phase transport rates of all species.

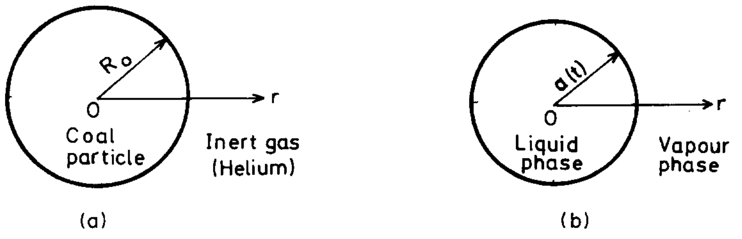

FIG. 1. Geometry and the coordinate system for a spherical liquid-like coal particle in an infinite stagnant gas: (a) $t = 0$, $T = 300$ K; (b) at time t, $T > 650$ K.

The unsteady state conservation law for species i in the liquid phase can be written as

$$\frac{\partial \omega_i}{\partial t} = \frac{D_l}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \omega_i}{\partial r}\right) + \left(\frac{r}{a}\right)\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right)\frac{\partial \omega_i}{\partial r} + \frac{\phi_i}{\rho}. \tag{9}$$

It is assumed that the coal particle composition is initially uniform, i.e.

$$\omega_i = \omega_{i0} \quad \text{at} \quad t = 0 \tag{10}$$

and the boundary conditions are

$$\frac{\partial \omega_i}{\partial r} = 0 \quad \text{at} \quad r = 0 \tag{11}$$

$$\frac{\partial \omega_i}{\partial r} + h(t)\omega_i = 0 \quad \text{at} \quad r = a \tag{12}$$

where

$$h(t) = \left(\frac{D_v}{D_l}\right)\left(\frac{P_i^0}{P_t}\right)\left(\frac{C_v}{C_l}\right)\left(\frac{1}{R_0}\right) + \frac{m_t}{\rho D_l}. \tag{13}$$

Note that the time dependence of $h(t)$ comes from the time dependence of the total mass from the particle, m_t, and the temperature dependence of D_v, P_i^0, and C_v. From ref. [4], the vapour pressure of the evaporative species i, P_i^0, can be estimated with

$$P_i^0(0.1\ \text{MPa}) = 5756 \exp\left[-255\frac{M_i^{0.586}}{T}\right] \tag{14}$$

where M_i is the molecular weight of species i and T is in kelvin. The vapour phase diffusivity, D_v, which is equal for all species i can be effectively modelled by [5]

$$D_v(\text{cm}^2\ \text{s}^{-1}) = 0.1(T/273)^{1.5}(1/P_t) \tag{15}$$

where T is in kelvin and P_t is in atm.

The chemical reaction term, ϕ_i, in equation (9) always shows a considerable variability due to the fact that it is dependent on material characteristics and the molecular structure of the particle in nature. In the case of coal pyrolysis, both a source and a sink are required. The evaporable species are formed, on a time scale comparable to evaporation, by depolymerization of the parent coal. In this case, coal decomposes into smaller molecular units termed 'metaplast' which is formed via a set of independent parallel first-order decomposition reactions represented by a Gaussian distribution of activation energies around a mean of 126 kJ mol^{-1} which is found to give better fit to the experimental data. Once formed, these metaplast species may evaporate to give tar or may repolymerize to promote a bigger molecule. The statistical average of the Gaussian distributed activation energies of species for formation has been used to determine the chemical rate for conversion of coal to so-called metaplast. The evaporable species are lost by reattachment to the crosslinked, non-volatile matrix, which eventually is observed as product 'char'. The same procedure is applied to determine the rate for gas formation.

The formation of species i is assumed to be controlled by a unimolecular decomposition of the parent coal structure. The volumetric production or mass formation rate of species i, ϕ_{pi}, is given by

$$\phi_{pi} = \alpha_i\left(\frac{R_0}{a}\right)^3 \rho k_p. \tag{16}$$

The loss of species i by reaction has been observed in non-isothermal experiments to occur over a narrower range of temperature than the formation of species i. The implication is that the loss process is characterized by a narrower distribution of activation energies. Though it is difficult to predict the form of the reaction rate term a priori, here the loss process is assumed characterizable by a single reaction which is first order in the mass of species i as follows:

$$\phi_{di} = k_{d0}\exp\left(-\frac{E_d}{RT}\right)\rho\omega_i. \tag{17}$$

Thus the net production rate of species i is

$$\phi_i = \phi_{pi} - \phi_{di}. \tag{18}$$

The overall reaction term is now explored. The rate constant or the rate of formation of species i, k_p, is governed by a Gaussian distributed activation energy model [1]. The rate constant, k_p, is given as follows [6]:

$$k_p = k_{p0}\exp\left(\frac{\sigma^2}{2R^2T^2} - \frac{E_0}{RT}\right)\frac{1}{2}\operatorname{erfc}(u_c) \quad \text{if} \quad u_c > 0 \tag{19}$$

or

$$k_p = k_{p0}\exp\left(\frac{\sigma^2}{2R^2T^2} - \frac{E_0}{RT}\right) \times \left(1 - \frac{1}{2}\operatorname{erfc}|u_c|\right) \quad \text{if} \quad u_c < 0 \tag{20}$$

where

$$u_c = \frac{E_c - E_0}{\sqrt{2}\sigma} + \frac{\sigma}{\sqrt{2}RT}. \tag{21}$$

The critical activation energy, E_c, is given by the formula [6]

$$E_c = RT\left(1 - \frac{\ln\ln A}{1 + \ln A}\right)\ln A \quad \text{where} \quad A = \frac{k_0 T}{b_h}. \tag{22}$$

Once the critical activation energy, E_c, is found then the rate constant, k_p, is calculable.

Since the transport equations for the vapour phase can be solved for the mass flux of individual species from the particle, then these mass fluxes of species can be related to the liquid phase by Raoult's law in making mass balance to produce a set of partial differential equations, namely equation (9). The number of PDEs, or the number of species, n, within the coal particle is taken to be 15 which is found to be reasonable for an adequate representation of all molecular weight classes. Then the molecular weight of individual species in the coal particle is given by

$$M_i = 100 + 200(i-1), \quad i = 1, 2, \ldots, 15. \tag{23}$$

Information on mass concentrations is needed to calculate metaplast formed and tar yield during the pyrolysis. To obtain a solution for the mass concentration of species i, ω_i, a Green's function method can be used. A similar approach has also been employed previously for the combustion of fuel droplets [7–9]. Now the mass concentration profiles for a small time interval, dt, can be obtained as follows [10]:

$$\frac{\omega_i(r,t)}{\omega_{i0}} = \sum_{m=1}^{\infty}\exp\left[-\frac{D_l\,\mathrm{d}t}{a^2}b_m^2\right] \times 2\left[\frac{b_m}{b_m - \sin b_m\cos b_m}\right]\frac{\sin(b_m x)}{x}\int_0^1 x'\sin(b_m x') \times \left[\frac{\omega_i(x',t_0)}{\omega_{i0}} + \frac{\mathrm{d}t}{\omega_{i0}}\Phi_i(x',t_0)\right]\mathrm{d}x' \tag{24}$$

where b_m's are the roots of the following equation:

$$b_m\cos b_m + (ah-1)\sin b_m = 0 \tag{25}$$

and $x = r/a$

$$\Phi_i = \frac{\phi_i}{\rho} + \frac{r}{a}\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right)\frac{\partial \omega_i}{\partial r}. \tag{26}$$

The mass concentration of species i, $\omega_i(r,t)$, can be calculated numerically, if the previous values of mass concentration of species i, $\omega_i(r,t_0)$, and the term $\Phi_i(r,t_0)$ are initially known. The new values of $\omega_i(r,t)$ and $\Phi_i(r,t)$ become the initial conditions for the next successive calculation.

RESULTS AND DISCUSSION

The present model developed for an isolated coal particle is tested against one set of experimental data [4]. One of the purposes of modelling is to develop a semi-analytical model that accurately predicts the experimental coal pyrolysis results, or at least improves our understanding of the mechanism of coal pyrolysis phenomena.

A limited amount of comparison of the model against experimental data is performed. It should be borne in mind that the model does not yet account for nearly all of the phenomena known to occur during pyrolysis. For example, there is no consideration of development of fluidity, of bubbling or of cenosphere formation, of pore development in the char, or a host of other phenomena, including many details of chemical alteration of the coal structure.

The key adjustable parameter in the transport model is the diffusion coefficient within the particle. The value of D_l was felt to be bracketed by the range 10^{-5}–10^{-9} cm^2 s^{-1}. This was therefore the only range explored in this work. Early on, it rapidly became apparent that regardless of any other parameter values, only values of $D_l > 10^{-7}$ cm^2 s^{-1} would permit reasonable tar yields. Whether such high diffusion coefficients are realistic (at 600–1000 K the real temperature range of relevance) may be open to much debate. Measurements of diffusion coefficients in softening coals are really difficult. Even if ultimately the true diffusion coefficients turn out to be somewhat lower than this range, it may be the case that an 'effective' diffusion coefficient reflecting enhanced transport via bubbles, may be in this range.

The comparison with experiments employed here is not a way of obtaining reliable values of diffusivity, as desirable as this would be. This is because many of the reaction rate parameters are unknown although they can be bounded by comparison with 'model' systems, and the vapour pressures of most of the heavy evaporating species are also unknown although we attempt to bound these based on the few experimental data available.

Another key parameter of the model is the total yield of metaplast, i.e. the fraction of coal that can be broken down into mobile, extractable species. The experimental data with which the model will be compared suggested that at least 30% of the coal could be so broken down (based on tar yields at vacuum conditions). Recent measurements at MIT [11] have, however, suggested that up to 60% by mass of a similar coal may be extractable into a good solvent (pyridine) if the coal is quenched quickly enough from reactive conditions. Hence, this parameter was generally bounded by values in the range from about 25 to 60% of the raw coal.

The kinetics of metaplast formation was modeled by a distributed activation energy model. This reflects the experimental observations that this material is formed over a broad range of temperatures. This in turn reflects a wide range of cleavable bonds in the coal.The choice of the pre-exponential factors for the model is, in fact, a priori. It can be calculated from transition state theory [12] and is of the order of 10^{13} s^{-1}. It should however be noted that the researchers at MIT [1] estimated lower pre-exponential factors (of the order of 10^9 s^{-1}) from experimental data. But they also calculated the pre-exponential factor by fitting the experimental data, and found it to be higher than 10^{13} s^{-1}. Thus the pre-exponentials for the present model were independently set to 10^{13} s^{-1} for all reactions. This meant that the truly adjustable parameters were the mean activation energy for metaplast formation, E_0, and the standard deviation of a Gaussian distributed set of activation energies, σ.

A comparison between the predicted tar yield from the present theory and the experimental tar yield is represented in Fig. 2. As mentioned previously, the coal was pyrolized with a heating rate of 1000 K s^{-1} to the indicated peak temperature under an atmosphere of helium, and immediately afterwards cooled to ambient temperature (300 K) with a heating rate of 200 K s^{-1}. Therefore, it is important that one realize that each data point represents a complete heating and cooling cycle. As can be seen in this figure, the agreement between theory and experiment is quite good with the parameter set of destruction activation energy $E_d = 252$ kJ mol^{-1}, species mean activation energy $E_0 = 147$ kJ mol^{-1} and the diffusion coefficient $D_l = 5 \times 10^{-6}$ cm^2 s^{-1}. However, the model predicts low tar yields for the diffusion coefficient of $D_l = 10^{-7}$ cm^2 s^{-1} at atmospheric pressure. This is not surprising because low D_l runs, i.e. as low as 10^{-7} cm^2 s^{-1} at atmospheric pressure, may neglect the phenomenon of 'internal nucleation'.

The model presented here does not take into account the bubbling phenomena but it is alert on the significance of the phenomena. If the temperature within the particle is high enough to raise the vapour pressure of trapped light species to their boiling points, then internal nucleation and bubbling may occur within the particle. It should, however, be noted that a vapour pressure internal to the particle that exceeds the ambient pressure does not necessarily assure nucleation of bubbles. The theoretical pressure within the particle has been checked with the actual pressure in each time step in the computer program and it has been found that the bubbling may occur in the particle where the model assumption of no bubbling may break down based on a calculation of internal vapour pressures. This occurs at temperatures

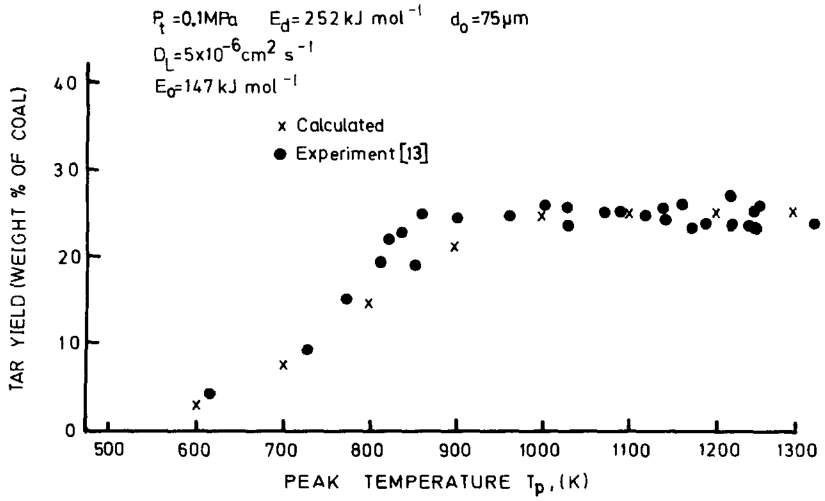

FIG. 2. Tar yield vs temperature.

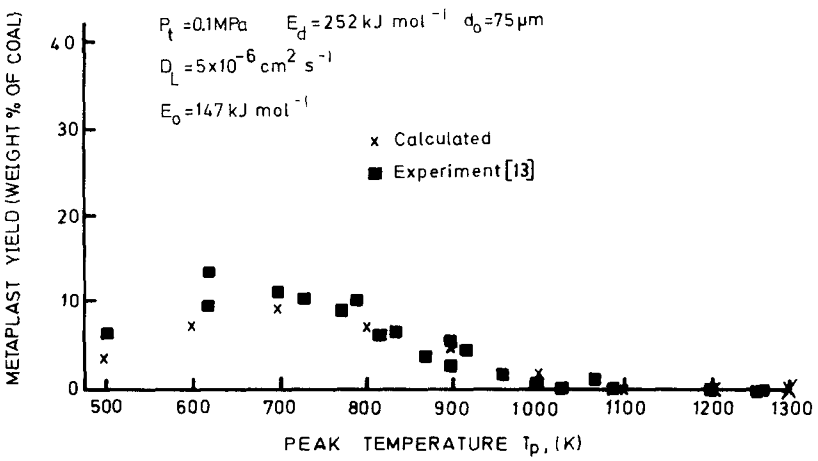

FIG. 3. Metaplast yield vs temperature.

of approximately 800 K for atmospheric conditions. No bubbling occurs at higher pressures such as 7 MPa.

The experimental metaplast yield is represented in Fig. 3 along with the predicted metaplast yield as a function of peak temperature. The term 'extract' on the figure may be viewed as 'metaplast' which has not yet escaped the particle by either evaporation or some other mechanism. Metaplast which is considered to be the source of the evaporative species continues to form up to temperatures of around 650 K. Above temperatures of 1000 K, metaplast concentration is generally very low and most of the time it is almost zero. Since a minute amount of metaplast is observed above the peak temperature of 1000 K, this in turn implies that no additional tar yield is expected after this temperature which is consistent with the tar yield in Fig. 2. As seen in Fig. 3, the prediction of the metaplast yield is reasonably matched to the experimental data for a given parameter set. It is noteworthy to mention that the prediction of where the metaplast formation ends is very good. This shows the power of using Gaussian distributed activation energies for the metaplast species because it permits one to adjust the width of the activation energies to be used for different species rather than using the same activation energy for all of them.

Figure 4 illustrates both experimental and predicted values of total weight loss from the coal particle as a function of peak temperature. At lower temperatures the gas yield is pretty low but at higher temperatures (say in the range 650–1000 K) it increases rapidly and relaxes above 1000 K. The agreement between the theory and experiment is excellent.

CONCLUDING REMARKS

In the present model, two empirical correlations concerning species vapour pressure, P_i^0, and vapour phase diffusion coefficient, D_v, play significant roles during the process. The liquid phase diffusion coefficient, D_l, is also important but there is no known correlation for this coefficient. Suggested values have been used in this study. Therefore, the present modelling effort is somewhat sensitive to the correlations, particularly that for vapour pressure and the determination of these liquid and vapour phase diffusion coefficients from experimental observations. Furthermore, because of the mathematical form of the empirical correlations, it is difficult to propose a mathematically convenient problem with the appropriate boundary conditions.

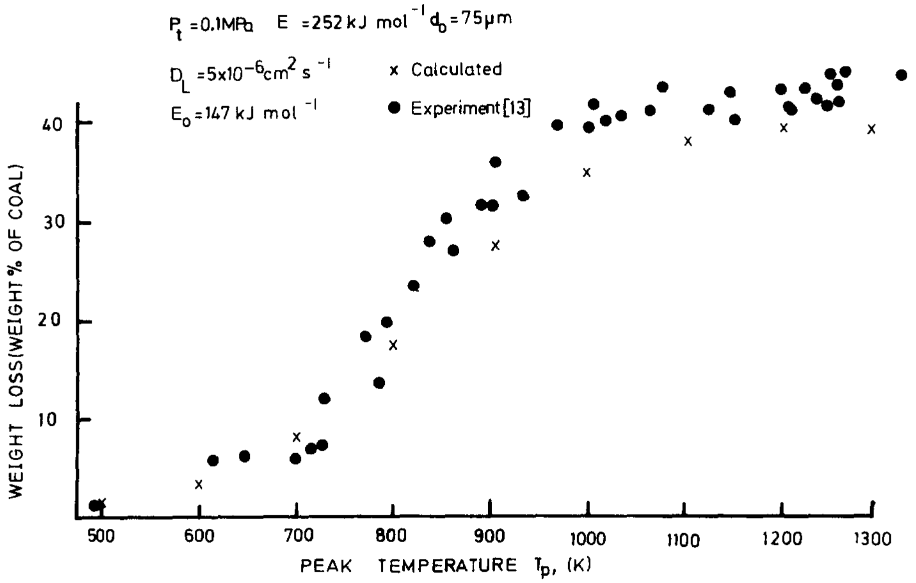

FIG. 4. Weight loss vs temperature.

In the limit of high mass transfer rates from the surface of the particle, there is set up a situation in which mass transfer is controlled through a thin 'boundary layer' of steep concentration gradients very near the particle surface.

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A note on the inverse problem of radial diffusion in a semi-infinite porous medium

G. F. Jones
Department of Mechanical Engineering, Villanova University, Villanova, PA 19085, U.S.A.

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INTRODUCTION

Contaminant transport in subsurface repositories and related systems is an issue of growing concern [1, 2]. The interest arises in part because of the need to assess the probability of release of contaminants and also to determine their rate of transport.

Vapors from a concentrated source are transported by molecular diffusion if the source pressure and the pore pressure of the surrounding porous medium are equal. Otherwise, pressure-driven flow contributes to the rate of transport. In the former case, only the porosity and mass diffusivity affect the rate of transport. Porosity is accurately determined from laboratory tests performed on samples of the medium. However, accurate estimates of diffusivity are found only through *in situ* methods for at least two reasons. First, preferential paths for diffusion that exist in the unstressed medium may not exist under *in situ* conditions where stresses can be large. Secondly, it is very difficult to replicate *in situ* moisture conditions in the laboratory.

Recent studies to determine thermal and mass transport molecular properties have focused on laboratory tests and theoretical analyses rather than *in situ* tests to calculate properties from global measurements [3–6]. These include laboratory tests to determine thermal diffusivity of gases in fibrous insulation materials [3], and mass diffusion coefficients for binary gas flow in closed-cell insulation systems [4]. One type of *in situ* test to determine effective mass diffusivity in homogeneous porous media consists of isolating an initially known concentration of gas in a well installed in the medium. The time-history of gas concentration is monitored and the data used in an appropriate model of mass diffusion from which mass diffusivity is estimated.

The solution for gas diffusion in a semi-infinite porous medium, with particular attention to solving the inverse problem for *in situ* effective mass diffusivity, is the focus of this note.

FORMULATION

An initially known concentration of gas is isolated in a circular well of radius R in a semi-infinite, isotropic, homogeneous porous medium of uniform porosity, ϕ, and effective mass diffusivity, D_{eff}. As time progresses, concentration of the isolated gas decreases because of diffusion of mass into the medium. We wish to determine the effective mass diffusivity for the medium of known porosity by measuring the time-history of this concentration.

If the length of the isolated gas is much larger than the penetration depth of the diffused mass, the diffusion process can be approximated as only radial. The diffusion equation for the scaled concentration, C (ratio of molar concentration and initial concentration of the isolated gas), in the porous medium is