APPENDIX A

TRANSPORT OF VOLATILE PRODUCTS IN POROUS COALS

E. M. Suuberg Division of Engineering Brown University Providence, RI 02912

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The transport of volatile products through coal is an important aspect of the coal pyrolysis process for a variety of reasons. Transport limitations affect the residence times of various primary decomposition products within the hot, reactive environment of the particle. This can affect the composition of the spectrum of products of pyrolysis, since increased residence time can promote both retrograde char-forming reactions and cracking or gasification reactions involving primary decomposition products.



As a result of the competitive transport and secondary reaction processes, the observed spectrum of products is a mixture of primary and secondary products.

The morphology of the nonvolatile product char is also potentially influenced by transport limitations. If the particle of coal is of the softening type, then retardation of gas escape can lead to pressure buildup in the interior of the particle, which in turn leads to swelling and hollow cenosphere formation. If the coal is of a non-swelling type, the build-up of pressure in pores may be sufficient to fracture the particle. The role of mass transfer in affecting pyrolysis behavior, and various models available for describing the mass transfer processes have been recently reviewed (1).

This report is concerned principally with the modeling of mass transfer in particles that do not soften during pyrolysis. Several models have been advanced in recent years to describe the process but none can be termed entirely satisfactory. From the perspective of understanding the basic physics of the process, several significant aspects need improvement. This stems from what is an

imperfect understanding of the nature of porosity in coals and coal char. Attempts at modeling the structure by assuming that it is: 1) random and crosslinked; or 2) of tree-like structure will be discussed below. Models embodying these different assumptions have enjoyed moderate successes in describing some aspects of the situation but are all subject to questions about "realism", based upon varying interpretations of the wealth of information on the nature of porosity in these materials. The fact that there remain questions about the basic nature of porosity in coal, particularly with respect to shape and connectedness, assures that modelers will be questioned from the outset concerning the physical basis of their models, regardless of which one they choose.

Contributing to the general debate over what constitutes an "appropriate" model is the fact that different modelers have different end uses in mind for their models. Some models which have been proposed on the basis of relatively simple pictures of pore structure have been computationally rather straightforward, involving simple analytic solutions or at least some significant closed form constituents in the full solutions. From the perspective of an end user who is developing a comprehensive pyrolysis and combustion model, computational convenience is certainly attractive, particularly if the impact of correctly accounting for porosity is considered to be of secondary importance in the application.

None of these aspects are unique to modeling of this particular transport/reaction system. The fact that modeling of transport in porous reacting solids continues to be an area of considerable research interest despite many years of effort is a testament to the difficult nature of the problem. One should not be unduly optimistic about a general breakthrough in this area. Advances in computational equipment assure that progressively more elaborate models will become computationally more feasible, but such work does not necessarily assure improved understanding in all cases. In the particular case of coal, the uncertainty in physical structure will continue to hamper even these efforts.

The present report will briefly review the current situations in the field, without an attempt at being exhaustive. Then a revised approach consistent with the goals of the present project (to provide a robust, but computationally efficient model of coal pyrolysis under a wide range of heating conditions), will be presented.

Models Based on the Assumption of Highly Crosslinked Porous Networks

The internal composition of a particle is often assumed to be a smooth function of position in the particle. For example, if the physical situation involves spherical coal particles, then volatiles compositions within the particles are assumed to be functions of radial position and time alone. Classic examples of this type of model are the so-called "dusty gas model" (2) and the model of Feng and Stewart (3). The model of Russel et al. (4), which is specific to the coal pyrolysis situation, involves application of what is essentially the dusty gas model in the continuum limit. The model of Gavalas and Wilks (5) mirrors some of the features of the Feng and Stewart approach.

The dusty gas model basically treats the solid matrix of coal as an assembly of particles, fixed in space and obstructing the motion of lighter gaseous species. Then, the ordinary flux equations for gases are modified to reflect the presence of a dummy species of very high molecular weight, which has a zero drift velocity (the "dust" in the gas is motionless). The dust is assumed uniformly dispersed and assumed to have a very small volume. The porosity in coal is thus not really at all represented in application of the diffusion part of the model. The contribution of viscous flow is introduced through an empirical approach in which viscous fluxes are simply added to calculated diffusive fluxes to obtain the total flux; calculation of the viscous flux is the only place in which pore structure quantitatively enters. We consider first the application of this model to coal by Russel et al (4).

The Model of Russel et al (4)

The general structure of this model is as shown:



the steps shown as type "c" are chemical reaction steps and those of type "t" are transport steps. It is with these latter steps that this discussion is mainly concerned.

In the representation of the model employed by Russel et al., bulk diffusion and viscous flow are assumed to control escape of volatiles, and thermal diffusion is neglected. In this case, the molar flux of species i (N_i) with respect to stationary co-ordinates (r) in a spherical particle is given in implicit form by:

$$\frac{\sum_{j=1}^{n} \frac{y_j N_j - y_j N_j}{D_{ij}^e}}{\sum_{ij}^{p} \frac{D_{ij}^e}{D_{ij}^e}} = -\frac{P}{R_g T} \frac{dy_i}{dr} - \frac{y_i}{R_g T} \begin{bmatrix} 1 - \frac{1}{\frac{n}{\sum_{j=1}^{n} \frac{1/2}{\sum_{j=1}^{n} \frac{1/2}{\sum_{j=1}^{n} \frac{1}{\sum_{j=1}^{n} \frac{$$

where P is pressure, T is temperature, R_b the gas constant, M_i is the molecular weight of i, y_i is the mole fraction of i, and n is the number of gas phase species. The diffusion coefficient D_{ij}^e is related to the true binary gas pair ij diffusion coefficient D_{ij} by:

$$\mathbf{D}_{ij}^{e} = \mathbf{K}_{l} \mathbf{D}_{ij} \tag{2}$$

The value of K_1 is unknown and must normally be determined experimentally. It is often taken as

$$K_1 = \epsilon / T \tag{3}$$

where ϵ is porosity and τ is the tortuosity of the pore system, but of course τ is generally not known a priori either. It should be noted that K_1 is <u>not</u> a function of pore size.

Only (n-1) flux relations of form Eq. 1 are independent, the one additional relation used for solving for the fluxes is the overall flux relation

$$\sum_{j=1}^{n} M_{j}^{1/2} N_{j} = - \frac{B_{0} P}{\mu R_{g} T} \sum_{j=1}^{n} M_{j}^{1/2} y_{j} \frac{dP}{dr}$$
(4)

where B_0 is a Darcy permeability and μ is a gas viscosity. The permeability B_0 is again generally not known a priori and must be determined experimentally. If the pores are of circular cross-section, then B_0 is proportional to the square of pore diameter (d). Russel et al. assume

$$B_0 = K_1 d^2$$
 (5)

It is apparent that the actual representation of pore structure in this model is quite crude. Even if the constants B_0 and K_1 were known in any particular case, the representation of the fluxes in the implicit form of Eq. 1 is unwieldy; often a simplification is effected based upon defining a few pseudo-species. This was ultimately the approach employed by Russel et al. They defined a ternary mixture consisting of reactive volatiles (reactive towards secondary reactions), nonreactive volatiles and inert gas. Thus, Eq. 1 is represented by:

$$N_{i} = y_{i} (N_{R} + N_{NR}) - \left(\frac{P_{o} D_{eff}}{R_{g}T}\right) dy_{i}/dr$$
(6)

where the subscript i refers to any species and R refers to reactive volatiles, NR the non-reactive volatiles. D_{eff} is assumed to be the diffusivity for <u>all</u> species (the equal binary diffusivity assumption). The pressure P_0 is the external pressure, as the internal pressure in the particle is <u>assumed</u> to not rise very much compared to ambient. The flux of inert gas is assumed to be zero, again according to pseudo-steady state. Equation 4 in this case becomes:

$$M_{NR}^{1/2} N_{NR} + M_{R}^{1/2} N_{R} = -\frac{B_{0}P}{\mu R_{g}T} \sum_{i=1}^{3} M_{j}^{1/2} x_{j} \frac{dP}{dr}$$
(7)

where the actual pressure gradient could be approximately determined from Eq. 7 given the N_{i} (in the case of small gradients only, given the assumption inherent in Eq. 6).

Actually, the model was extended to consider hydropyrolysis in which a fourth component, H_2 , was also considered, but the solution of the four component problem was not necessary because of the assumption of a thin reaction zone involving H_2 and reactive volatiles in the particle; this solution will not be considered here. Russel et al. assumed that the inventory of vapor phase volatiles in the particle was always small enough so that pseudo-steady state could be assumed for all the vapor phase species in the particle. As a result, species conservation for any vapor phase species in the particle pore structure could be taken as,

$$(1/r^2) d/dr (r^2N_i) = R_i$$
 (8)

where R_i is the volumetric generation rate of species i in the particle. For the - inert gas that bathes the particle, $R_i = 0$.

If it is possible to assume that the net production rate for volatiles (including any cracking reactions) is independent of position and thus of concentration in the vapor phase, then integration of Eq. 8 is straightforward, yielding:

$$N_{i} = rR_{i}/3$$
(9)

Symmetry was assumed at r = 0. The assumption of concentration-independent cracking reaction rate is rather severe. Also, the fact is that gases probably are yielded upon cracking reactive volatiles, thus affecting R_i for non-reactive volatiles (which are mainly light gases) and thus coupling the equations, greatly complicating solution.

The actual solution for composition profiles within the particle involves combination of Eq. 6 and Eq. 9, and the assumption that the volatiles composition is zero at the exterior of the particle (r = R). This is actually a procedure involving simultaneous solution for two fluxes (N_R and N_{NR}) and three composition variables (y_R , y_{NR} , y_{inert}) using Eq. 9 for the two volatile species, and the fact that the mole fractions sum to unity. The solutions are given in Russel et al. and will not be repeated here. Since validation was performed against experimental data on a <u>softening</u> coal, it cannot be said that the model has really been rigorously tested.

In trying to apply the model to coal pyrolysis in the general case, the following difficulties will be encountered:

1. It will not be obvious a priori how to best relate the pore structure to K_1 and B_0 . In addition, the present simplified formulation was developed based upon the assumption that the diffusional processes are describable in terms of a strictly Fickian model; Knudsen processes were ruled out on the basis that diffusion in micropores would be too slow to be of consequence. Thus, the model really applied only to pores larger than $10^{-2} \mu m$, unless a more general form of Eq. 1 is used. In this case, yet another parameter would be needed to characterize Knudsen diffusion in the particular pore structures of interest.

2. The assumption concerning the concentration and position independence of the reaction source-sink term in Eq. 8 may be unrealistic, as already noted. Also, the assumption of pseudo-steady state in the species conversation equation may be poor, particularly if the particles are large, or prone to forming cavities.

3. The a priori assumption of a small ΔP within the particle is unattractive, since this quantity may not always be small, and in fact, an important purpose of the model might be to calculate it. This assumption may be relaxed, of course, but at the price of computational complexity.

These criticisms are not intended as a basis for quickly disregarding this or similar models-rather they should serve as a reminder of the difficulty of the task.

The Model of Gavalas and Wilkes (5)

In an effort to represent more realistically the pore structure of coals in a transport pyrolysis model, Gavalas and Wilks (5) developed a model that was somewhat simpler in chemical structure than the previous model:



While it was recognized that competitive processes involving the species are important, this model did not take into account explicitly the competition between tar transport and retrograde reactions involving the tar. Thus, the effects of particle diameter or pressure on total product yields were not directly calculable. Instead, attention was focused on the issue of connectivity of pores of differing sizes, and what implications this would have in transport. As opposed to the approach of Russel et al., which requires the assumption of a well connected pore network and an empirical method for estimating effective diffusivity and permeability, the Gavalas and Wilks approach considers first what the pore structure of the coal must look like and then uses this to attempt to predict transport coefficients.

As did Russel et al., Gavalas and Wilks also solve the Equations (8) for tar, gaseous volatiles, and inert gas. Again, an assumption of pseudo-steady state was made, and the R_i terms were also assumed spatially invariant. The key difference comes in the expressions for the fluxes N_i , which naturally contain all the information about pore structures. Note that Gavalas and Wilks deal with a well-connected pore network model, as do Russel et al., since all gradients are assumed as desirable in terms of a radial position variable (r) in a spherical particle. The main difference is that Gavalas and Wilks assume their network to be dominated

by pores in the "small macropore" range. Once this assumption is made (it will be explored further below), the calculation of permeabilities and diffusivities is based solely upon a consideration of these pores, and the flux relations are in essence the same as those expressed in Equation (1), except the Knudsen diffusion is explicitly considered:

$$\sum_{\substack{j=1\\j\neq i}}^{n} \frac{y_{j}N_{i}^{D} - y_{i}N_{j}^{D}}{D_{ij}^{e}} + \frac{N_{i}^{D}}{D_{iK}^{e}} = -\frac{1}{R_{g}T} \frac{dP_{i}}{dr}$$
(10)

$$N_{i}^{v} = -\frac{y_{i}B_{0}P}{\mu R_{g}T} \frac{dP}{dr}$$
(11)

$$N_i = N_i^{v} + N_i^{D}$$
(12)

where the symbols are as defined before, except N_i^{V} is the flux of i due to convection alone, N_i^{D} is the flux of i due to diffusion alone, P_i is the partial pressure of species i (= Py_i), and D_{iK}^{e} is the effective Knudsen diffusivity of i. An alternative, still equally general form of these flux relations is (see Jackson (6)):

$$\frac{N_{i}}{\substack{\mathbf{c}\\ \mathbf{D}_{iK}}}_{iK} + \sum_{\substack{j=1\\ i\neq i}}^{n} \frac{\mathbf{y}_{j} N_{i} - \mathbf{y}_{i} N_{j}}{D_{ij}^{\mathbf{c}}} = -\frac{P}{R_{g}T} \frac{d\mathbf{y}_{i}}{d\mathbf{r}} - \frac{\mathbf{y}_{i}}{R_{g}T} \left[1 + \frac{B_{o}P}{\mu D_{iK}} \frac{d\mathbf{p}}{d\mathbf{r}}\right]$$
(13)

Regardless of the form in which written, these flux relations, when compared with those of Russel et al., suggest that there is really little difference between the approaches. Gavalas and Wilks retain greater generality by considering Knudsen diffusion while Russel et al. do not. There are only minor difference in the

calculations of parameters related to the pore struct e. Gavalas and Wilks obtain the permeability from:

$$B_0 = \frac{d_3^2 \epsilon_3}{96}$$
(14)

where the significance of the pore diameter (d_3) and porosity (ϵ_3) will be explored below. As assumed by Russel et al., Gavalas and Wilks assume permeability as proportional to the square of a pore diameter. The Knudsen diffusion coefficient for species i is calculated from the standard equation for this purpose:

$$D_{iK} = 4.85 \times 10^3 d_3 \sqrt{\frac{T}{M_i}}$$
 (15)

where d_3 is given in cm and D_{iK} in cm²/s. This D_{iK} is related to the Knudsen diffusivity in a porous matrix by:

$$D_{iK}^{e} = \frac{\epsilon_{3}}{\tau} D_{iK}$$
(16)

The calculation of the bulk diffusion coefficient is from:

$$\mathbf{D}_{ij}^{\mathbf{e}} = \frac{\epsilon_3}{\tau} \frac{\mathbf{D}_{ij}}{\mathbf{P}}$$
(17)

where De_j is the binary pair ij diffusivity in the bulk gas at atmospheric pressure, and P is the actual pressure in the pore.

As compared to the approach involving the dusty gas model in its original form, in which the diffusivities were strictly empirical quantities, the approach by Gavalas and Wilks seeks to relate the diffusivities to the pore structure more directly. However, the introduction of the unknown quantity τ , the tortuosity, into Equation (17) is exactly equivalent to introducing the constant K₁ into Equation (2)--both are necessarily empirically determined constants. Only in the fact that the tortuosity can by physically rationalized in terms of deviation of the pores from cylindrical shape and that it can be related to the nature of pore crosslinking, has a real step been taken towards developing a link between the dusty gas formulation and the true nature of pore structure. Fundamentally, the approaches are still basically the same. When considering the handling of permeability in the two models, the Gavalas and Wilks approach apparently removes a degree of freedom from the calculation, by not including an adjustable parameter in (14).

Particularly valuable incights were provided in the Gavalas and Wilks analysis concerning the nature of porosity in coal and how it is crosslinked. The analysis considered the porosity of coal divided into five general size ranges as shown in Table 1. The division of pores into micro-, transitional-, and macropore categories follows traditional size criteria, but the further subdivision into three classes of macropores is for convenience of discussion. Mean pore diameters characteristic of each range are presented (d_i) . Values of porosity in each size range are taken from typical literature data (e.g., Gan et al. (7)), as well as from Gavalas and Wilks' own measurements. It is now known that near zero values of micro and tran.itional porosity can be of questionable validity in low rank coals, which tend to partially "collapse" upon removal of moisture in preparation for traditional porosity testing (Evans (8), Lavine and Gauger (9), Gorbaty (10), Deevi and Suuberg (11)). It is therefore important to know what the preceding thermal history of low rank sample is in order to have an accurate indication of its porous structure at the time of onset of pyrolysis. It should, however, be noted that a previous collapse of pore structure due to moisture removal does not assure that the structure will necessarily be in such a collapsed state at the onset of pyrolysis. Disruption of hydrogen bonds would be expected, long before pyrolysis begins. These issues will not be considered further here.

The random capillary model of Gavalas (12) has been used to estimate certain features of the porous structure, such as the length of pores and the frequency of intersections of pores with each other and/or with the surface of the coal. The results are summarized in Table I. The relevant working equations are:

$$\frac{1}{L_{i}} = \sum_{j=i}^{N} \frac{\epsilon_{j}}{d_{j}} \left[1 + \frac{d_{i}}{d_{j}} \right]$$
(18)

$$\frac{1}{L_{i}} = \sum_{j=i+1}^{N} \frac{\epsilon_{j}}{d_{j}} \left[1 + \frac{d_{i}}{d_{j}} \right] = \frac{1}{L_{i+1}}$$
(19)

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TYPICAL FEATURES OF POROSITY

(Based on Gavalas ans Wilks)

Pore Classification	Diameter Range (µan)	Hean d _i	Porosity E ₁	ել (ա տ) L ₁	L1/41	^m i (¹ _µ ¹ ¹ ₃) ¹	ng (4m=2)	Opening onto (Pore/Surface)
Hicropores (d ₁)	4 x 10 ⁻⁴ to 1.2 x 10 ⁻³ (4 to 12 Å)	8 x 10-4	1×10^{-7} to 0.1	0,008	0.74	10	6.8 x 10 ⁴	5 x 10 ⁴	26.3
Transitional Pores (d ₂)	1.2 × 10 ⁻³ to 3 ¥ 10 ⁻² (12 to 300 Å)	fl x 10-3	0 to 0.1 (0.005)	0.74	4.6	93	10.7	49.7	4.1
Hacropores (d ₃)	3×10^{-2} to 0.3	0.1	0 to 0.1 (0.01)	4.6	29.7	46	0.21	0.64	U.6
Hacropores (d ₄)	0.3 to 3	1	0 to 0.1 (0.015)	29.7	158	30	7 × 10 ⁻⁵	0.01	0.1
Macropores (d5)	3 to 10	6	0 to 0,1 (0,019)	158	•_	26	-	3 x 10 ⁻⁴	0

PORE TREE MODEL

Surface area (m ² /y)	L	Lı/ai	Openiny onto (Pore/Surface)
193	U.004	5.4	3.8×10^{3}
2	0.04	5.4	375
0.3	U.54	5.4	30
0.05	5.4	5.4	3
0,01	32.4	5.4	0.5

where L_i = average length of a pore of diameter d_i , between intersections with pores of diameter d_i or larger, and L_i = average length of a pore of diameter d_i , between intersections with pores of diameter d_{i+1} .

$$\frac{1}{L_{i}} = \frac{1}{L_{i+1}}$$
(20)

The lengths given in Table 1 are for the indicate ϵ_i in square brackets, for a particular sample studied by Gavalas and Wilks.

In addition to the average length of pores, the statistical analysis of Gavalas and Wilks yields the predicted number of intersections of d_i pores with d_j pores per unit volume:

$$m_{ij} = \frac{4\epsilon_i \epsilon_j}{\pi d_i^2 d_j^2} \quad (d_i + d_j)$$
(21)

Since microporosity was disregarded by Gavalas and Wilks, they provided no estimates for pore lengths and parameters in this size range. These have been added here, assuming $\epsilon_1 = 0.05$. Because a "typical" 100 μ m particle has a surface area of 3.14 x 10⁴ μ m² and a volume of 5.23 x 10⁵ μ m³, it is clear how few d₅ pores there are in the particle.

The column headed Pore/Surface considers how many pores in a particular size range terminate on other pores as compared to on the surface. It is apparent that micro- and transitional pores mainly feed into other pores, rather than to the surface.

The column headed Pore/Surface indicates for an assumed particle density of 1.3 g/cm^3 , what the contribution of each pore size range would be to surface area, assuming cylindrical pores.

Having thus characterized the porosity in what seems to be a fairly reasonable manner, Gavalas and Wilks proceed to develop a simplified transport model based upon the postulated central role of only one range of pore sizes.

Gavalas and Wilks maintain that the only significant range of porosity which need be considered are the macropores of size d_3 . This conclusion was based upon

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the following arguments concerning the role of other pore sizes in determining transport rates:

- 1. Diffusion in micropores (range d_1) is activated and slow, compared to the timescale for pyrolysis, except for small gas phase species. The decision is made to treat the micropores as part of the bulk phase and neglect transport within these pores.
- 2. Transitional pores (range d_2) are assumed to provide the surface area for product evolution and possible recombination reactions of tars. It is stated that, "This pore range makes a relatively small contribution to mass transfer because of low permeability and Knudsen diffusivity, although the porosity is comparable to that in other ranges." It is noted that d_2 pores are well crosslinked, and feed larger pores. Most d_2 pores are linked to other pores rather than to the surface of the particle, as noted above.
- 3. The d_4 pores are <u>assumed</u> to not support a large pressure gradient and are thus treated by a mathematically convenient assumption of decreased particle diameter, to account for the fact that all d_3 pores end on the <u>surface</u> of the particle rather than in the interior on either d_4 and d_5 pores.
- 4. The d5 size range pores are thus automatically neglected, based on the same reasoning as in 3 above. It is further noted that the number of intersections of transitional pores with these larger macropores is small compared to the number of intersections of transitional pores with small macropores (d3), so that one need not be concerned about there being a direct feeding of large macropores from the bulk reactions--what flow occurs in the large pores must be fed through progressively smaller pores. A variant of this physical picture underlies the "pore tree" model to be described further below.

Even with this somewhat restrictive set of assumptions, only a numerical solution was possible for the ternary system of light product gases, tar, and inert ambient gas. These calculations by Gavalas and Wilks suggested that, at atmospheric pressure pyrolysis conditions, the maximum pressure drop in d₃ pores is less than 0.1 atm for an 80 μ m particle, but the details of the calculations were sketchy. As a limiting case, it is noted by Gavalas (13) that is the molar production rate

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of light gases is high compared to that of tar, and if pyrolysis is carried out in a self-generated atmosphere:

$$\Delta P = \left[\frac{R_G + R_T \sqrt{M_T/M_G}}{24}\right] \left[\frac{R_g T d_p^2}{D_{GK}^e + \frac{B_0 P_0}{\mu}}\right]$$
(22)

where R_{G_1} R_T are the net molar volumetric production rates of light gases and tar, the M_i are molecular weights, d_p is the particle diameter, and R_g is the gas constant. This result is obtained by summing the equations (10) for both tars and light gases, combining with (9), and solving for dP/dr explicitly. Integration yields (23) for the case in which $R_T << R_G$ and $y_T << y_G$. Also, it was noted that

$$\frac{D_{GK}^{e}}{D_{TK}^{e}} = \sqrt{\frac{M_{T}}{M_{G}}}$$
(23)

Note that the procedure is a bit more involved if the presence of an inert gas (I) is allowed:

$$\frac{dP}{dr} = \frac{-R_g T \left[\frac{R_G}{D_{GK}^e} + \frac{R_T}{D_{TK}^e} \right] (r/3)}{1 + \frac{B_0 P}{\mu} \left[\frac{y_G}{D_{GK}^e} + \frac{y_T}{D_{TK}^e} + \frac{y_I}{D_{IK}^e} \right]}$$
(24)

If, again $R_T \ll R_G$ and thus $y_T \ll y_G$,

$$\frac{dP}{dr} = \frac{-R_g T \left[R_G + R_T \left[\frac{D_{GK}^e}{D_{TK}} \right] \right] r/3}{D_{GK}^e + \frac{B_o P}{\mu}}$$
(25)

where it has also been assumed that $D_{GK}^e = D^e I_K$ and $y_I + y_G = 1$. Since this is

precisely the starting point from which Equation (23) was derived, it will naturally yield the same result upon integration. The fact that ordinary bulk diffusion does not enter into the calculation of pressure drop via (23) or (25) may at first viewing be surprising, since there was not a specific ruling out of this mechanism. The fact that it does not appear in the equation for pressure drop does <u>not</u> suggest that it is of no consequence in the process; to solve for composition profiles in the particle requires returning to Equation (10), which does include bulk diffusion terms. It is only the pressure gradient which does not depend explicitly upon the magnitude of bulk diffusion rates.

A quick consideration of the magnitude of pressure gradients within the particle is possible from Equation (23). The calculations assume a temperature of T = 1000 K, μ = 4 x 10⁻⁴ g/cm-s (typical of air), M_T = 400, M_G = 40, B_O from Equation (14), D_{GK} from Equations (15) and (16) with τ = 3, viz:

$$D_{GK}^{c}$$
 (cm²/s) = 8.08 x 10³ d₃e₃ = 8.08 x 10⁻⁴ cm²/s

with

$$d_3 = 1 \times 10^{-5} \text{ cm}, \epsilon_3 = 0.01.$$

$$\Delta P (atm) = \left[\frac{R_G + 3.2R_T}{24} \right] \left[\frac{8.2 \times 10^4 d_p^2}{8.08 \times 10^{-4} + 2.6 \times 10^{-5}} \right]$$
(26)
= 4.1 x 10⁶ (R_G + 3.2 R_T) d_p²

with d_p in cm and the P_i in moles/cm³ sec. For a particle of density ρ_p , and for pyrolysis involving a timescale Δt , f_G mass fractional yield of gas, f_T of tar.

$$R_{G} = \frac{f_{G} \rho_{p}}{\Delta t M_{G}}$$
(27)

$$R_{T} = \frac{f_{T} f_{p}}{\Delta t M_{T}}$$
(28)

Thus,

$$\Delta P = \frac{4.1 \times 10^6 \, d_p^2 \, \rho_p}{\Delta t} \left[\frac{f_G}{M_G} + \frac{3.2 \, f_T}{M_T} \right]$$
(29)

Letting $f_G = 0.1$, $f_T = 0.2$, $\rho_p = 1.3$ g/cm³, $d_p = 100 \ \mu m = 10^{-2}$ cm, $\Delta t = 1$ msec, $\Delta P \doteq 2200$ atm. The rather large disagreement with the earlier cited result of Gavalas and Wilks is a consequence of assuming a much higher reaction rate and not allowing for the decrease in effective particle size, assumed by those workers. The larger of these factors is the assumption of reaction rates which are four orders of magnitude larger than those of Gavalas and Wilks, who assumed the characteristic times scale of pyrolysis was 10 seconds rather than 1 msec. It is worth noting again that the analysis performed here is a pseudo steady state analysis, meaning that the formulation of the problem shown here assumes constant formation and transport at steady rates. Consideration of transients considerably complicates the analysis.

The Pore Tree Approach

Simons and coworkers (14-19) have developed an alternative to the randomly crosslinked pore structure approach presented above. In this approach, all pores are assumed connected only at their ends, and small pores are only connected to the end of the next larger size of pores. Each size of pore has a particular average length. As opposed to the physical picture proposed by Gavalas, small pores never join directly to pores of a much larger size class. This, in practice, is not too different from the picture that emerges from the Gavalas model, since generally for any size of pore:

$m_{i,i+1} >> m_{i,i+2}$

The m_{ij} ar the number of intersections per unit volume of size i pores with size j pores, with j representing the larger of the pores, by convention. What is substantially different in the Simons picture is the end-connectivity requirement; pores are pictured as trees in which no branches enter the middle of a "trunk". The mathematical convenience of such an assumption is that there is a one-to-one mapping of length down a particular pore and the diameter of the pore. The actual length of a pore is given by

$$L_{i} = K_{0}d_{i}/2 \epsilon_{TOT}^{1/3}$$
(30)

where $K_0 \neq 5$. Comparison of the predicted lengths of pores using this model, with those from the Gavalas approach, are shown in Table 1, for a typical porosity $\epsilon_{TOT} = 0.1$. The L_i/d_i aspect ratio is naturally constant for this model, and in general, the pores are somewhat shorter than pictured in a random by crosslinked pore model, such as that of Gavalas and Wilks. The fraction of pores of any size that reach the surface directly is given by Simons and Finson (16) as:

$$\frac{f(r_i) 4\pi d_p^{3/24}}{\bar{g}(r_i) 4\pi d_p^{2/4}} = \frac{d_p}{L_i 6} = \frac{d_p \epsilon_{TOT}^{1/3}}{3K_0 d_i} = 0.03 \frac{d_p}{d_i}$$
(31)

where $f(r_i)$ and $\overline{g}(r_i)$ are distribution functions defined by Simons. This quantity is tabulated for a 100 μ m particle in Table 1. Note that in the case of a pore tree, a far larger number of small pores open onto other pores than onto the surface of the particle. In the Gavalas and Wilks formulation, it is quite probable that small macropores (d₃) will open to the surface, whereas in the Simons formulation it is quite improbable that this is the case. It is useful to note at this point that both formulations involve considering basically the same range of pore sizes. In the Simons approach r_{max} is calculated from the distribution cited above, and is given by

$$r_{max} = d_p \epsilon_{TOT}^{1/3} / 3K_0$$
(32)

for $d_p = 100 \ \mu m$, $\epsilon_{TOT} = 0.1$, $r_{max} = 6.2 \ \mu m$. The minimum size of pore is calculated from

$$r_{\min} = 2\epsilon_{TOT} / B\rho_{S}(S.A.)$$
(33)

where $\beta = \ln(r_{max}/r_{min})$, S.A. is the specific particle surface area and ρ_s is the particle <u>bulk</u> density (this density was correctly give in another version of Eq. 33 in Simons and Finson (16) as a true solids density, but incorrectly given in Simons (14) as a true solids density; it should be a bulk density, including porosity). With this relation, assuming $\epsilon_{TOT} = 0.1$, $\rho_s = 1.3$ gm/cm³, and S.A. = 100 m²/g (typically), then $R_{min} = 1.5$ Å. This lower bound is smaller than what is

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normally thought to be accessible to molecular probes, and may reflect the difficulty in representing the actual pore structure with a tree-like model with its end connectivity requirement.

Transport in the pore tree is modeled on the individual pore level, as opposed to the earlier approaches which modeled transport on the particle level. The basic transport equation is:

$$\frac{d}{dz} \left[\frac{\rho_{\rm G} \, \mathrm{U} \, \pi d_{\rm i}^2}{4} \right] = m_{\rm W} \tag{34}$$

where P_G is the mass density of volatiles, \overline{U} their average velocity, d_i the pore diameter, \overline{m}_W the mass generation rate at the walls of all pores, and z is a pore co-ordinate, related to the diameter of the pore by:

$$d(d_i)/dz = d_i/L_t$$
(35)

where L_t is the length of a pore tree trunk.

The mass generation at the walls of the pores is related to the rate of change of porosity, as mass leaves the wall (Simons (14)):

$$\mathbf{m}_{\mathbf{w}} = 3\pi \rho_{\mathbf{S}} \, \mathbf{d}_{\mathbf{i}} \mathbf{d}(\mathbf{d}_{\mathbf{i}})/\mathbf{d}_{\mathbf{t}} \tag{36}$$

But for pore growth:

$$d(d_i)/d_t = (d_i/3\epsilon) d\epsilon/d_t$$
(37)

and

$$d\epsilon/d_t = k(\epsilon_F - \epsilon) \tag{38}$$

where ϵ_F is the final porosity and k is the rate constant for pyrolysis.

Combining (34) and (38) yields:

$$\frac{d(\rho_G \ U)}{d(d_i)} = \frac{\rho_s \ L_t \ k(\epsilon_F - \epsilon)}{\epsilon \ d_i}$$
(39)

The mass flux is zero at the minimum pore size $d_m = 2 r_{min}$, and thus integration

yields, using this boundary condition:

$$\overline{\mathbf{U}} = \left[k \mathbf{L}_{t} \, \rho_{s}(\epsilon_{\mathbf{F}} - \epsilon) / \epsilon \rho_{\mathbf{G}} \right] \ln \, (\mathbf{d}_{i} / \mathbf{d}_{\mathbf{m}}) \tag{40}$$

If \vec{U} is predicted to be greater than the speed of sound at the exit of the pore, the flow is choked, and \vec{U} is the speed of sound at $d_i = d_t = 2r_{max}$. Otherwise, the pressure at the pore mouth will be P_0 , the ambient pressure. Since $PG = P\vec{M}/k_gT$, this allows solving (40) for pressure:

$$P = \left[kL_t \rho_s R_g T (\epsilon_s - \epsilon) / \epsilon \overline{MU}\right] \ln (d_i/d_m)$$
(41)

Letting

$$k(\epsilon_{s} - \epsilon)\rho_{s} = R_{G}M_{G} + R_{T}M_{T}$$
⁽⁴²⁾

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and assuming, again, that $y_G >> y_T$

$$P = \left[L_t R_g T \left[R_G + R_T (M_T / M_G) \right] / \tilde{c} \tilde{U} \right] \ln(d_i / d_m)$$
(43)

The calculation of pressure then depends upon a good knowledge of \overline{U} , which depends upon the mechanism of transport. The following factors may all help determine \overline{U} , in the Simons model:

- 1. Activated diffusion.
- 2. Knudsen diffusion.
- 3. Fickian diffusion.
- 4. Viscous Convection.
- 5. Drag induced by injection of mass from the walls into the flow.

It is likely that the smallest pores (d_1) are entirely in the activated diffusion regime, for which the application of equations such as (34), (41) or (42) is inappropriate because one is dealing with a condensed phase. Consequently, the real minimum diameter (d_m) is most likely to be about 1.2 x 10^{-3} µm (i.e., the smallest transitional pores).

The applicability of the Knudsen diffusion regime requires that pores be of diameter comparable to or smaller than the mean free path of the gas phase species. This suggests that pores in the size ranges d_2 and d_3 might be appropriately examined in this way.

By arguments based on the comparability of fluxes due to various controlling mechanisms, Simons suggests that the entire pore tree switches from Knudsen diffusion to viscous convection controlled flow at a critical trunk radius given by:

$$r_{t}^{*} = \frac{\epsilon_{\text{TOT}}^{1/3}}{K_{0}} \sqrt{\frac{\mu \, s \, \epsilon_{\text{TOT}}}{k \rho_{\text{S}} \, \pi(\epsilon_{\text{F}} - \epsilon)}}$$

$$= \frac{\epsilon_{\text{TOT}}^{1/3}}{K_0} \sqrt{\frac{\mu \ 8 \ \epsilon_{\text{TOT}}}{\pi \ (R_G M_G + R_T M_T)}}$$
(44)

Again, using $\Delta t = 1$ msec, and thus

 $R_G = 3.3 \frac{mol}{s cm^3}$, $R_T = 0.65 \frac{mol}{s cm^3}$, $M_G = 40$, $M_T = 400$, $\mu = 4 \times 10^{-4} \text{ g/cm-s}$, $\epsilon_{TOT} = 0.1$, $K_0 = 5$.

$$r_t^* = 4.7 \text{ x } 10^{-5} \text{ cm} = 0.47 \ \mu\text{m}$$

This confirms the expected result. Thus, pore trees with trunks in the d_4 or d_5 class would be expected to be controlled by convection. This does not mean that the smallest pores of a tree with a large trunk should in some sense be different from the smallest pores of a tree with a small trunk. Rather, the critical radius within the pore tree at which transition from Knudsen to viscous control depends upon the size of the trunk carrying the flow away from the pore.

Considering first only pore trees having trunks of size class d_3 , and thus entirely in the Knudsen regime, \overline{U} can be obtained from a pseudo Knudsen diffusion analysis:

$$N_{G} = \frac{\rho_{G}\bar{U}}{\bar{M}_{G}} = -D_{GK} \left(\frac{P}{R_{g}T}\right) \frac{dy_{G}}{dz}$$
(45)

In the analysis performed by Simons, no distinction was drawn between volatile products, so here we neglect the contribution to the flux due to tar species. Strictly speaking, multicomponent flux relations should be written, but this was not considered. The value of D_{GK} is obtained from (15), and the co-ordinate z can be eliminated using (35). To a crude approximation

$$\overline{U} = -\frac{D_{GK}}{\rho_{G}} \frac{d\rho_{G}}{dz}$$
(46)

from which by combining with (15) and (40) gives:

$$\overline{U}\left(\frac{cm}{s}\right) = \frac{4.85 \times 10^{3} (d_{1})^{2} \sqrt{T/M_{G}}}{2P_{G} L_{t}} \frac{dp}{d(d_{i})}$$
(47)

Eliminating \overline{U} between (47) and (40) gives

$$\frac{dP}{d(d_i)} = - \frac{kL_t^2 \rho_s(\epsilon_F - \epsilon)R_g T}{4.85 \times 10^3 (d_i)^2 \epsilon M} \ln (d_i/dm)$$
(48)

which upon integration yields

.

$$P = \frac{kL_t^2 \rho_s R_g T (\epsilon_F - \epsilon)}{4.85 \times 10^3 (d_i) \epsilon M} \left[1 + \ln \left(\frac{d_i}{d_m} \right) \right] + A_1$$
(49)

where A_1 is an arbitrary constant of integration, determined by the fact that $P = P_t$ at $d_i = d_t = 2(r_{max})$, determined as discussed in connection with Eqs. (40) and (41).

$$A_{1} = P_{t} - \frac{kL_{t}^{2} \rho_{s} R_{g} T (\epsilon_{F} - \epsilon)}{4.85 \times 10^{3} (d_{t}) \epsilon \overline{M}} \left[1 + \ln \left(\frac{d_{t}}{dm}\right)\right]$$
(50)

For $d_i \ll d_t$, Simons claims that the pressure is independent of the background pressure, since the second term on the right hand side of (50) will be small

compared to the first term on the right hand side of (49). This does not necessarily mean that P_t will be small compared to the first term in (49). Solving for ΔP in the particle:

$$\Delta P = P(d_{\rm m}) - P_{\rm t} = \frac{kL_{\rm t}^2 \rho_{\rm s} R_{\rm g} T(\epsilon_{\rm F} - \epsilon)}{4.85 \times 10^3 d_{\rm m} \epsilon \bar{\rm M}}$$

$$= \frac{(R_{\rm G} M_{\rm G} + R_{\rm T} M_{\rm T}) L_{\rm t}^2 R_{\rm g} T}{4.85 \times 10^3 d_{\rm m} \epsilon \bar{\rm M}}$$
(51)

Lt is given by:

$$L_{t} = K_{0}d_{t}/2 \epsilon_{TOT}^{1/3}$$
(52)

where $(d_t/2) = r_t^* = 4.7 \ 10^{-5} \text{ cm}$.

 $L_{t} = 5 \times 10^{-4} \text{ cm}$

Simple application of previously cited parameter values leads to an estimate of ΔP of order 10^4 atm, even if d_m is taken as the lower limit of pores of size d_2 . Clearly, such high pressures are of little physical significance, and probably serve to suggest only that the concept of diffusional pore transport is of questionable validity in this case.

If viscous flow controls the rate of escape:

$$\overline{U} = -\frac{(d_{\bar{i}})^2 d\dot{P}y_{\bar{G}}}{32\mu dz}$$
(53)

Again, combining with (35) yields:

$$\overline{U} = -\frac{(d_i)^3 \, dPy_G}{32L_t \mu \, d(d_i)}$$
(54)

And again eliminating \tilde{U} between (54) and (40), followed by integration gives for $d_i \ll d_t$

$$\Delta P = (L_t/d_i) \sqrt{[\mu k \rho_S R_g T(\epsilon_F - \epsilon)/\epsilon M]}$$

= $(L_t/d_i) \sqrt{\mu [R_G M_G + R_T M_T] R_g T/\epsilon M}$
= $3.6 \times 10^{-2} (L_t/d_i) \text{ atm}$ (55)

(Note $R_g = 8.31 \times 10^7 \text{ erg/K}$ -Moi, and 1 atm = 1.01 x 10⁶ $\frac{\text{dyne}}{\text{cm}^2}$. This again will yield quite high pressures in small transitional-size pores (of order 10^3 atm).

Comparison of Models

Recall that the pressure drop in the model of Gavalas and Wilks was calculable from Eq. (29), and gave for the pore structure described in Table I $\Delta P = 2200$ atm for a pyrolysis timescale of 1 msec. The pressure drop is inversely proportional to the timescale. It should at this point be emphasized also that the indication of two significant figures in the result of the calculation is only for the convenience of sample calculations - the results should only be interpreted in terms of orders of magnitude, given the crude nature of the estimates in this section.

If we compare the results of the random pore model calculation to that of the pore tree calculation, assuming that the viscous transport controls, we see both predict the same order of magnitude in pressure drop - namely 1000 atm. However, it may legitimately be asked if such a pressure has any physical significance, when discussing transport in pores that are tens to hundreds of angstroms in size. Such a pressure is well above the critical pressure, and the temperature is generally going to be well above the critical temperature, so the distinction between a condensed phase and the vapor phase no longer exists. One then has a choice of developing a separate modeling strategy for the supercritical fluid state in fine pores, or an arbitrary choice can be made to apply the models at hand only to situations in which they make physical sense.

As an illustration of this point, consider an arbitrary cutoff of 100 atm on the pressure (actual critical pressures for hydrocarbons are often half this

value). This means that we would be concerned with modeling gas phase transport only if $\Delta P < 100$ atm. In the case of the random pore model, this could only be satisfied if the timescale of pyrolysis were lengthened to order 10 msec from 1 msec, for the sample calculation discussed in connection with Eq. 29. If we now apply this slower rate to the pore tree model, but assume that the viscous flow control model still applies, then Eq. 55 becomes:

$$\Delta P = 1.1 \times 10^{-2} (L_{+}/d_{1}) \text{ atm}$$
(56)

If the appropriate pore characterization parameters for the pore tree model are taken from Table I, $L_t = 32 \mu m$, and:

$$\Delta P (atm) = 0.35/d_{1} (\mu m)$$
 (57)

Assuming that the value of ${\it \Delta}$ P must be less than 100 atm suggests that the smallest pores within which this is true are of order $10^{-3} \mu m$, which are in the d₂, or transitional porosity regime. It should be noted that if one assumed $d_1 = d_3 = 0.1 \ \mu m$, to be consistent with the random pore model, $\Delta P = 3.5$ atm, far below the prediction of that model. This comparison is not, however, significant, since all that this says is that the randomly crosslinked pore model lumps all of its resistance in do pores, whereas the pore tree has more resistance in pores smaller than d_3 . It should also be noted that in the case of the randomly crosslinked pore model, the volatiles must traverse a length of comparable magnitude to the particle radius in such small pores, while in the case of the pore tree model, the volatiles quickly exit into larger pores from the d₃ size pores (see Table I). Since the pressure drop in the randomly crosslinked pore model is proportional to the square of particle radius, a decrease of the particle diameter by an order of magnitude, so that the length the volatiles must travel is comparable to the length of a pore tree in the other model, would bring the pressure drops into order of magnitude agreement.

Thus it cannot really be said that there is a fundamental difference in the magnitude of the pressure drops predicted by the two approaches, if a comparable basis of comparison is assumed. The main difference in the models comes in variation of ΔP with parameters. The pressure drop in the case of the randomly crosslinked pore model varies with the square of particle radius and with the first power of pyrolysis rate, while the pressure drop in the case of the pore tree model varies directly with particle radius (by virtue of the proportionality of tree length to radius) and with the square root of pyrolysis rate.

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For present purposes, it is felt that the pore tree model is the more interesting for detailed modeling of pyrolysis. This is not because the physical picture it presents is necessarily any more realistic than that of the randomly crosslinked pore model, but because it permits the estimation of pressure along pores of well characterized geometry. If the model of particle swelling during pyrolysis is to be based upon growth of pores due to high internal pressures in a softened material (such as in the model of Melia and Bowman (20)), then the pore tree model is the only approach which allows calculation of swelling given a knowledge of original pore structure. The randomly crosslinked pore model would only be useful to a basis for a swelling model if symmetrical swelling about the center were of interest, where it is assumed that the particle as a whole behaves as a "balloon". Naturally both of these approaches would be quite different than the nucleation and growth in liquid media models of Lewellen (21) or Oh et al. (22), and address specifically the question of what happens in the transition from non-softened to softened coals. As such, the presently explored approaches may be complementary to those earlier approaches.

What remains to be established in utili is the pore tree approach is whether the viscous transport controlled limit applies over the entire range of practical interest. Also, it needs to be established how precisely the limits of pressure must be set, for which the postulated gas phase transport applies, and how the pseudo-evaporative process should be handled at the intersections with pores which are so small that the gas phase transport cannot be assumed. Finally, the question of transport in the condensed phase must be examined more closely, and an appropriate model of activated diffusion developed for it.

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These above topics will all be discussed in future reports.

REFERENCES

- Suuberg, E.M. in <u>Chemistry of Coal Conversion</u>, Ch. 4, (R. Schlossberg, Ed.) Plenum, 1985.
- 2. Evans, R.B., III, Watson, G.M. and Mason, E.A., J. Chem. Phys., 35, 2076 (1961); 36, 1894 (1962); 38, 1808 (1963). Also Mason, E.A. and Malinauskas, A.P., Jo. Chem Phys., 41, 3815 (1964); 46, 3199 (1967).
- 3. Feng, C. and Stewart, W.E., I & EC Fundamentals, 12, 143 (1973).
- 4. Russell, W.D., Saville, D.A. and Greene, M.I., AIChE. J., 25, 65 (2979).
- 5. Gavalas, G.R. and Wilks, K.A., AIChE J., 26, 201 (1980).
- 6. Jackson, R., Transport in Porous Catalysts, Elsevier, 1977.
- 7. Gan, H., Nandi, S.P. and Walker, P.L., Jr., Fuel, 51, 272 (1972).
- 8. Evans, D.G., Fuel, 52, 155 and 186 (1973).
- 9. Lavine, I. and Gauger, A., I&EC, 22. 1226 (1930).
- Gorbuty, M., Fuel, 57, 706 (1978).
- 1. Deeir, S.C. and Suuberg, E.M., Fuel, **56**, 454 (1987).
- 12. Gavalas, G.R. and Wilks, K.A., AIChE J., 26, 577 (1980).
- .3. Gavalas, G.R., Coal Pyrolysis, Elsevier, Ch. 5, 1982.
- '4. Simons, G.A., Combustion Flame, 53, 83 (1983).
- 15. Simons, G.A., Combustion Flame, 53, 181 (1984).
- .6. Simons, G.A. and Finson, M.L., Comb. Sci., Techn., 19, 217 (1979).
- 17. Simons, G.A., Comb. Sci., Techn., 19, 227 (1979).
- -8. Simons, G.A., 19th Symp. (Int) on Combust., p. 1067, The Comb. Inst., 1982.
- 19. Simons, G.A., Comb. Sci., Techn., 20, 107 (1979).
- 20. Melia, P.F. and Bowman, C.T., Comb. Sci. Techn., 31, 195 (1983), also Western States Section Meeting of the Combust. Inst., Salt Lake City, April, 1982.
- 1. Lewellen, P.C., S.M. Thesis, Dept. of Chem. Eng., MIT, Cambridge, MA, 1975.
- 12. Oh, M., Peters, W.A. and Howard, J.B., Proc. 1983 Int. Conf. on Coal Sci., IEA, p. 483 (1983).



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