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On the Short-Residence Time Hydropyrolysis of Single Coal Particles: The Effect of Unequal Diffusivities

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A relatively simple single-particle model recently developed by Russel, Saville, and Greene (1979) apparently explains the pressure and particle-size dependence of the weight loss in the rapid hydropyrolysis of coal. As in the kinetic model of Anthony, et al. (1976) the volatile products are divided into stable and reactive fractions, the latter of which can react further by depositing within the particle or combining with hydrogen to form a stable product. The predicted pressure and particle size effects reflect the competition between the kinetic rates and the diffusion of hydrogen into the particle against the outward flow of volatiles. The hypotheses of the model were supported by order of magnitude estimates based on experimental data or established theories with the exception of the equal binary diffusivities assumed for the gas phase components. These actually can differ significantly, so we have tested the sensitivity of the results by analyzing the alternative limiting case with at least one relatively small, and hence "controlling," binary diffusivity. Only the rapid devolatilization step is considered because the slower hydrogenation of the solid coal is relatively insensitive to diffusion.

The mathematical analysis parallels that in the original paper; only the differences will be discussed in detail here. Conservation equations for the gaseous constituents are integrated and the instantaneous yield η calculated as a function of the dimensionless particle size α^2, pressure π, the fraction of reaction volatiles ν, and the mole fraction of hydrogen in the bulk gas $x^o_{H_2}$.

The actual range of diffusivities can be estimated by characterizing the reactive volatiles with benzene, the stable volatiles with methane and the inert gas with helium so that (Reid and Sherwood 1958)

	pD_{ij}
H_2-He	16.6 N/s
H_2-CH_4	6.4
He-CH_4	6.9
He-C_6H_6	3.8
C_6H_6-CH_4	1.0

In slow devolatilization reactive volatiles are stabilized instantaneously throughout the particle leaving a ternary mixture in which the binary diffusivity for He-H_2 exceeds those for H_2-CH_4 and He-CH_4 by a factor of two and a half. Thus we assume that $D_{V,H_2} = D_{V,I} << D_{I,H_2}$. During rapid devolatilization the ternary mixture in the hydrogen-depleted core has the benzene-methane diffusivity controlling or $D_{V,V*} << D_{V,I}$, $D_{V*,I}$. Clearly the numerical differences fall short of the mathematical idealization and the chemical characterization of the components could be questioned, but this limiting case should accurately measure the influence of the original assumption of equal diffusivities on the predictions of the model.

GENERAL FORMULATION

The ternary mixtures within the particle during devolatilization require three conservation equations and three independent flux relations to determine the two independent mole fractions, the three fluxes, and the pressure. Our earlier order of magnitude estimates indicated that rapid equilibration of the pressure and concentration profiles should sustain a pseudo-steady state. Consequently, the flux of inerts (component 3) must be zero leaving five unknowns and five independent dimensionless equations:

$$\frac{1}{r^2}\frac{d}{dr} r^2 N_i = R_i \quad i = 1, 2 \tag{1}$$

$$\alpha^{-2}\frac{dx_1}{dr} = \gamma_1(x_1N_2 - x_2N_1) - x_3N_1 \tag{2}$$

$$\alpha^{-2}\frac{dx_2}{dr} = \gamma_1(x_2N_1 - x_1N_2) - x_3\gamma_2N_2 \tag{3}$$

$$\alpha^{-2}\frac{dx_3}{dr} = x_3(N_1 + \gamma_2N_2) \tag{4}$$

with $x_3 = 1 - x_1 - x_2$. The fluxes are scaled on the instantaneous devolatilization rate and the radial position on the particle radius. The additional dimensionless groups are

$$\gamma_1 = \frac{D^e_{13}}{D^e_{12}} \quad \text{and} \quad \gamma_2 = \frac{D^e_{13}}{D^e_{23}}.$$

Only two of the three flux relations are independent; the final equation relating the pressure gradient to the total flux has been omitted because an explicit solution for the pressure is unnecessary.

SLOW DEVOLATILIZATION

When the hydrogen flux permits instantaneous stabilization of the reactive volatiles throughout the particle the remaining

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TABLE 1. RATIO OF α^2_{crit} WITH UNEQUAL DIFFUSIVITIES TO THAT FOR EQUAL DIFFUSIVITIES

ν \ $x^0_{H_2}$	0	.1	.5	1.0
0	∞	1.0	1.0	1.0
.1	∞	1.6	1.1	1.0
.3	∞	2.3	1.2	1.0
.5	∞	2.8	1.3	1.0
.7	∞	3.5	1.4	1.0
.9	∞	3.6	1.5	1.0
1.0	∞	3.9	1.6	1.0

components are stable volatiles (1), hydrogen (2), and inerts (3) with rates $R_1 = 1$ and $R_2 = -\nu$ and diffusivity ratios $\gamma_1 = 1$, $\gamma_2 << 1$.

The corresponding solution to (1-4) for hydrogen, for example, is

$$x_{H_2} = \frac{1}{1-\nu}\exp\left\{\frac{\alpha^2(1-\nu)}{6}(r^2-1)\right\} - \frac{\nu}{1-\nu} - (1-x^0_{H_2})\exp\left\{\frac{\alpha^2}{6}(r^2-1)\right\}. \quad (5)$$

Since all reactive volatiles are stabilized upon release, the instantaneous yield, the ratio of volatiles escaping to those evolved, is unity.

The critical value of α, i.e., the conditions at which the hydrogen flux just suffices to stabilize all the reactive volatiles, is found by setting $x_{H_2} = 0$ at $r = 0$ or

$$0 = \frac{1}{1-\nu}\exp\left\{-\frac{\alpha^2_{crit}(1-\nu)}{6}\right\} - \frac{\nu}{1-\nu} - (1-x^0_{H_2})\exp\left\{-\frac{\alpha^2_{crit}}{6}\right\}. \quad (6)$$

The comparison in Table 1 between the resulting values for α^2_{crit} and those obtained for equal diffusivities reveals similar trends with ν and $x^0_{H_2}$ but a larger critical particle size because of the large hydrogen-inerts diffusivity.

RAPID DEVOLATILIZATION

When $\alpha^2 > \alpha^2_{crit}$ a core depleted of hydrogen forms bounded by an interface at $r = \lambda$ at which the outward-flowing reactive volatiles and the inward-diffusing hydrogen react instantaneously. Generally $\alpha^2 >> 1$ as well so that bulk flow dominates diffusion in the core, forcing the concentration of reactive volatiles to adjust to its interfacial value of zero through a thin diffusional boundary layer.

In the core $x_1 = x_V$, $x_2 = x_{V*}$, and $x_3 = x_I = 0$ so that $\gamma_1 >> 1$ and $\gamma_2 \sim 0\,(1)$. With $\alpha^2 >> 1$ (2) and (3) reduce to

$$x_{V*}N_V - x_V N_{V*} = 0 \quad (7)$$

which with $R_V = 1 - \nu$ and $R_{V*} = \nu - \pi x_V$ allows (1) and (4) to be integrated to

$$x^c_{V*} = 1 - x^c_V = \frac{1}{2\pi}\{1 + \pi - (\pi^2 + 2(1-2\nu)\pi + 1)^{1/2}\}. \quad (8)$$

Rescaling the flux expressions near $r = \lambda$ to retain diffusion produces two boundary layers. The more rapidly diffusing inert gas penetrates a distance $y = \alpha^2(\lambda - r) \sim 0\,(1)$ into the core with profile

$$x_I = x^\lambda_I \exp\left\{-\frac{\lambda}{3}\frac{1-\nu}{1-x^c_{V*}}(1 + x^c_{V*}(\gamma_2 - 1))y\right\} \quad (9)$$

and the volatiles concentrations decrease in accord with (7). x^λ_I is the unknown inerts concentration at $r = \lambda$. Within a still thinner boundary layer with $y\lambda_1 \sim 0\,(1)$ the reactive volatiles concentration adjusts from $x^c_{V*}(1 - x^\lambda_I)$ to zero as

$$x_{V*} = (1 - x_I)x^c_{V*}\left\{1 - \exp\left(-\frac{\lambda}{3}\frac{1-\nu}{1-x^c_{V*}}\gamma_1 y\right)\right\} \quad (10)$$

while $x_I = x^\lambda_I$ and $x_V = 1 - x^\lambda_I - x_{V*}$.

Conditions within the sheath correspond to those for slow devolatilization except that $x_{H_2} = 0$ and the fluxes must balance at $r = \lambda$ as

$$\begin{aligned} N_V|_{\lambda^+} &= (N_V + N_{V*})_{\lambda^-} \\ &= \frac{\lambda}{3}(1 - x^c_{V*}) \end{aligned} \quad (11)$$

$$\begin{aligned} N_{H_2}|_{\lambda^+} &= -N_{V*}|_{\lambda^-} \\ &= -\frac{\lambda}{3}(1 - x^c_{V*}) \end{aligned} \quad (12)$$

$$x_{H_2} = 0 \text{ at } r = \lambda.$$

As a result

$$\begin{aligned} x_V &= -c\exp\left(\frac{\alpha^2(1-\nu)}{6}r^2\right) + \frac{1}{1-\nu} - f\left(\left(\frac{1-\nu}{6}\right)^{1/2}\alpha r\right) \\ x_I &= (1 - x^0_{H_2})\exp\left\{\frac{\alpha^2}{6}(r^2-1) + \frac{\lambda^3\alpha^2\pi x^c_{V*}}{3}\left(\frac{1}{r} - 1\right)\right\} \\ x_{H_2} &= 1 - x_I - x_V \end{aligned} \quad (13)$$

where

$$c = \left\{\frac{1}{1-\nu} + f\left(\left(\frac{1-\nu}{6}\right)^{1/2}\alpha\right)\right\}\exp\left(-\frac{\alpha^2(1-\nu)}{6}\right)$$

$$f(R) = \frac{\pi\alpha^3\lambda^3}{3}\left(\frac{(1-\nu)}{6}\right)^{1/2} x^c_{V*}\left\{\frac{1}{R} + \sqrt{\Pi}e^{R^2}\mathrm{erf}R\right\}.$$

The requirement that $x_{H_2} = 0$ at $r = \lambda$ then determines implicitly the position of the reactive interface as

$$0 = \left\{\frac{1}{1-\nu} - f\left(\left(\frac{1-\nu}{6}\right)^{1/2}\alpha\right)\right\}\exp\left\{\frac{\alpha^2(1-\nu)}{6}(\lambda^2-1)\right\}$$

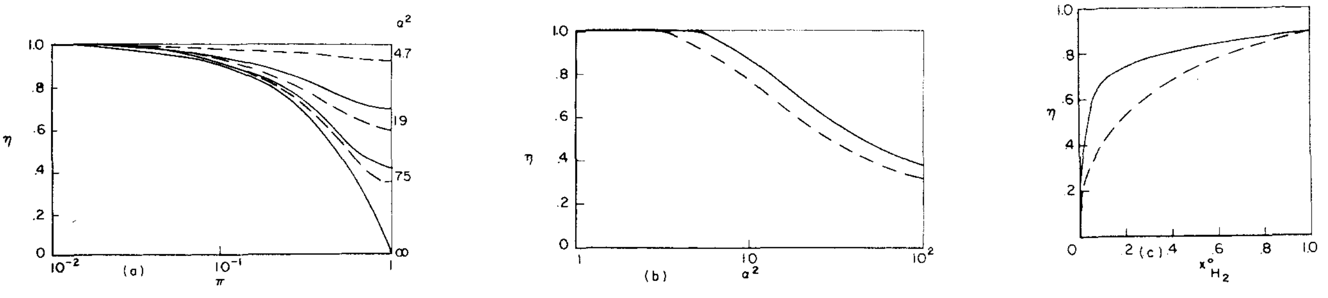

Figure 1. Instantaneous yield versus (a) dimensionless pressure: $\nu = 1.0$, $x^0_{H_2} = 0.5$; (b) dimensionless particle size: $\nu = 1.0$, $\pi \geq 1.0$, $x^0_{H_2} = 0.5$; (c) mole fraction of hydrogen: $\nu = 1.0$, $\pi \geqq 1.0$, $\alpha^2 = 10$. ——— controlling diffusivity. – – – – equal diffusivities.

$$-\frac{\nu}{1-\nu}+f\left(\left(\frac{1-\nu}{6}\right)^{1/2}\alpha\lambda\right)$$

$$-(1-x^o_{H_2})\exp\left\{\frac{\alpha^2}{6}(\lambda^2-1)+\frac{\lambda^3\alpha^2\pi x^c_{V*}}{3}\left(\frac{1}{\lambda}-1\right)\right\}. \tag{14}$$

The case of $\nu = 1$ requires special treatment, because when $\alpha > \alpha_{crit}$ and $\pi > 1$ all volatiles released in the core deposit before reaching the reaction interface. The boundary layer analysis then breaks down as stable volatiles and inerts diffuse in from the sheath to fill the core. Otherwise the analysis parallels that above and determines the position of the reactive interface through

$$1=\frac{\alpha^2}{6}(2\lambda^3-3\lambda^2+1)$$

$$+(1-x^o_{H_2})\exp\left\{-\frac{\alpha^2}{6}(2\lambda^3-3\lambda^2+1)\right\}. \tag{15}$$

In both cases the rapid I-H_2 diffusion increases the penetration of hydrogen and thereby reduces λ, the size of the core.

INSTANTANEOUS YIELD

For rapid devolatilization the deposition within the core reduces the instantaneous yield

$$\eta = 3N_V|_{r=1} = 1-\pi x^c_{V*}\lambda^3 \tag{16}$$

with x^c_{V*} from (8) and λ from (14) or (15). Typical numerical results for η as a function of π, α^2, and $x^o_{H_2}$ are plotted in Figure 1. As indicated above the results differ most from those for equal diffusivities when $\nu \rightarrow 1$ and $x^o_{H_2} \rightarrow 0$ and least when $\nu \rightarrow 0$ or $x^o_{H_2} \rightarrow 1$.

The most important conclusion rests on the qualitatively similar trends. The quantitative differences are significant, but may not be detectable experimentally unless the effective diffusivities within the coal particle are measured independently. If they must be deduced from hydropyrolysis data, the two models may be indistinguishable.

NOTATION

c = constant defined after Eq. 13
D_{ij}, D^e_{ij} = binary diffusivities in gas and within particle, respectively
f = function defined after Eq. 13
N_i = flux of i^{th} species
p = pressure
r = radial position
R = dummy variable
R_i = rate of reaction producing i^{th} species
x_i = mole fraction of i^{th} species
x^o_{H2} = mole fraction of H_2 in bulk gas
y = position measured inward from reaction interface
α^2 = dimensionless particle size (Russel et al., 1979)
γ_1, γ_2 = ratios of binary diffusivities within particle defined after Eq. 4
λ = dimensionless position of reaction interface
η = dimensionless yield (Russel et al., 1979)
π = dimensionless pressure (Russel et al., 1979)
Π = 3.1415 . . .
ν = fraction of volatiles which are reactive

Subscripts

I = inerts
H_2 = hydrogen
V, $V*$ = unreactive and reactive volatiles, respectively.

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Solubility Extrema in Solid-Fluid Equilibria

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Experimental data and theory both support the contention that there is a maximum solubility in solid-fluid equilibria. An example system, naphthalene-ethylene, at temperatures between the upper and lower critical end points and at pressures from 1 to 1000 bar is considered. There is also a solubility minimum in this system.

Recently, several research papers have addressed the question of the solubility of solid, pure solutes into supercritical fluids (Francis and Paulaitis (1980), Johnston and Eckert (1980), Kurnik et al. (1980), Mackay and Paulaitis (1979), McHugh and Paulaitis (1980), Van Leer and Paulaitis (1980). In some of these, naphthalene-ethylene was one of the systems studied. Experimental solubilities could then be compared to earlier data of Tsekhanskaya et al. (1964) to validate the experimental procedure. In the ethylene-naphthalene system, the temperature range is limited to that between the two critical end points (283.9 and 325.3 K). Experimental pressures ranged up to 400 bar. Various equations of state were employed to estimate the fugacity coefficient of naphthalene in ethylene so as to allow a correlation to be developed between experimental solubilities

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