Rapid Hydropyrolysis of Softening Coal Particles—A Modeling Study

Part I: Model Formulation and Parameter Values

A mathematical model is developed for rapid hydropyrolysis of softening coal particles. It is aimed to represent previously measured effects of pressure and particle size on product yields. The model includes a global chemical reaction scheme combined with diffusional transport of hydrogen dependent on the transient physical properties of the coal. Model predictions are compared with experimental data in a companion paper.

GEORG SCHAUB,
W. A. PETERS and
J. B. HOWARD
Department of Chemical Engineering and
Energy Laboratory, Massachusetts Institute
of Technology
Cambridge, MA 02139

SCOPE

The objective of this study was to define and formulate a mathematical model for rapid hydropyrolysis of softening coal particles consistent with the drastic changes in physical properties associated with softening and resolidification. Rapid hydropyrolysis, where coal particles are heated at rates of 100 to 10,000 K/s under high H_2 pressure, is of interest not only as a process for converting coal into CH_4-rich gas and liquids but also in coal gasification with steam where significant partial pressures of H_2 occur. Previous experimental studies (Anthony et al., 1976; Suuberg et al., 1980) indicate that the coal's transient fluidity plays an important role with respect to transport mechanisms involved. For example, a particle size effect on integral product yields had been found with Pittsburgh Seam bituminous coal, a strongly caking—i.e., softening—coal, but not with a lignite which retains a porous structure throughout the experiment. Previous modeling work has either concentrated on hydropyrolysis of coals which retain their porosity (Russel et al., 1979), or—in the case of softening coals—on pyrolysis, i.e., thermal decomposition in the absence of H_2. The resulting models therefore could not adequate represent the experimental results with softening coals.

This modeling study takes advantage of kinetic information from previous investigations of coal hydrogasification and pyrolysis. The study addresses the questions of intra- and extraparticle transport limitations for hydrogen and develops a tentative description of the coal's transient fluidity and its implication for hydrogen transport. The model leads to predictions of particle size and pressure effects which are compared with trends previously measured in a screen heater apparatus.

CONCLUSIONS AND SIGNIFICANCE

A mechanistic concept has been formulated for the chemical reactions and mass transport processes involved in rapid hydropyrolysis of softening coal particles. A global chemical reaction scheme borrowed from previous coal pyrolysis and hydrogasification studies is combined with a concept of intraparticle hydrogen transport, seen as diffusion of either hydrogen dissolved in the coal melt during the plastic period or of gas phase hydrogen in a reconstituted pore matrix after resolidification. The transient coal fluidity is expressed in terms of appearance and disappearance of a plasticizing material called metaplast, which is generated during the coal's pyrolysis reactions. Transport of metaplast away from the coal particle to yield tar is modeled as evaporation-diffusion from the liquid coal surface during the plastic period. The model considers the limiting case of small particles only ($\leq 300\ \mu m$), in order to avoid intraparticle heat and metaplast mass transfer limitations.

Parameter values are obtained from literature data on the kinetics of primary and secondary pyrolysis and hydrogasification reactions, viscosities of gases, liquids and coal-liquid dispersions, H_2 solubility in coal-derived liquids, gas and liquid diffusion, and vapor pressure of tar-related model compounds. Thus the model contains a collection of available information on the individual processes which constitute the complex interaction of H_2 and softening coal particles during rapid hydropyrolysis. It presents a unified conceptualization of the mutual effects of chemical reactions and mass transfer related to the softening process in coal hydropyrolysis.

Georg Schaub is currently with Lurgi GmbH, 6000 Frankfurt 11, West Germany.

INTRODUCTION

The potential of high methane-formation rates during the early stages of coal hydropyrolysis has been known for about 40 years. Various studies, reviewed by Howard (1981), were carried out to elucidate the effect of reaction conditions on these rapid methane-forming reactions.

In the case of bituminous or softening coal, H_2 pressure, temperature and particle size were each found to have a major effect on methane formation rates during the coal's high reactivity period. The experimental data have been used in the formulation of kinetic models, and important progress has been made toward describing some of the effects on reactions rates. However, the detailed coal particle chemistry and physics underlying hydropyrolysis remain poorly understood.

Previous experimental and modeling studies listed in Tables 1 and 2 indicate that the complex interaction of H_2 with coal during and after its thermal decomposition involves coupled chemical reactions and transport processes. Measured effects of particle size on CH_4 and tar yields indicate that transport of H_2 within the coal particle is hindered. This transport limitation has not been analyzed with respect to the drastic changes in the coal's physical properties, namely softening (or melting), resolidification, and changes in pore structure. Another experimental finding is that H_2 pressure exerts a strong effect not only on hydrogasification rates but also on the transient plasticity of bituminous coal, as is found in plasticity measurements. The mechanism of this effect, as well as an analogous effect of inert gas pressure, is not well understood at present.

Given the lack of understanding of rapid hydropyrolysis of bituminous coal, the present study was directed toward the development of a mathematical model based on a quantitative description of the kinetics of the global chemical reactions and transport processes involved.

MODEL DESCRIPTION

General Features

The model has been developed using hydropyrolysis data from a screen heater apparatus which minimizes, by rapid quenching, extraparticle secondary reactions of hydropyrolysis products. This feature is advantageous in studying the processes occurring within the coal particles. A thin layer of pulverized coal is sandwiched between the layers of an electrically heated folded strip of stainless steel screen and subjected to a prescribed temperature-time history which is recorded in each run. Figure 1 shows conditions of a typical screen heater run (Suuberg, 1977) and its representation in the model. In the case of a softening coal, the initially distinct coal particles soften during the plastic period and coalesce to form a thin layer under the combined effects of gravitational forces, swelling, and gas evolution. Since under the present high heating rate conditions the presoftening period contributes only little to the overall hydropyrolysis process, the coal geometry is represented here by a time-invariant rectangular film of thickness equal to that of the original particle diameter.

TABLE 1. STUDIES OF HYDROPYROLYSIS KINETICS AND PRODUCT DISTRIBUTIONS AS BASES FOR THE PRESENT MODEL

Anthony (1974) Anthony et al. (1976)	Screen heater experiments with lignite and bituminous coal; modeling of weight loss kinetics during (hydro-)pyrolysis.
Johnson (1977)	Hydrogasification experiments with low-rank coals in a helical coiled transport reactor; modeling of CH_4 and C_2H_6 formation kinetics.
Suuberg (1977) Suuberg et al. (1979) Suuberg et al. (1980)	Screen heater experiments with lignite and bituminous coal; modeling of individual product formation kinetics during pyrolysis.
Russel et al. (1979)	Modeling of weight loss kinetics during (hydro-)pyrolysis for nonsoftening coals, based on screen heater data.
Sprouse (1980)	Entrained flow reactor model for hydrogasification of bituminous coal tested against experimental data.

TABLE 2. STUDIES OF COAL PLASTICITY AND TAR TRANSPORT EFFECTS DURING (HYDRO-)PYROLYSIS AS BASES FOR THE PRESENT MODEL

Loison et al. (1963)	Review of experimental and modeling studies related to the plastic properties of coal.
Fitzgerald (1956)	Low heating rate plastometer experiments; modeling of coal softening behavior.
van Krevelen (1956)	Low heating rate plastometer experiments; discussion of mechanisms involved.
Kaiho and Toda (1979)	Experiments in a high pressure, low heating rate plastometer in H_2, N_2, Ar, He, CO_2.
Lloyd et al. (1980)	Model for the isothermal behavior of different coals.
Lewellen (1975)	Modeling of volatiles transport and thermal decomposition in plastic coal pyrolysis.
Suuberg et al. (1979) Zacharias (1979) Unger and Suuberg (1981)	Modeling studies of tar formation, transport, and secondary reaction kinetics, based on screen heater experiments with bituminous coal.
Neavel (1982)	Discussion of coal plasticity mechanisms based on liquefaction studies.

The temperature-time history is idealized as a linear heat up and cool down, with a constant maximum temperature during an isothermal holding period. This study concentrates on a regime of coal film thickness where intraparticle heat transfer is not limiting and therefore the coal temperature can be considered to be spatially uniform at all times. The exothermic hydrogenation reaction affects the intraparticle temperature distribution in a direction contrary to the sensible heat transfer. Given the uncertainty in heat of hydrogenation (ΔH_h) during the pyrolysis reactions, its effect was studied by performing model calculations for values of ΔH_h from zero (which corresponds to pyrolysis) to 30 kcal/mol CH_4 formed. Solution of the unsteady heat transfer equation indicates that for the standard temperature-time history in this study

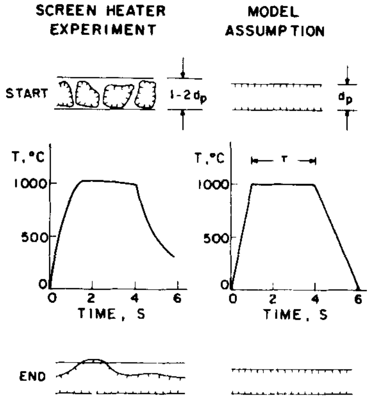

Figure 1. Screen heater experiment and its representation in the model.

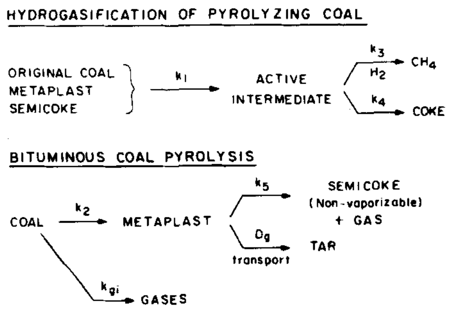

Figure 2. Reaction scheme for bituminous coal hydropyrolysis.

(heating rate 1,000 K/s, final temperature, 1,000°C) and a coal film thickness of up to 300 μm, the temperature difference between the film center and surface never exceeds 2% of the final temperature.

Chemical Reaction Scheme

Since the emphasis in this study is on mass transfer involved in hydropyrolysis, the chemistry is described empirically. Reactant and product species are lumped into groups in a manner based on various earlier studies (see below) of coal hydrogasification and pyrolysis. The lumping criteria are solely the products formed and the characteristic time scales of the reactions, not any mechanistic consideration. As shown in Figure 2, two main features can be distinguished.

1. CH_4 formation through uptake of externally provided H_2 is modeled as a consecutive-competitive reaction scheme, the kinetics and nomenclature of which are similar to a scheme suggested by Johnson (1977) for low-rank coal hydrogasification. During the coal's pyrolysis reactions, a reactive species called active intermediate is formed which can either be hydrogenated to yield CH_4 if H_2 is present or otherwise crosslinked to form a relatively unreactive coke.

2. Access of H_2 to the location of the active intermediate is controlled by the changing physical properties of the coal which are linked with the progress of its pyrolysis reactions. Thus coal fluidity, assumed to govern H_2 penetration into the coal mass during the plastic period, is correlated with appearance and disappearance of a primary coal pyrolysis product called metaplast (van Krevelen et al., 1956). This plasticizing material is generated in depolymerization of the coal and can either decompose or repolymerize to form a semicoke and gas or be transported away from the coal to yield tar. The scheme and rate expressions for coal pyrolysis are based on modeling studies by Suuberg et al. (1979) and Zacharias (1979).

The active intermediate is generated in a first-order reaction from either the original coal, from metaplast still present in the coal mass, or from semicoke. It is implied that part of the active intermediate precursor, namely the metaplast, is transportable and thus subject to a competition between transport, which leads to tar escape from the coal, and secondary reactions, which form gas and semicoke including nontransportable material. This concept is a working hypothesis of the model. The rate expression for CH_4 formation through uptake of external H_2 is Eq. 1 in Table 3. This equation incorporates the effect of H_2 concentration and is the linearized form of an expression suggested by Johnson (1977). The variable x denotes the spatial coordinate along the depth of the coal film, as can be seen in Figure 3.

It is assumed that the concentration of active intermediate C^* is very small and therefore subject to a pseudosteady-state description. The rate constants of the competing hydrogenation and crosslinking reactions k_3 and k_4 appear only as their ratio, which

TABLE 3. CHEMICAL RATE EXPRESSIONS

CH$_4$ Formation

$$r_{CH_4}(x,t) = r_{C^*}(t)\begin{cases} \dfrac{k_3}{k_4} C_{H_2}(x,t) & \text{for } \dfrac{k_3}{k_4} C_{H_2} < 1 \\ 1 & \text{for } \dfrac{k_3}{k_4} C_{H_2} \geq 1 \end{cases} \tag{1}$$

$$r_{C^*(t)} = V_{C^*}(t) k_1 \tag{2}$$

H$_2$ Consumption

$$r_{H_2}(x,t) = 2 r_{CH_4}(x,t) \tag{3}$$

Pyrolysis Gas Formation
During nonisothermal period (linear heat up):

$$r_i(T) = V_i^* k_{io} \exp\left[-\frac{E_{Ai}}{RT} - \frac{k_{io} R T^2}{m E_{Ai}} \exp\left(-\frac{E_{Ai}}{RT}\right)\right] \tag{4a}$$

During isothermal period:

$$r_i(t) = V_i(t) k_i \tag{4b}$$

Metaplast Formation

$$r_{\gamma i \text{ formation}}(t) = (V_\gamma(t) + V_{\gamma H}(t) \nu_\gamma(t)) f(M_{\gamma i}) \sigma_M k_2(t) \tag{5}$$

$$f(M_{\gamma i}) = \frac{1}{\sigma_M \sqrt{2\pi}} \exp\left(-\frac{1}{2} \frac{(M_{\gamma i} - M_0)^2}{\sigma_M^2}\right) \tag{6}$$

$$M_{\gamma i} = M_0 + (i - 4)\sigma_M \qquad i = 1,2, \ldots, 7 \tag{7}$$

$$\nu_\gamma(t) = \frac{1}{L} \int_0^L \begin{Bmatrix} a_1 C_{H_2}(x,t) \\ 1 \end{Bmatrix} dx \quad \begin{matrix} \text{for } a_1 C_{H_2} < 1 \\ \text{for } a_1 C_{H_2} \geq 1 \end{matrix} \tag{8}$$

Metaplast Decomposition

$$r_{\gamma i \text{ decomposition}} = \frac{\rho_{\gamma i}(t)}{\rho_C} k_5(t) \tag{9}$$

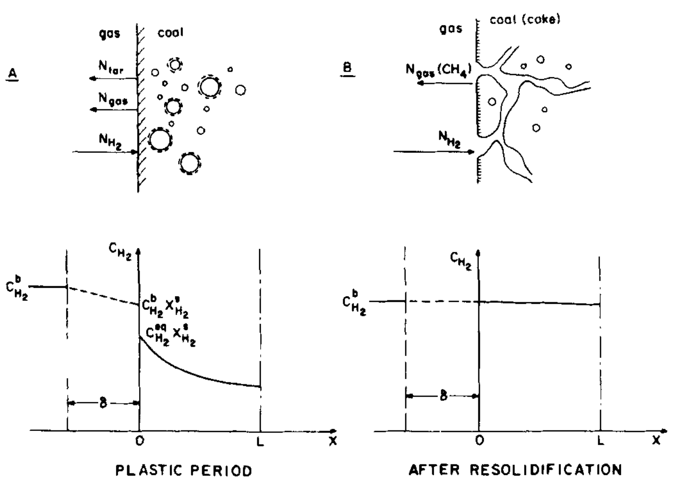

Figure 3. Schematic representation of softening coal hydropyrolysis and mass transfer resistances for H_2 involved during the plastic period (A) and after resolidification (B).

is approximated as being temperature-independent. The amount of active intermediate yet to be formed, V_{C^*}, can be approximated initially as the organic coal fraction reduced by the yields of pyrolysis gases.

Metaplast formation rate, given by Eq. 5, is first-order in the amount yet to be formed ($V_\eta + V_{\gamma H}$). Metaplast, being fragments of the coal's depolymerization reactions, is assumed to consist of many compounds having a Gaussian distribution of molecular weights, Eq. 6. The molecular weight distribution function for the products of coal depolymerization was introduced in earlier studies by Suuberg et al. (1979), Zacharias (1979), and Unger and Suuberg (1981). In the present model the distribution function is represented by seven discrete species, Eq. 7, whose molecular weight affects their transport to yield tar but not the rate constants of their formation and decomposition, the latter being also modeled as a first-order reaction, Eq. 9.

Furthermore, metaplast potential yield is divided into a part, V_γ, which is unaffected by the presence of H_2, and a part, $V_{\gamma H}$, formed only if externally provided H_2 is available. The formation rate of the latter is assumed to be linearly dependent on the average H_2 concentration in the coal film, Eq. 8, with a_1 being an empirical proportionality constant. The concept of the enriching effect of H_2 on metaplast formation is borrowed from a mechanistic view of coal liquefaction (Neavel, 1982) where the presence of hydrogen is considered crucial for stabilization of coal depolymerization products.

The working hypothesis that the effect of H_2 on metaplast reactions is seen as an enhancing effect on formation only is consistent with the observed thermal decomposition behavior of simple aromatic hydrocarbons which Virk et al. (1974) found to decompose with the same rate in H_2 as in inert gas, although the H_2 does affect the product spectrum. However, the effect of molecular size (and thus molecular weight) on thermal decomposition rate that was also analyzed by Virk et al. is not included here for the following two reasons:

(1) The range of molecular weights investigated by Virk et al. (up to chrysene) does not cover the range considered here (250–1,750 g/mol. For aromatic molecules of this size no adequate correlations exist for the molecular weight dependence of the kinetic parameters for thermal decomposition.

(2) Given the lack of experimental data on product tar molecular weight distribution in rapid hydropyrolysis, the main focus of the present study was not product distributions and kinetics of the metaplast decomposition. Variations of metaplast decomposition rates with molecular weight would affect the product tar molecular weight distribution but not necessarily the integral concentration of all metaplast species in the coal particle, the quantity that is being linked to H_2 diffusivity and therefore relevant in the present study.

Formation rates of active intermediate, metaplast, and pyrolysis gases are each described by one activation energy and one preexponential factor. Given the complexity of the chemical reactions involved, this is a simplistic approach. As the thermal decomposition of coal can be assumed to consist of a large number of independent parallel reactions, use of activation energy distribution functions is suitable for kinetic representation (Howard, 1981). However, it is known that sets of parallel reactions can be approximated by one reaction having an activation energy lower than those of the set (Jüntgen and van Heek, 1970), as shown by Zacharias (1979) for tar formation during coal pyrolysis.

Rate expressions for pyrolysis gas formation during the nonisothermal periods are used in the simplified analytical form of Eq. 4a, which is valid here since the rates of heating and cooling of the coal film are linear and the activation energies are much larger than RT.

Hydrogen Continuity Equation

Diffusion and reaction of H_2 in a coal film with half-thickness L under transient conditions is described by the equation of continuity:

$$\frac{\partial C_{H_2}(x,t)}{\partial t} = \left\{\begin{matrix} D_{H_2/CH_4}\mathrm{eff}_{\mathrm{coal}} \\ D_{H_2}(t, \sum \rho_{\gamma i}) \\ D_{H_2/CH_4}\mathrm{eff}(t)_{\mathrm{coke}} \end{matrix}\right\} \frac{\partial^2 C_{H_2}(x,t)}{\partial x^2} - \rho_c r_{H_2}[t, C_{H_2}(x,t)] \quad (10)$$

with initial condition

$$\mathrm{I.C.}\; C_{H_2}(x, t=0) = C^0_{H_2} \quad (11)$$

and boundary conditions

$$\mathrm{B.C.}\; C_{H_2}(x=0,t) = \left\{\begin{matrix} C^b_{H_2}(t) \\ C^{eq}_{H_2}(t) \\ C^b_{H_2}(t) \end{matrix}\right\} x^s_{H_2}[t, C_{H_2}(x,t)]$$

$$\frac{\partial C_{H_2}}{\partial x}(x=L, t) = 0 \quad (13)$$

Equations 10 through 13 apply to the presoftening period as well as the plastic and resolidified stages, with the upper, middle, and lower expressions in braces valid before softening, during the plastic region, and after resolidifcation, respectively.

Equations for multicomponent coupled diffusion can be avoided since diffusion involving several products occurs primarily during the plastic period. This process is modeled as diffusion of dissolved gases in a liquid where coupling is considered not to be important for relatively low gas concentrations. Furthermore, the multicomponent effect can be regarded as lumped into the diffusivity, which is affected by variations in liquid properties due to the presence of dissolved gases. But given other uncertainties in predicting liquid diffusivities at the high temperatures of interest here, neglect of this effect can be regarded as justified. When the coal resolidifies, most of the pyrolysis products have escaped the particle. The gas phase in the reconstituted pore system then mainly consists of H_2 and CH_4, so that diffusion occurs in a binary mixture. Deviation from equimolar counterdiffusion is neglected, given the uncertainty in the stoichiometry of the gasification reaction.

The spatial boundaries of the integration domain are taken as time-invariant, since changes in the shape of the coal film due to coalescence and swelling are not accounted for. The H_2 consumption rate, Eq. 3, represents the stoichiometric relation between CH_4 formation, Eq. 1, and H_2 consumption.

The gas phase mole fraction of H_2 at the coal surface $x^s_{H_2}$, Eq. 12, is affected by H_2 concentration gradients across the external boundary layer due to the countercurrent flow of pyrolysis gases and CH_4 evolving from the coal particle. The resulting drop in $x^s_{H_2}$ is calculated based on the following assumptions:

1. No homogeneous gas phase reactions occur within the boundary layer.
2. Steady state prevails, i.e., extraparticle concentration profiles follow infinitely fast the changes in fluxes due to changes in intraparticle chemical reaction rates.

The resulting expression for the gas phase mole fraction of H_2 at the coal surface $x^s_{H_2}$ is:

$$x^s_{H_2}(t) = \frac{\dfrac{N_{gas}(t)}{N_{H_2}(t)} \exp\left(- \dfrac{N_{H_2}(t)\delta(t)\left(\dfrac{N_{gas}(t)}{N_{H_2}(t)} - 1\right)}{D_g(t)c_g(t)} \right) - 1}{\left(\dfrac{N_{gas}(t)}{N_{H_2}(t)} - 1\right)} \tag{14}$$

where the boundary layer thickness δ and fluxes

$$N_{gas}(t) = \frac{\sum r_{gasi}(t) + r_{CH_4}(t)}{A} \tag{15}$$

$$N_{H_2}(t) = \frac{2r_{CH_4}(t)}{A} \tag{16}$$

are defined as positive quantities in Eq. 14, although in vectorial notation N_{gas} and N_{H_2} should have opposite signs. In Eqs. 15 and 16, r_{CH_4} stands for the overall CH_4 formation rate, which is obtained by integrating Eq. 1 over all x from 0 to L. An expression for the boundary layer thickness δ is derived in the metaplast transport section, below.

The beginning and end of the plastic period and thus use of the appropriate expressions in Eqs. 10 and 12 are defined by means of a critical metaplast concentration. This approach is different from the one proposed by van Krevelen et al. (1956) where the transitions are defined by means of a critical viscosity.

Metaplast Balance Equations

The changing physical properties of the coal are linked with appearance and disappearance of metaplast. The concentration of this plasticizing material is modeled as the sum of concentrations of seven individual species with differnent molecular weights. Each concentration is determined by integration of its balance, Eqs. 17–23:

$$\begin{aligned}\frac{1}{\rho_C}\frac{d\rho_{\gamma 1}(t)}{dt} &= r_{\gamma 1\ \text{formation}}(t, C_{H_2}(x,t)) \\ &\quad - r_{\gamma 1\ \text{decomposition}}(t, \rho_{\gamma 1}) \\ &\quad - r_{\gamma 1\ \text{transport}}(t, \rho_{\gamma 1}, \rho_{\gamma 2}, \ldots, \rho_{\gamma 7})\end{aligned} \tag{17}$$

$$\begin{aligned}\frac{1}{\rho_C}\frac{d\rho_{\gamma 2}(t)}{dt} &= r_{\gamma 2\ \text{formation}}(t, C_{H_2}(x,t)) \\ &\quad - r_{\gamma 2\ \text{decomposition}}(t, \rho_{\gamma 2}) \\ &\quad - r_{\gamma 2\ \text{transport}}(t, \rho_{\gamma 1}, \rho_{\gamma 2}, \ldots, \rho_{\gamma 7})\end{aligned} \tag{18}$$

$$\cdot \qquad \cdot \qquad \cdot \tag{19}$$

$$\cdot \qquad \cdot \qquad \cdot \tag{20}$$

$$\cdot \qquad \cdot \qquad \cdot \tag{21}$$

$$\begin{aligned}\frac{1}{\rho_C}\frac{d\rho_{\gamma 7}(t)}{dt} &= r_{\gamma 7\ \text{formation}}(t, C_{H_2}(x,t)) \\ &\quad - r_{\gamma 7\ \text{decomposition}}(t, \rho_{\gamma 7}) \\ &\quad - r_{\gamma 7\ \text{transport}}(t, \rho_{\gamma 1}, \rho_{\gamma 2}, \ldots, \rho_{\gamma 7})\end{aligned} \tag{23}$$

with initial conditions of the type

$$\rho_{\gamma i}(t = 0) = \rho^0_{\gamma i} \tag{24}$$

Metaplast Transport

Transport of the different molecular weight species away from the coal film is assumed to involve evaporation and diffusion from a liquid surface at which vapor and liquid are in equilibrium. No homogeneous gas phase reactions of the metaplast are considered to occur, given the rapid quenching of the evolving products in the screen heater apparatus. Thus the rate of transport $r_{\gamma i,t}$ is proportional to a diffusion coefficient D_g, a vapor concentration equivalent to the equilibrium vapor pressure p_{vi} at the prevailing temperature, and the external coal surface per unit mass A. For the rectangular coal-film geometry, the transport rate is given by Eq. 25 in Table 4, where f_c accounts for metaplast convection in the gaseous volatiles evolving from the coal, Eq. 26. Calculation of the stagnant gas boundary layer thickness on both sides of the coal film is based on a mass transfer analysis (Zacharias, 1979) for the rectangular film geometry and screen heater conditions. The natural convection of bulk gas around the coal surface is assumed to be driven by a rising column of hot gas above the heated screen. The boundary layer thickness δ, determined by simulating the flow as stagnation flow near a flat plate, is given by Eq. 28. The function ψ in Eq. 29, which is related to the flow field in the vicinity of the stagnation point, is derived from an analysis presented by Schlichting (1960), and is used here as a closed form approximation (Zacharias, 1979).

The velocity of the rising gas column v is given by Eq. 30, where $\Delta\rho_g$ is the difference between the gas density at room temperature (298 K) and at the column temperature, and μ_g is the gas viscosity at the column temperature, which is taken to be the average between that of the screen and room temperature.

Use of Eq. 25 for metaplast transport implies that no metaplast is released from the coal particle as liquid droplets entrained in the flow of gaseous pyrolysis products. Furthermore, it implies that transport is governed solely by the rate of removal of vapor in the external stagnant gas boundary layer. As mentioned earlier, no intraparticle metaplast concentration gradients are considered. A theoretical parametric study of intraparticler metaplast diffusion during the plastic period indicates as follows that this is a good approximation for hydropyrolysis of the thin coal films examined here (thickness up to 300 μm). Steady state metaplast concentration profiles were calculated for a range of metaplast diffusivities in the

TABLE 4. EQUATIONS FOR THE METAPLAST TRANSPORT MODEL

$$r_{\gamma i\ \mathrm{transport}} = f_c A D_g M_{\gamma i} \frac{x_{\gamma i} p_{vi}}{RT\delta} \qquad (25)$$

$$f_c = \frac{\phi}{1-\exp(-\phi)} \qquad (26)$$

$$\phi = u\delta/D_g \qquad (27)$$

$$\delta = \left[\psi\left(\frac{P^*}{100}\right)\right]\left(\frac{1.5\,\mu_g}{2V\rho_g}\right)^{1/2}\left(\frac{\mu_g}{\rho_g D_g}\right)^{1/3} \qquad (28)$$

$$\psi\left(\frac{P^*}{100}\right) = 0.6899\left(\frac{P^*}{100}\right)^3 - 0.2828\left(\frac{P^*}{100}\right)^2 + 1.003\left(\frac{P^*}{100}\right) \qquad (29)$$

$$v = 529.8\,\frac{\Delta\rho_g}{\mu_g}\,\frac{\mathrm{cm}}{\mathrm{s}} \qquad (30)$$

• SI conversion: Pa·s = Poise × 0.1

fluid coal from 10^{-7} to 10^{-3} cm^2/s. The resulting profiles for a film thickness of 300 μm indicate that under typical hydropyrolysis conditions of $p_{H_2} = 69$ atm (6.99 MPa), a metaplast diffusivity of 10^{-5} cm^2/s is high enough to keep the difference between maximum and minimal concentration below 10% of the maximum value. Although estimation of metaplast liquid diffusivity at such high temperatures is questionable, the value 10^{-5} cm^2/s appears adequate in the light of pyrolysis gas bubbles enhancing metaplast diffusion by their growth and motion. The absence of considerable intraparticle metaplast gradients can be attributed to the following phenomena. The elevated external pressure in hydropyrolysis leads to increased transport resistance outside compared to inside the particle. Furthermore, secondary reactions, assumed to be first-order in metaplast concentration, and metaplast formation, correlated with intraparticle H_2 concentration profiles, Eq. 5, smooth the metaplast concentration gradients which would result from transport limitations alone. Thus, in the absence of intraparticle transport limitations for metaplast, the average H_2 concentration defined in Eq. 8 is used to describe a H_2 concentration effect on metaplast formation, Eq. 5.

Introduction of the molecular weight effect on metaplast transport away from the particle adds another aspect to the intraparticle metaplast transport problem. The lower molecular weight and hence more volatile species evaporate faster, leaving the higher molecular weight species behind. The result is a multicomponent diffusion process in the plastic coal, which is not accounted for in the present model.

Presoftening Period

The presoftening period under high heating rate conditions does not significantly contribute to total product formation. The H_2 diffusivity in Eq. 10 is approximated as a time-invariant effective diffusivity in the pore system of the original coal, Eq. 31, Table 5. The boundary condition, Eq. 12, is defined in terms of the H_2 bulk gas phase concentration $C^b_{H_2}$.

TABLE 5. EQUATIONS FOR H_2 DIFFUSIVITY AND SOLUBILITY MODEL

Before and After Plastic Period

$$D_{H_2/CH_4}\mathrm{eff} = \epsilon D_{H_2/CH_4} \qquad (31)$$

Plastic Period

$$D_{H_2} = (k^m_D + k^e_D \sum r_{\mathrm{gas}})\frac{1}{\mu_c} \qquad (32)$$

$$\mu_c(t) = \mu_0 \exp\left(\frac{E_\mu}{RT(t)}\right)\left(\frac{\rho_c}{\sum_i \rho_{\gamma i}(t)}\right)^{2.5} \qquad (33)$$

$$C^{eq}_{H_2} = \mathrm{H}p_{H_2} \qquad (34)$$

$$H = H_0 \exp\left(-\frac{E_s}{RT}\right) \qquad (35)$$

Plastic Period

Once the defined critical metaplast concentration is reached due to the increased formation of metaplast, the coal particles are considered to become plastic. Intraparticle H_2 transport is seen as diffusion of a dissolved gas in a liquid solvent, enhanced by mixing of the solvent caused by growth and motion of bubbles of gas from coal pyrolysis reactions. The plastic coal mass is considered as the solvent, its viscosity varying over a wide range during the plastic period. Hence H_2 diffusivity is modeled in terms of the solvent viscosity μ_c and the formation rate of coal pyrolysis gas, Eq. 32, Table 5. Both k^m_D and k^e_D are empirical proportionality constants, the former describing the molecular diffusivity, the latter an eddy contribution due to the pyrolysis gas stirring the solvent. They must be considered empirical as little is known about multiphase diffusion processes on a molecular scale at temperatures as high as 1,000°C and in a solvent of very complex and transient composition such as the plastic coal mass. The inverse proportionality between D_{H_2} and μ_c stems from information available on diffusion of a small molecule in a viscous solvent. Solute diffusivity at low concentrations, low temperatures, and moderate viscosities was found to be proportional to μ^q where q varies from -0.5 to -1.0, depending on the system (Reid et al., 1977). The diffusivity does not contain any coupling of the various species diffusing in the liquid solvent (H_2 and pyrolysis gases), given the uncertainty in single component diffusivities.

For describing viscosity, the plastic coal is seen as a liquid-solid system with highly transient concentration of the plasticizing material (metaplast). The expression for the actual coal viscosity, Eq. 33, has a temperature-dependent part which gives viscosities of an idealized pure metaplast (at different temperatures) and a second part representing the effect of metaplast concentration. The pure metaplast viscosity does not reflect any non-Newtonian behavior known for coal-related materials such as pitches (e.g., Balduhn and Fitzer, 1980; Nazem, 1980) because of a lack of quantitative information which could be translated into a mathematical representation. The effect of chemical composition is not represented although known from coal liquefaction products as an effect of asphaltene and preasphaltene content, average molecular weight, and H-bonding interactions. However, the high heating rates of interest here, together with high effective activation energies for viscosities of coal-related viscous fluids are assumed to make the temperature effect stronger than any effect of chemical composition.

The effect of metaplast concentration in Eq. 33 is described by a correlation suggested by Fitzgerald (1956) for pyrolyzing coal. It is based on a rigorous theoretical approach for suspended spheres in a liquid. Use of this correlation here implies extrapolation to low concentrations of the plasticizing material, at the beginning and toward the end of the plastic period. It stands among many others developed on a theoretical, semiempirical, or empirical foundation for dispersed systems (Rutgers, 1962).

Formulation of the boundary condition, Eq. 12, implies validity of Henry's law at the coal surface during the plastic period, Eqs. 34, 35, based on experimental data for systems and conditions pertinent to coal hydroliquefaction (Guin et al., 1977; Lin et al., 1981). Thus, Henry's law is assumed to be valid at the higher temperatures of interest in rapid hydropyrolysis.

Period After Resolidification

Once the metaplast concentration goes through its maximum and decreases below the defined critical value, the coal film is assumed to resolidify and form a porous coke structure, Figure 3B. Most of the metaplast has either evaporated or decomposed. Consequently, instead of the liquid phase diffusivity for dissolved H_2, an effective pore diffusivity is used in the continuity expression, Eq. 10. Most of the coal pyrolysis gases have escaped the particle by that time and the gas phase in the pores consists essentially of H_2 and the main hydrogasification product CH_4. Therefore, an effective binary pore diffusivity is used, Eq. 31.

The geometrical factor ϵ in Eq. 31 includes the porosity of the resolidified coke and the tortuosity of the pore system, and is assumed to remain invariant with extent of reaction. The binary diffusivity is considered to be a bulk diffusivity, given the short mean free path under H_2 pressure in hydropyrolysis and the high large-scale porosity of the coke (Howard, 1981). The rate parameter k_3/k_4 in the CH_4 formation rate expression, Eq. 1, now has a different value than during the plastic period, as the appropriate H_2 concentration in Eq. 1 is no longer a liquid phase concentration but the gas phase concentration in the pores.

As during the presoftening period, the boundary condition, Eq. 12, is defined in terms of the H_2 bulk gas phase concentration instead of the Henry's law equilibrium concentration used during the plastic period.

Predicted Quantities

Solution of the equations yields intraparticle H_2 concentration profiles, intraparticle metaplast concentration, coal mass viscosity, H_2 diffusivity, gas phase mole fraction of H_2 at the coal surface, and global chemical reaction rates during hydropyrolysis. Integration of CH_4 formation rate, as affected by intraparticle H_2 concentration profiles, over time leads to the integral CH_4 yield:

$$\text{yield } CH_4 = \int_0^{t'} r_{C^*}(t)\left[\frac{1}{L}\int_0^L \left\{\begin{matrix}\frac{k_3}{k_4} C_{H_2}(x,t) \\ 1\end{matrix}\right\} dx\right] dt \quad (36)$$

This quantity corresponds to the yield determined experimentally in the screen heater reactor, where t' is taken as the duration of the experiment Similarly, the total tar yield results from integration of the metaplast transport rates, Eq. 25, over time.

$$\text{yield tar} = \sum_i \left(\int_0^{t'} f_c(t) A D_g(t) M_{\gamma i} \frac{x_{\gamma i}(t) P_{vi}(t)}{R T(t) \delta(t)} dt\right) \quad (37)$$

Numerical Solution

The continuity equation for H_2, Eq. 10, and the coupled balance equations for the different metaplast species, Eqs. 17–23, were integrated numerically using implicit finite-difference techniques. Backward differences in the time variable were used for both the H_2 continuity equation, a linear parabolic *PDE*, and the metaplast balance equations. The solution method for the latter, however, was explicit with respect to C_{H_2}, Eqs. 5 and 8. Step sizes in time and in the dimensionless spatial variable $\bar{x} = x/L$ were 0.025 s and 0.05, respectively.

PARAMETER VALUES

Chemical Reaction Rates

Rate parameters for formation of the reactive species and its subsequent hydrogenation/crosslinking are calculated from data obtained by Johnson (1977) and given in Table 6. Although Johnson's hydrogasification experiments were carried out with low rank coals, the resulting rate parameters were shown to yield reasonable consistency when applied to bituminous coal data. In this study the parameters from his distributed activation energy model are represented by one activation energy E_{A1} and the proper preexponential factor k_{1o}, derived from a best-fit analysis. The parameter values for k_3/k_4 before and after resolidification incorporate linearization of Johnson's original expression, with the ratio k_3/k_4 assumed to be independent of temperature. The value for the ultimate yield of reactive species $V^*_{C^*}$ is based on the assumptions that all organic material in the coal, less the ultimate pyrolysis gas yields, potentially is hydrogentable and that its carbon content is higher (82 wt. %) than in the original coal (67.8 wt. %) (Suuberg et al., 1980).

TABLE 6. RATE PARAMETERS FOR C^* AND CH_4 FORMATION (CALCULATED FROM JOHNSON, 1977)

$V^*_{C^*}$ = 0.04 mol.·C/g coal[†]
k_{1o} = 2.4×10^2 s^{-1}
E_{A1} = 15,900 cal/mol
k_3/k_4 = 1,250 cm^3/mol during plastic period
k_3/k_4 = 460 cm^3/mol after resolidification

[†] Estimate for Pittsburgh Seam bituminous coal (see text).

TABLE 7. RATE PARAMETERS FOR METAPLAST AND PYROLYSIS GAS FORMATION (FROM ZACHARIAS, 1979)

	V^* g/g coal[*] mol/g coal[**]	k_o s^{-1}	E_A cal/mol
Metaplast	0.420[†]	1.23×10^3	14,900
	0.162[†]	1.23×10^3	14,900
Pyrolysis gas			
CH_4	1.03×10^{-3}	5.13×10^{15}	72,900
CO	7.46×10^{-4}	9.55×10^{14}	71,100
CO_2	1.95×10^{-4}	4.47×10^7	33,900
	1.39×10^{-3}	2.82×10^{11}	70,500
C_2H_4	1.79×10^{-3}	4.17×10^{12}	57,700
C_2H_6	1.40×10^{-4}	6.03×10^{12}	57,400
HC gas	3.07×10^{-4}	1.15×10^{12}	52,900
HC liq	2.03×10^{-4}	6.31×10^{11}	52,200
H_2O	2.16×10^{-3}	3.24×10^{12}	71,800

---

[*] For metaplast.
[**] For pyrolysis gas.
[†] Authors' estimate (see text).
$a_1 = 5.0 \times 10^3$ cm^3/mol
$M_o = 1.0 \times 10^3$ g/mol
$\sigma_M = 2.5 \times 10^2$ g/mol

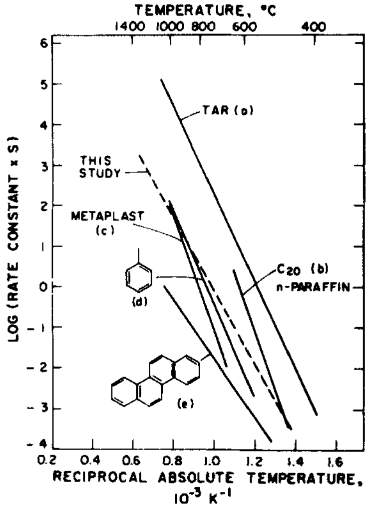

Figure 4. Rate constants for decomposition of metaplast and related model compounds. (a) Zacharias, 1979; (b) Fabuss et al., 1964; (c) Unger and Suuberg, 1981; (d) Benson, 1967; hydrodealkylation P_{H_2} = 69 atm (6.99 MPa); (e) Virk et al., 1974.

Rate parameters used for metaplast and pyrolysis gas formation are noted in Table 7. With the exceptions mentioned below they are all taken from a best-fit analysis of rapid pyrolysis of Pittsburgh Seam bituminous coal (Zacharias, 1979), based on experimental work by Suuberg (1977). The ultimate yield of metaplast represents the organic fraction of Pittsburgh Seam bituminous coal less the ultimate yields of pyrolysis gases. It is subdivided into two parts, one unaffected and one affected by the presence of H_2, as defined in Eq. 5. The subdivision, together with the definition of the constant a_1, Eq. 8, is purely empirical. Mean and standard deviations of the metaplast molecular weight distribution function are in a range indicated in related pyrolysis studies (Zacharias, 1979; Unger and Suuberg, 1981; Gavalas and Oka, 1978).

The choice of rate parameters for metaplast decomposition reactions is based on kinetic information on pyrolysis reactions of related model compounds and on other modeling studies of tar and metaplast secondary reactions. Rate parameters used in this study ($k_{5o} = 1.0 \times 10^9\ s^{-1}$, E_{A5} = 42,000 cal/mol result in rate constants which are representative of the range given in the related literature, as shown in Figure 4.

Physical Properties

Direct measurements of the activation energy and preexponential factor for metaplast viscosity, Eq. 33, were not available. These quantities were therefore estimated from data on related materials and extrapolated to the high temperatures of interest here. Coal-derived pitches and products from various coal liquefaction processes are most closely related to the metaplast formed in the primary coal decomposition reactions. The parameter values $\mu_o = 4.8 \times 10^{12}$ P, and E_μ = 45,830 cal/mol for the shear rate independent activation energy used in this study are extracted from Nazem's (1980) work on different pitches. The preexponential factor for metaplast is assumed to be a factor of 100 larger than the one for the pitches. The critical metaplast mass concentration which defines the beginning and end of the coal's plastic period is assumed to be 10^{-2} g/cm^3. The initial coal density ρ_c^o is 1.0 g/cm^3.

For the empirical constants in the H_2-diffusivity expression during the plastic period, Eq. 32, k_D^m and k_D^e values of 10^{-4} g·cm/s^2 and 1.0 g^{2}cm/mol·s respectively are used. The range of resulting H_2 diffusivities is reasonable for diffusion of a gas dissolved in a liquid solvent. Values of the activation energy and preexponential factor for H_2 solubility in the plastic coal mass, Eq. 35, are E_μ = 750 cal/mol and $H_o = 1.2 \times 10^{-5}$ mol/cm^2·atm, as calculated from data by Guin et al. (1977).

Gas phase diffusivity of tar vapor in a mixture with H_2 as the predominant compound—Eqs. 14, 25, and 28—is assumed to be

$$D_g = 0.1 \left(\frac{T}{273}\right)^{1.5} \left(\frac{1}{P}\right) \tag{38}$$

(Suuberg et al., 1979). In the absence of data on high-temperature gas phase diffusivities in H_2 of tar molecules of different size and structure, the above expression developed for the similar system tar/He is assumed to be a reasonable approximation. For estimating vapor pressures of the different molecular weight metaplast species, in Eq. 25, an empirically based correlation is used (Homann, 1977):

$$p_{v_i} = 1.23 \times 10^5 \exp\left(-\frac{236\, M_{\gamma i}^{0.654}}{T}\right) \tag{39}$$

This equation was shown to apply to aromatic and partially hydrogenated aromatic hydrocarbons with or without small aliphatic side chains (Zacharias, 1979). Its application here implies that the enthalpies of vaporization of the metaplast species have the same empirical molecular weight dependence as the aromatic and partially hydrogenated hydrocarbons. For calculation of μ_g and ρ_g, Eq. 28, the boundary layer is assumed to be isothermal at the temperature of the screen and coal, and to be composed mostly of H_2. The H_2 viscosity is given by

$$\mu_g = 2.2222 \times 10^{-6}\ T^{0.6487} \tag{40}$$

according to a correlation based on Chapman-Enskog theory and suggested by Reid et al. (1977). For calculation of ρ_g, H_2 is assumed to behave as an ideal gas.

NOTATION

A = external surface area of coal, cm^2/g
a_1 = proportionality constant in metaplast formation rate, cm^3/mol
C = molar concentration, mol/cm^3
$C_{H_2}^{av}$ = molar concentration H_2, average over x, mol/cm^3
d_p = particle diameter, cm
D_{H_2} = H_2 diffusivity in plastic coal mass, cm^2/s
$D_{H_2/CH_4}{}^{eff}$ = effective pore diffusion coefficient for the binary mixture H_2/CH_4, cm^2/s
D_g = binary gas phase diffusivity H_2/tar, cm^2/s
E_{Aj} = activation energy for reaction j, cal/mol
E_S = heat of solution of H_2 in plastic coal mass, cal/mol
E_μ = activation energy of metaplast viscosity, cal/mol
$f(M_{\gamma i})$ = distribution function for metaplast molecular weight
f_c = multiplying factor, convective contribution to tar evaporation
H, H_o = Henry's law constant, preexponential factor, respectively, mole/cm^2·atm
k_1 = rate constant for active intermediate formation, s^{-1}
k_2 = rate constant for metaplast formation, s^{-1}
k_3/k_4 = ratio of rate constant for hydrogenation and cross-linking of the active intermediate, cm^3/mol
k_5 = rate constant for metaplast decomposition, s^{-1}
k_{jo} = pre-exponential factor for reaction j, s^{-1}
k_D^m, k_D^e = proportionality constants in D_{H_2}—correlation, gcm/s^2, g^{2}cm/mol·s
L = half-thickness of coal film, cm or μm
M = molecular mass, g/mol

M_o = mean, molecular mass distribution function, g/mol
m = heating rate, K/s
N = flux, molar, mol/cm^{2}s
p = pressure, atm
p_{H_2} = partial pressure H_2, atm
p_{vi} = vapor pressure, pure metaplast species i, atm
r_i = formation rate of species i (except metaplast), mol/g·s
$r_{\gamma i}$ = chemical reaction or evaporation rate for metaplast species i, mass fraction of original coal per second, s^{-1}
R = the gas constant, cal/mol·K
T = temperature, K or °C
t = time, s
t' = overall duration of a screen heater experiment, s
u = linear velocity of evolving pyrolysis gas, cm/s
v = linear velocity of rising gas column above heated screen, cm/s
V_i^* = ultimate yield of species i (except metaplast), mol/g coal
V_γ^* = ultimate yield of metaplast, g/g coal
$V_{\gamma H}^*$ = ultimate additional yield of metaplast in the presence of H_2, g/g coal
V_i = amount of species i yet to be formed, mol/g coal or g/g coal
x = space coordinate, cm
x_{H_2} = mole fraction of H_2 in gas
$x_{\gamma i}$ = mole fraction of metaplast species i in mixture of metaplast species

Greek Letters

γ = metaplast (subscript)
δ = thickness of stagnant gas boundary layer, cm
ϵ = geometrical factor, effective pore diffusivity
μ_c = viscosity of coal mass, Poise
μ_o = preexponential factor in Andrade equation, Poise
μ_g = viscosity of gas phase, Poise
ν_γ = fraction of metaplast formed in the presence of H_2
ρ_c = mass density of coal, g/cm^3
$\rho_{\gamma i}$ = intraparticle mass concentration of metaplast species i, g/cm^3
ρ_g = mass density of gas phase, g/cm^3
σ_M = standard deviation of molecular mass distribution function, g/mol
ϕ = mass Peclet number, $\phi = u\delta/D$
ψ = stream function, used in stagnation flow analysis

Superscripts

b = bulk
eq = equilibrium
o = value at $t = 0$
s = at the coal surface

Subscripts

C^* = active intermediate
g = bulk gas phase
γ_i = metaplast species i

LITERATURE CITED

Anthony, D. B., "Rapid Devolatilization and Hydrogasification of Pulverized Coal," Sc.D. Thesis, *Dept. Chem. Eng.*, M.I.T., Cambridge, MA (1974).

Anthony, D. B., et al., "Rapid Devolatilization and Hydrogasification of Bituminous Coal," *Fuel*, **55**, 121 (1976).

Balduhn, R., and E. Fitzer, "Rheological Properties of Pitches and Bitumina up to Temperatures of 500°C," *Carbon*, **18**, 155 (1980).

Benson, S. W., and R. Shaw, "Kinetics and Mechanism of Hydrogenolysis," *J. Chem. Phys.*, **47**, 4,052 (1967).

Fabuss, B. M., J. O. Smith, and C. N. Satterfield, "Thermal Cracking of Pure Saturated Hydrocarbons," *Adv. Petr. Chem. Ref.*, **9**, 156 (1964).

Fitzgerald, D., "Kinetic Study of Coal Carbonization in the Plastic Zone," *Fuel*, **35**, 178 (1956).

Gavalas, G. R., and M. Oka, "Characterization of the Heavy Products of Coal Pyrolysis," *Fuel*, **57**, 285 (1978).

Guin, J. A., et al., "Kinetics and Solubility of Hydrogen in Coal Liquefaction Reactions," *Liquid Fuels from Coal*, R. T. Ellington, Ed., 133, Academic, New York (1977).

Homann, K. H., 16th Int. Symp. on Combustion, 717, Combustion Inst., Pittsburgh (1977). This was a comment on a presented paper. Many comments and author(s)' replies are reproduced in final version of Proceedings.

Howard, J. B., "Fundamentals of Coal Pyrolysis and Hydropyrolysis," *Chemistry of Coal Utilization*, 2nd supp. vol., M. A. Elliott, Ed., Ch. 12, Wiley, New York (1981).

Johnson, J. L., "Kinetics of Initial Char Hydrogasification Stages," Am. Chem. Soc., Div. of Fuel Chem., *Preprints*, **22**(1), 17 (1977).

Jüntgen, H., and K. H. van Heek, "Reaktionsabläufe unter nichtisothermen Bedingungen," *Fortschritte der Chemischen Forschung*, **13**, 601, Springer-Verlag, Berlin (1970). (Translated by Belov and Assoc., Denver, CO, APTIC-TR-0776).

Kaiho, M., and Y. Toda, "Change in Thermoplastic Properties of Coal Under Pressure of Various Gases," *Fuel*, **58**, 397 (1979).

Lewellen, P. C., "Product Decomposition Effects in Coal Pyrolysis," M.S. Thesis, Dept. Chem. Eng., M.I.T., Cambridge, MA (1975).

Lin, H. M., et al., "Solubilities of Hydrogen and Methane in Coal Liquids," *Ind. Eng. Chem. Proc. Des. Dev.*, **20**, 253 (1981).

Lloyd, W. G., H. E. Francis, and M. R. Yewell, Jr., "A Model for the Isothermal Plastometric Behavior of Coals," Am. Chem. Soc., Div. of Fuel Chem., *Preprints* **25**, 128 (1980).

Loison, R., et al., "The Plastic Properties of Coal," *Chemistry of Coal Utilization*, Suppl. Vol., H. H. Lowry, Ed., Wiley, New York (1963).

Nazem, F. F., "Rheology of Carbonaceous Mesophase Pitch," *Fuel*, **59**, 851 (1980).

Neavel, R. C., "Coal Plasticity Mechanism: Inferences from Liquefaction Studies," *Coal Science*, Vol. 1, M. L. Gorbaty, J. W. Larsen, I. Wender, Eds., 1, Academic Press, New York (1982).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd Ed., 392, 567, McGraw-Hill, New York (1977).

Russel, W. B., D. A. Saville, and M. I. Greene, "A Model for Short Residence Time Hydropyrolysis of Single Coal Particles," *AIChE J.*, **25**, 65 (1979).

Rutgers, J. R., "Relative Viscosity and Concentration," *Rheologica Acta* **2**, 305 (1962).

Schlichting, H., *Boundary Layer Theory*, 4th Ed., 78, McGraw-Hill, New York (1960).

Sprouse, K., "Modeling Pulverized Coal Conversion in Entrained Flows," *AIChE J.*, **26**, 964 (1980).

Suuberg, E. M., "Rapid Pyrolysis and Hydropyrolysis of Coal," Sc.D. Thesis, Dept. Chem. Eng., M.I.T., Cambridge, MA (1977).

Suuberg, E. M., W. A. Peters, and J. B. Howard, "Product Compositions and Formation Kinetics in Rapid Pyrolysis of Pulverized Coal—Implications for Combustion," 17th Int. Symp. on Combustion, 117, Combustion Inst., Pittsburgh (1979).

Suuberg, E. M., W. A. Peters, and J. B. Howard, "Product Compositions in Rapid Hydropyrolysis of Coal," *Fuel*, **59**, 405 (1980).

Unger, P. E., and E. M. Suuberg, "Modeling the Devolatilization Behavior of a Softening Bituminous Coal," 18th Int. Symp. on Combustion, 1203, Combustion Inst., Pittsburgh (1981).

van Krevelen, D. W., F. J. Huntgens, and H. N. M. Dormans, "Chemical Structure and Properties of Coal, XVI," *Fuel*, **35**, 462 (1956).

Virk, P., L. E. Chambers, and H. N. Woebcke, "Thermal Hydrogasification of Aromatic Compounds," *Coal Gasification*, Adv. in Chem. Ser. No. 131, 237, Am. Chem. Soc., Washington, DC (1974).

Zacharias, M. W., "Analysis of Product Yields from Rapid Pyrolysis of Bituminous Coal," M.S. Thesis, Dept. Chem. Eng., M.I.T., Cambridge, MA (1979).

Manuscript received Aug. 12, 1983; revision received Sept. 5, 1984, and accepted Sept. 11.