

**The Significance of Transport Effects in Determining
Coal Pyrolysis Rates and Yields**

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INTRODUCTION

The recent search for robust but mathematically simple models of coal pyrolysis has led to many significant advances in the area of modeling the wide range of chemical reactions responsible for many key phenomena (gas release, tar formation). It has also become clear that transport phenomena cannot be disregarded in such models. There has emerged a debate concerning the role of heat transfer and various mass transfer processes in determining both the overall timescales of pyrolysis, and the compositions of products from these processes. Many of the earlier theories concerning the role of transport processes in coal pyrolysis were reviewed in various recent publications (Howard, 1981; Gavalas, 1982; Suuberg, 1985). It seems appropriate in the context of this symposium to review some recent developments and conclusions.

THE ROLE OF HEAT TRANSFER

THE HEAT OF PYROLYSIS

It is instructive to consider exactly what is meant by the term "heat of pyrolysis". This term has been used in many different ways by many different workers, and as a result there is some confusion about the magnitude of the term and whether it even warrants inclusion in any particular analysis. The various possible components of the heat of pyrolysis are:

1. The sensible enthalpy of heating the coal and its decomposition products to a particular temperature.
2. The enthalpy of the actual decomposition reactions.
3. The heat of vaporization of any condensed phase decomposition products that ultimately escape the particle by evaporation (i.e. not all tar molecules evaporate immediately when formed in the coal- they must diffuse first to a surface at which they can evaporate).

Some species essentially evaporate as they are formed (e.g. CO₂), and it is customary to lump the heat of evaporation and heat of reaction into a single term (the enthalpy of reaction) in those cases. Under the conditions of relevance in coal pyrolysis, only in the case of formation of the heavy tars will the distinction between steps 2 and 3 above be important.

Most, though not all workers in the field, have sought to distinguish between the contributions of items 1 and 2 to the heat of pyrolysis. Few workers have tried to distinguish between all three effects. Many of the experiments upon which estimates of the heat of pyrolysis are based simply are not designed so as to permit the distinctions to be drawn. For example, a calorimetric experiment in which a sample is pyrolyzed in the interior of a calorimeter (Davis, 1924) will not take into account the heat effect due to item 3 above- in addition to the recondensation of tars inside the calorimeter, one will also have to generally contend with condensation of water and lighter oils as well. The corrections due to such condensation effects (which are

generally unlikely in actual pulverized gasification or combustion processes) may be difficult to make, even if the composition of the products is known. Other types of experimental systems have not lent themselves well to separation of sensible enthalpy and reaction enthalpy effects. Much of the difficulty derives from the fact that the enthalpy effects due to reaction and evaporation processes are small, and of the same order of magnitude as sensible enthalpy effects.

The work of Davis and Place (1924) is often cited as evidence that the heat of pyrolysis is small enough to neglect. These workers however pointed out several important facts:

1. The net heat of pyrolysis varies quite a bit with rank
2. The heat of pyrolysis that will be reported from any experiment depends upon the conditions under which pyrolysis is performed.
3. Related to the above, the heat effects of pyrolysis involve a series of endo- and exotherms which sum to the total heat of pyrolysis.

Davis and Place reviewed some earlier relevant literature that suggested many of the same uncertainties that are cited today--the variability of apparent heats of pyrolysis was large, with values ranging from 1060J/g endothermic to 837J/g exothermic. In their own calorimetric work, Davis and Place found apparent enthalpies of reaction that were in all cases less than 400J/g endothermic. The lower ranks of coal were observed to exhibit the largest endothermic reaction enthalpies, when a correction was applied to take into account the latent heat of condensation of water. Higher temperatures seemed to promote the occurrence of more endothermic processes, as did the addition of hydrogen to the gaseous environment (Davis, 1924). It is important to note that this work involved slowly heated samples, pyrolyzed at low temperatures. No corrections were included for the latent heat of evaporation of tars. It is not clear how reliably these results can be extrapolated to the higher temperature and heating rate conditions of pulverized coal processing.

Some years later, Mahajan et al. (1975) studied the same problem using differential scanning calorimetric techniques (DSC). They obtained qualitatively similar results to those of Davis and Place, in that their enthalpies of pyrolysis ranged from about 80J/g exothermic to 250J/g endothermic.

Burke and Parry (1927) provided a different viewpoint to the study of this problem. They distilled coals to 870K in an open retort, such that all the tar that was evolved from the bed could escape in the vapor state, and thus at least some contribution of a latent heat of tar evaporation was included. Also, they did not separate out sensible enthalpy effects from reaction enthalpy and latent heat effects in their experiments. The net heat consumed by a Colorado subbituminous coal was 1109J/g, while a Pittsburgh high volatile bituminous coal consumed 946J/g. An attempt was made by the authors to factor out the contribution of sensible enthalpy, and they concluded that the values of 16J/g (Pitt. coal) and 198J/g (Colo. coal), both exothermic, were in reasonable agreement with the results of Davis and Place (not including latent heat corrections). These values demonstrate very well the difficulty that will be encountered in any attempt to factor out sensible enthalpies by calculation--the values are sufficiently large compared to the reaction enthalpy terms that the calculations cannot be considered reliable, except to provide an order of magnitude estimate.

A number of subsequent attempts have been made to estimate the heats of pyrolysis, including the sensible enthalpy terms. The work of Kirov (1965) has led to a correlation for the heat of coking:

$$Q(J/g) = 343 + 1.20T$$

where T is the temperature of coking in centigrade (see also Sharkey and McCartney, 1981). The work of Lee (1968) suggests a similar correlation:

$$Q(J/g)=[0.728+8.28 \times 10^{-4}T+ (1.38+2.30 \times 10^{-3}T)V](T-21)$$

where V is the volatile matter content of the coal. Using either method yields fair agreement with the earlier cited data of Burke and Parry, though obviously the first correlation's use is restricted to coking coals. The success of such simple correlations must again be ascribed to the fact that sensible enthalpy terms dominate the estimates.

The above viewpoint is apparently at odds with that of Baum and Street (1971), who imply that there is a distinct heat of vaporization which has to be supplied in order for volatiles to escape. The value cited in that work is 627.9J/g of coal, and is based upon the authors' own experiments. This value is considerably higher than most estimates of the heat of reaction, and most estimates of the latent heat of tar volatiles evaporation. It is difficult to obtain data on the latent heats of vaporization of the heavy tars of interest in coal pyrolysis. Briggs and Popper (1957) proposed a correlation for the latent heat of vaporization of "tar oils" which has the form:

$$\Delta H_V(J/g)=S_{20}(485.8-0.598T_b)$$

where S_{20} is the specific gravity of the tar at 20°C and T_b is its boiling point in K. The difficulty in using this correlation for coal tars is that their boiling points are not well known. To address the need for estimates of tar vapor pressures, Unger and Suuberg (1983) developed a crude correlation as a function of molecular weight alone, based on limited data on the vapor pressure of ring compounds with sidechains:

$$P^{\circ}(\text{atm})=5756 \exp(-255M^{.586}/T)$$

where M is the molecular weight of the tar, T is the temperature in K. A "typical" tar molecular weight of 600 (see Unger and Suuberg, 1984) would be estimated to have $T_b=1250\text{K}$. This is clearly outside the range of applicability of the above correlation. Instead, applying the Clausius-Clapeyron equation to the vapor pressure equation itself yields

$$\Delta H_V(J/g) \approx 2120M^{-0.414}$$

Another similar analysis by Homann (1976) yields:

$$\Delta H_V(J/g) \approx 1960M^{-0.346}$$

These correlations give estimates for a typical tar species of 600 molecular weight of $\Delta H_V=150$ to 215J/g. To compare this value to earlier cited estimates of heats of pyrolysis, one can note that tar yields represent typically no more than 1/4 to 1/3 the mass of a particle; thus the latent heat of tar evaporation is a sink of order 70J/g coal if all tar had $M=600$. A lower assumed molecular weight does not change the conclusion much--e.g. $M=200$ gives a latent heat requirement of about 100J/g coal. Thus, the latent heat term is of the same order of magnitude as the measured heats of pyrolysis reported earlier.

Estimation of the reaction enthalpy term is also quite difficult, because there are so many possible contributing processes. Attempts at estimation of this term by measurement of pyrolysis products, and then comparing heats of combustion of starting material and final products have been difficult (one such attempt is described in Suuberg et al., 1978). All that can be said as a result of these efforts is that at high heating rates (1000K/s), the general conclusion of near-thermoneutrality seems to still apply. Recent experiments in which the temperature response of a coal-loaded, electrically heated wire grid is carefully examined seem, upon rough calculation, to support the earlier estimates of the magnitude of the heat of pyrolysis as well (Freihaut and Seery, 1983).

HEAT TRANSFER CONTROL

It appears, then, that the weight of evidence still favors the viewpoint that the heat of pyrolysis is dominated by sensible enthalpy requirements for heating the particle to reaction temperature, and that the reaction enthalpy requirements and

latent heat requirements are both modest (not more than 1/4 to 1/2 of the total). This means that the classical analysis of heat conduction in a solid, in which the reaction enthalpy and latent heat effects are neglected, still appears reasonable. Under these circumstances, the characteristic time for diffusion of heat in the absence of reaction heat effects is:

$$t_H = 0 \quad (r^2/\alpha)$$

where r is the particle radius and α the thermal diffusivity of the particle; the latter is temperature dependent, but of order $1 \times 10^{-3} \text{cm}^2/\text{s}$ at low temperatures (Badzioch et al., 1964). The timescale for pyrolysis reaction may be defined:

$$t_R = 0 \quad [A \exp(-E/RT)]^{-1}$$

Naturally, the absence of heat transfer limitations during reaction is assured by $t_R \gg t_H$, or, approximately:

$$r < [0.1\alpha \exp(E/RT)/A]^{-1}$$

This is similar to the criterion suggested by Gavalas (1982). The selection of A and E has a significant effect on the conclusions, however. A conservative approach might involve selection of these parameters for the fastest reaction of interest. This might be, for example, the initial CO_2 evolution reactions in pyrolysis of lignites, for which $A = 2.1 \times 10^{11} \text{s}^{-1}$, $E = 151 \text{kJ/mol}$ (Suuberg et al., 1978). Selecting as an arbitrary ambient temperature 1650K, heat transfer limitations are apparently not important only if $r < 0.05 \mu\text{m}$! For a temperature of 1200K, $r < 0.4 \mu\text{m}$. These radii are considerably smaller than those calculated by Gavalas, and serve to illustrate the importance of the choice of kinetic constants in such analyses. Recognizing that coal pyrolysis involves a broad spectrum of reactions, each with its own kinetic parameters, the so-called distributed activation energy models have been developed. If one uses a mean activation energy to obtain a characteristic timescale for all pyrolysis reactions, the conclusions change markedly. For example, Anthony et al. (1975) report that for pyrolysis of a lignite, the mean value of E is 204kJ/mol , $A = 1.07 \times 10^{10} \text{s}^{-1}$. With these kinetic parameters, such a timescale analysis suggests that at 1200K, $r < 30 \mu\text{m}$ is sufficient to assure the absence of heat transfer limitations. It is also apparent that the choice of temperature has an effect on the conclusions reached above. It may legitimately be asked if the use of the ambient temperature as the characteristic temperature may not be too conservative, since the particle may be well below this temperature during much of the process. This aspect will be clarified below.

Another analysis that has been suggested as a method of determining whether heat transfer limitations are significant is that due to Field et al. (1967). In this analysis, the magnitude of the temperature gradient in a particle is examined (generally the center of the particle is cooler than the ambient). The magnitude of the surface to center temperature gradient is, conservatively:

$$\Delta T = rq/2k$$

where q is the surface heat flux and k the thermal conductivity of the particle. For a $100 \mu\text{m}$ particle being radiatively heated in a 1650K environment, the maximum value of q is roughly 40W/cm^2 . Taking a typical $k = 2.5 \times 10^{-3} \text{W/cm-K}$ (Badzioch et al., 1964), the maximum ΔT is calculated to be roughly 40K. Field et al. cite this as evidence that pulverized fuel particles, which are generally less than $100 \mu\text{m}$ in diameter, may be taken as essentially spatially isothermal. For any particle that does have an internal temperature gradient, the relative rates of pyrolysis at its surface and center may be estimated from:

$$k_s/k_c = \exp[(1/T_c - 1/T_s)E/R] = \exp[\Delta TE/RT_s^2]$$

where the k 's are rate constants and the subscripts c and s refer to center and surface, respectively. For $E = 151 \text{kJ/mol}$ and the above $\Delta T = 40 \text{K}$, apparently the ratio is 1.65 at

$T_s=1200K$ or 1.3 at 1650K. Thus the rates throughout the particle are reasonably constant. The ratio increases with increasing E and decreasing T_s , but even if $E=204kJ/mol$ and $T_s=1200K$, the ratio is but 2. Thus the rates at the surface and center of the particle are both of the same order of magnitude in such a case.

The two different methods of analysis apparently yield contradictory conclusions about the importance of internal heat transfer limitations for particles in the 30-100 μm size range. This is symptomatic of the confusion that exists concerning the role of heat transfer in pyrolysis. The resolution of the apparent conflict comes in closer examination of the criteria for heat transfer control. It was noted above that the use of the ambient temperature in the calculation of characteristic times for reaction was unduly conservative. The more reasonable approach involves examining the timescales for pyrolysis of both the center and the surface of the particle, given an estimate of the actual ΔT in the particle. Only if the latter quantities differ significantly is there an important internal heat transfer limitation.

There has also been some confusion caused by imprecise discussion of the role of external heat transfer limitations. For the purposes of illustration, assume that pyrolysis can be modeled as a simple first order process with a rate:

$$dM/dt = -A M \exp(-E/RT)$$

where M is the mass of unpyrolyzed material remaining at time t . Further, assume that the particle heats up at a linear rate $dT/dt=B$, then it has been shown numerous times that it is possible to approximately integrate the rate expression above to obtain conversion $(1-M/M_0)$ as a function of maximum temperature achieved (T_m):

$$(1-M/M_0) = \exp\{-A \exp(-E/RT_m) [t_i + RT_m^2/EB]\} \quad (\text{Eqn. A})$$

where t_i is the time of any isothermal period during which the particle is held at T_m . Since the conversion as a function of time is determined by B , which in turn is a function of external heat transfer rate, this has in some cases been interpreted as an example of an "external heat transfer limitation". But it should be noted that chemical kinetics do indeed play a role in determining the time necessary to achieve complete conversion. Also, the case in which B is infinite can be recognized as the familiar case of complete chemical rate control.

RELEVANCE FOR PULVERIZED COAL DEVOLATILIZATION

From a simple heat balance, the surface heat flux to particles being uniformly heated at a constant rate $B(K/s)$ must be given by:

$$q = d\rho_C B/6 = dkB/6\alpha$$

where d is the particle diameter. Assuming $B=1000K/s$, $d=75\mu m$, and previously cited values, $q=3.1W/cm^2$, which implies that $\Delta T=2.4K$. Thus the particles are essentially uniform in temperature and the many experiments on pulverized particles heated at these rates (common for heated grids) would be expected to be governed by the nonisothermal kinetic expressions of the form of eqn. A. These experiments then do indeed yield information on true kinetics. If particles of 1mm are examined under the same conditions, $\Delta T=430K$, and the interpretation of the results in the same terms is questionable at best.

At a nominal average heating rate of $B=10^4K/s$, 75 μm particles would support a temperature gradient of about 24K, given the present assumptions. At a surface temperature of 1000K, the rate of a pyrolysis reaction with 210kJ/mol activation energy would be 1.8 times as high on the surface as in the center of the particle. However, it should be noted that about 60% of the mass of the particle is within 10 μm of its surface. At a depth of 10 μm , the temperature will lag that of the surface by only 12K, and the reaction rate will be only 35% lower. Such small differences in rate would normally not be apparent within the uncertainty of measurements in such high heating

rate experiments.

Only at particle average heating rates of 10^5K/s and above do internal heat transfer limitations become important for typical pulverized-size particles. The surface heat fluxes implied by such heating rates are 300W/cm^2 for $75\ \mu\text{m}$ particles, and temperature gradients of order 240K may be expected, based on the above analysis. It is then not surprising that at such fluxes (produced by laser radiation), Hertzberg and Ng (1987) observed a particle diameter effect on devolatilization half-life, with particles in the range $51\text{--}105\ \mu\text{m}$. At 100W/cm^2 irradiation, the effect of particle size was seen to be very small. The implication is that for typical pulverized coal particles heated at ordinary rates ($<10^4\text{K/s}$ or $<100\text{W/cm}^2$ flux), pyrolysis can be well described by a standard Arrhenius rate expression that accounts for the temporal nonisothermality of the process (e.g. equations of the form of A), without specifically accounting for internal heat transport limitations.

At higher fluxes, pyrolysis is expected to exhibit the observed "wave" character, in which the onset of reaction coincides with penetration of the thermal wave into the coal. The temperature of the wavefront is easily predicted from equation A, setting $t_1=0$ and assuming for example that the appearance of the wavefront coincides with about 50% conversion for the most facile reaction (kinetic parameters cited earlier for such a reaction were $A=2.11 \times 10^{11}\text{s}^{-1}$, $E=151\text{kJ/mol}$). For a heating rate $B=10^5\text{K/s}$, the calculated $T_m=960\text{K}$ is the apparent wavefront temperature. For $B=10^4\text{K/s}$, which would yield pyrolysis wave behavior only in "large" particles according to the above analysis, the apparent wavefront temperature is calculated to be about 870K , in good agreement with the observations of Hertzberg and Ng.

It may be concluded further that for high fluxes or large particles, that the standard Arrhenius kinetic expressions, combined with standard heat transfer analysis, are sufficient to describe the rate of pyrolysis, without the need to resort to the concept of a "decomposition temperature". As shown above, such a temperature would be a function of heating rate and reaction kinetics, and thus not a fundamental quantity.

More detailed analyses of the combined heat transfer-reaction processes in coal are still hampered by the lack of good thermodynamic and transport data on these systems. Even if the data on heats of reaction and latent heats were available, construction of a robust heat transfer model would have to wait for simultaneous development of a mass transfer model, since the location of evaporative tar loss (and thus the associated heat sink) would not necessarily coincide with the location of the reaction front in the coal.

THE ROLE OF MASS TRANSFER

There has recently appeared an extensive review on modeling of mass transfer limitations in coal pyrolysis (Suuberg, 1985), and this material will not be repeated here. Since the publication of that review, there have been a number of developments in understanding the processes involved, and these will be briefly summarized. As usual, a distinction is drawn between processes that are mainly of relevance in softening coals, and those that occur in the porous structure of non-softened coals.

Mass Transfer in Softening Coals

A major unresolved issue is that concerning the handling of bubble transport of volatiles, and whether it plays the dominant role in determining tar yields during pyrolysis. It has been shown that models which involve transport of volatiles out of the coal through bubbling-type behavior can indeed capture many essential features of the process (Lewellen, 1975; Oh et al., 1983, 1984). However, it has also been shown that a simple model in which liquid phase diffusion controls the rate of escape of tars might also explain the tar yield data equally well for pulverized particles (Suuberg and

Sezen, 1985). Thus it is not yet clear what role the bubbles must play in transporting tars. Further work on this latter model has, not surprisingly, revealed that liquid phase diffusion is most likely not fast enough to explain tar yields from particles much larger than about 100 μ m, under high heating rate conditions. Consequently, the evidence favors at least some role of bubbles in helping remove the tar from the particles, since no other convective mechanism is evident. A new, semi-empirical model of bubble transport has recently been proposed.

This new model of bubble transport of tar volatiles proposes that the tars are carried out in small bubbles that are nucleated by light gaseous species and oils. Solomon (1987) proposes an analogy of cups on a conveyor belt—each cup can carry out a certain amount of tar, as determined by the saturation vapor pressure of the tar. The effect of pressure on tar yields is seen through the effect on the size of the cups—the higher the pressure, the smaller the cup, and the less tar it transports. The smaller the rate of tar transport out via the cups, naturally the longer the residence time of tars in the particle, and the greater the opportunity for yield reducing cracking/coking reactions. More formally, each bubble is assumed saturated with respect to all tar species present in the surrounding liquid. Assuming ideal vapors and liquid solutions, the total number of moles of a tar species of molecular weight M_i in a bubble is:

$$n_i = P_i v_b / RT = P_i^0 x_i (v_g + \sum v_j) / RT$$

where v is a volume, with the subscript b referring to the whole bubble, g referring to the fixed gases in the bubble, and j to the volume contribution of the tars themselves. The quantity x_i is a liquid phase fraction of species i and P_i^0 is its vapor pressure. The rate of escape of the tar species i is governed by the rate of escape of bubbles from the particle, which is given, at constant pressure, by the total volumetric rate of escape of bubbles:

$$dn_i/dt = (P_i^0 x_i / RT) dv_t/dt = (P_i^0 x_i / P_{tot}) dN_t/dt$$

where N_i is the same as n_i multiplied by the total number of bubbles that escape, and V_t is the total volume of all volatiles, which is related by the ideal gas law to the total number of moles of volatiles, N_t . The pressure P_{tot} is the prevailing ambient pressure. The implied inverse pressure dependence of the rate of tar escape is the same as was previously noted based on another model—one in which film diffusion controls the rate of tar escape (Suuberg et al., 1979, 1985; Unger and Suuberg, 1981). In that model, the rate of tar escape was given for a particle of radius R by:

$$dn_i/dt = 4\pi R D x_i P_i^0 / RT$$

where the inverse pressure dependence is implicit in the vapor phase diffusion coefficient of tar in the gas film around the particle (D). Either model will predict a variation of molecular weight distribution with pressure (see Suuberg et al. 1985).

Solomon (1987) has noted that the rate of escape of the bubbles from the coal should be linked to the size of the particle, the viscosity of the coal melt (μ), and the pressure difference between bubble and ambient (ΔP). The latter effect is proportional to dN_t/dt , leading to the following suggested empirical form for the rate of tar escape:

$$\begin{aligned} dn_i/dt &= (c_1 P_i^0 x_i / R P_{tot} \mu) (dN_t/dt) [1 / (P_{tot} + \Delta P)] \\ &= (c_1 P_i^0 x_i / R P_{tot} \mu) (dN_t/dt) [1 / (P_{tot} + c_2 (dN_t/dt))] \end{aligned}$$

As of this writing, equations of this form are being tested.

Porous Transport

There has been relatively little new work in this area since it was last reviewed, except that the standard pore transport analysis has been extended to account for temporal nonisothermality (Blik et al., 1985). This area awaits further work on the question of how pressures affect yields of tar volatiles in non-softening coals. It

seems clear that pressure affects the rate of convection and diffusion. But is this in turn affecting tar yields by virtue of an impact on the residence times of vapor phase species in pores (affecting the residence time for vapor phase cracking/coking) or by virtue of an impact on evaporation rate of tar species (affecting the residence time for condensed phase cracking/coking)? It also appears necessary to clarify what role if any, is being played by microporous transport, under reactive conditions. The distinction between micropore transport and bulk diffusion remains hazy.

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