Pyrolysis temperature [K]

Bituminous Coal

	Char	T & L	
Ohio #2	○	●	(Solomon and Colket, 1979)
Pittsburgh #8	▽	▼	(Suuberg et al., 1979)
Arkwright	□	■	(Blair et al., 1977)
Illinois #6	◇	◆	(Blair et al., 1977)

Other Gases
HC
$CO + CO_2$
Total Gas
Tar & Liquids
Char

Percent product, ash free [wt %]

Pyrolysis temperature [°C]

Lignite Coal

Other Gases
HC
$CO + CO_2$
Total Gas
Tar & Liquids
Char

	Char	T & L	$CO + CO_2$	HC	
Montana Lignite	○	●	■	□	(Solomon and Colket, 1979)
Montana Lignite	▽	▼	▲	△	(Suuberg et al., 1979)

Percent product, ash free [wt %]

Pyrolysis temperature [°C]

Figure 3.9. Comparison of coal pyrolysis product distributions at various temperatures from three independent investigators. d_p = coal diameter, h = heating rate, HC = hydrocarbons, T and L = tar and liquids. Data not shown for gaseous components for bituminous coal. For Suuberg et al. (1979), d_p = 74–1000 μm, in helium, 10^2–10^4 atm, $h < 10^4$ K/s; for Blair et al. (1979), d_p = 500–600 μm, in helium/argon, 1 atm, $h = 2$–8×10^4 K/s; for Solomon and Colket (1979) $d_p > 100$ μm, vacuum, 1 KPa (0.01 atm), $h < 10^3$ K/s.

These data are for rapid heating rates and for particles ranging from 74–1000 μm, and for a wide range of pressures. For the range of small particles tested, neither the product distribution nor the rate of devolatilization seem to vary significantly with the particle diameter. Several studies noted by Anthony and Howard (1976) also provided observations that weight loss was not size dependent for particles up to 400 μm in diameter. However, very large particles behave differently from finely pulverized coal. Larger particles will not heat rapidly or uniformly, so that a single temperature cannot be used to characterize the entire particle. The internal char surface provides a site where secondary reactions occur. Pyrolysis products generated near the center of a particle must migrate to the outside to escape. During this migration, they may crack, condense, or polymerize, with some carbon deposition taking place. The larger the particle, the greater the amount of deposition, and hence the smaller the volatiles yield.

Devolatilization processes during gasification are thought to be quite similar to that during combustion. Major differences are elevated pressure and a more fuel-rich environment that often occur in gasification. Anthony et al. (1975) reported that a lower ambient pressure favors the liberation of a greater mass of volatiles. Weight loss of a bituminous coal had declined from 50 to 55% [dry ash-free] (daf) for pressures under 10 kPa (0.1 atm) to below 40% at 10 mPa (100 atm) (Howard, 1981). This appears to be consistent with other results, since an increase in pressure also increases the transit time of volatiles within the particle. An increase in pressure thus has an effect analogous to an increase in particle size. Howard (1981) more recently reviewed the data available on effects of elevated pressure. Howard notes results of approximately 20 devolatilization studies at elevated pressures up to 50 mPa.

3.5b.   Devolatilization Models

Badzioch and Hawksley (1970) postulated that the devolatilization was a first-order reaction process, with the reaction rate being proportional to the amount of volatile matter still remaining in the coal:

$$dv/dt = k(v_\infty - v) \tag{3.1}$$

with

$$k = A \exp(-E/RT) \tag{3.2}$$

This treatment required a method for relating the amount of "total" volatile matter v_∞ to that obtained from proximate analyses. The correlation used was

$$v_\infty = Q(1 - v_c)v_p \tag{3.3}$$

The parameters Q and v_c were empirically determined, although a value of 0.15 for v_c was suitable for all of the nonswelling coals tested. This is a satisfactory single-step reaction to describe pyrolysis. However, it lacks the flexibility required to describe much of the experimental data available and may be inadequate to describe nonisothermal pyrolysis. The fact that the parameters v_p, Q, v_c, A, and E may depend upon the specific coal dust also limits the generality of this model.

Kobayashi et al. (1977) suggested that pyrolysis could be modeled with the following pair of parallel, first-order, irreversible reactions:

$$C \xrightarrow{k_1} (1 - Y_1)S_1 + Y_1 V_1$$

$$(3.4)$$

$$C \xrightarrow{k_2} (1 - Y_2)S_2 + Y_2 V_2$$
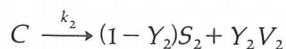
with the rate equations

$$dc/dt = -(k_1 + k_2)c \tag{3.5}$$

and

$$\frac{dv}{dt} = \frac{dv_1 + dv_2}{dt} = (Y_1 k_1 + Y_2 k_2)c \tag{3.6}$$

Again, k_1 and k_2 are Arrhenius-type rate coefficients. An important feature of the model is that $E_1 < E_2$. This approach satisfactorily correlates the data of Badzioch et al. (1970) and Kimber and Gray (1976), and the more recent data of Kobayashi et al. (1977) obtained under conditions of transient temperature as illustrated in Figure 3.8. In fact, the agreement for weight loss is very impressive for both coals and for a range of temperatures. Computations were made with a single set of parameters shown in Figure 3.8. The model is conceptually sound in that the variation in volatiles yield with temperature is explained by a second reaction rather than by a correlating parameter like that of Eqn. (3.3). As before, the general utility may be limited because the parameters Y_1, Y_2, A_1, A_2, E_1, and E_2 will depend on the specific coal dust. The stoichiometric parameters Y_1 and Y_2 can be estimated as the fraction of coal devolatilized during proximate analysis (Y_1) and the fraction that can be devolatilized at high temperatures (Y_2, often near unity).

In another treatment, Anthony et al. (1975) postulated that pyrolysis occurs through an infinite series of parallel reactions. A continuous Gaussian distribution of activation energies is assumed, along with a common value for the

frequency factor so that

$$\frac{v_\infty - v}{v_\infty} = [\sigma(2\pi)^{1/2}]^{-1}\left\{\int_0^\infty \exp\left[-\left(\int_0^t k\, dt\right)f(E)\, dE\right]\right\} \tag{3.7}$$

with

$$f(E) = [\sigma(2\pi)^{1/2}]^{-1} \exp\left(\frac{-(E - E_0)^2}{2\sigma^2}\right) \tag{3.8}$$

This approach also provided very good correlation of the data from Anthony et al. (1975) as well as the more recent experimental results of Suuberg et al. (1977). However, minimal comparison has been made with the data of other investigators. The model is attractive because it requires only four correlating constants. However, the utility of this model too, may be restricted by the need to determine the parameters v_∞, k, E_0, and σ for the specific coal dust of interest.

Sprouse and Schuman (1981) have compared the lignite data of Figure 3.8 (1000–2100 K) with predictions from Eqns. (3.7) and (3.8) as shown in Figure 3.10a. Parameters shown in Figure 3.10 provided near optimum agreement with the data. The authors note the excellent agreement with four parameters (σ, E_0, k, v_∞), compared to five for comparisons of Figure 3.8. A further comparison for lignite data of Anthony et al. (1975) for lower temperatures (973–1273 K) but for variable heating rates (10^2–10^4 K/s) is shown in Figure 3.10b. Again, agreement is very good with the same parameters. It is also interesting to note the absence of significant effect of heating rate on the maximum extent of devolatilization.

Both methods (i.e., Eqn (3.6) and Eqns. (3.7) and, (3.8)) give very good results. Differences in the number of coefficients (4 vs. 5) is considered secondary, since it is likely that a priori information may be available for coefficients for Eqn. (3.6). For example, Y_1 could be taken as the proximate volatiles level while Y_2 may be near unity on a daf basis. More complex reaction mechanisms were reviewed by Anthony and Howard (1976), and often involved several coal reaction steps.

In addition, comprehensive codes require a devolatilization model that will produce the composition of the volatile gaseous products and the residual char, as well as the rate of volatiles evolution. The two-step model of Eqn. (3.4) produces these compositions. Knowing the elemental composition of the raw coal (daf coal) and specifying the char composition (mostly carbon), the volatiles composition V_1 and V_2 can be calculated by mass balance. The total volatile matter evolved from the competing two-step process produces different amounts and composition of volatile matter from different temperature histories. The infinite series of parallel reactions of Eqns. (3.7) and (3.8) does not lend itself to a description of the composition of the resulting products.
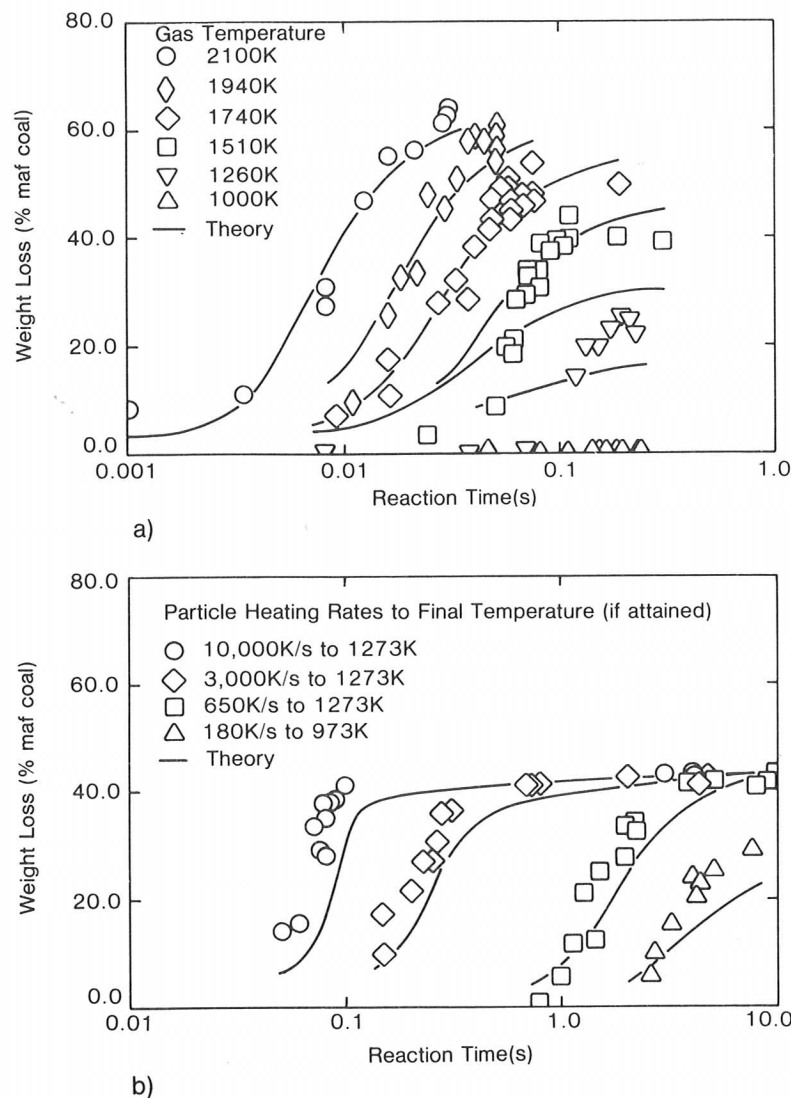
a)

b)

Figure 3.10. Comparison of measured lignite-weight-loss data (0.1 mPa) and predictions from Eqns. 3.7 and 3.8. (a) effects of temperature, laminar flow reactor; (b) effects of temperature and heating rate from electric screen (data from Anthony *et al.*, 1975). $\sigma = 1 \times 10^5$ J/mole, $v_\infty = 63.5$ wt %, $E_0 = 3.15 \times 10^5$ J/mole, $k = 1.67 \times 10^{13}$ s^{-1}. Parameters were not quite optimum but were common in both figures. (Figure used with permission from Sprouse and Schuman, 1981.)

A more recent method for predicting both devolatilization rates and product distribution has been developed by Solomon and co-workers (Solomon and Colket, 1979; Solomon, 1980). Prediction of time and temperature variation in these two properties is based on coal structural group, using general kinetic parameters for each of the coal constituents. Key observations upon which this technique was based are:

1. While the overall rates of devolatilization of coal vary with coal type, the rates of individual functional groups in the coal (i.e., ether groups, hydroxyl groups, tar, etc.) are *independent* of coal type.
2. The chemical composition of the tars is essentially that of the raw organic coal.

Thus, predictions can be made from quantitative measurements of coal composition and the set of parameters for each of the functional groups which are taken to be valid for all coals.

Figure 2.4 showed a model of the raw coal organic structure, while Figure 3.11 illustrates a model for thermal decomposition of this same raw coal. The raw organic coal is thus identified as being composed of a series of chemical constituents as illustrated in Figure 3.12. These include carboxyl (producing CO_2), hydroxyl (producing H_2O), ether (producing CO), aromatic hydrogen, aliphatic hydrogen, nitrogen, and nonvolatile carbon. It has been observed experimentally that the tars produced during the devolatilization process have a very similar structure to the raw organic coal. This close similarity is illustrated in the infrared spectra of Figure 3.13 for four different coals and their associated tars. Agreement for the lignite is not as good as for the bituminous coal. However, for many coals, the general composition of these tars can be identified from the parent coal.

Thermal decomposition is postulated to follow separate activated chemical reaction processes for each of these functional groups as also illustrated in Figure 3.12, including the tar. A given chemical species such as CO, OH, or CH_4 then is evolved from the coal by two independent, first-order processes—one for the species directly, and the second for the fraction of that chemical species in the tar as the tar is evolved. The rates of reaction for thermal decomposition for each species including the tar are assumed to be first order:

$$W_i = W_i^0[1 - \exp(k_i t)] \tag{3.9}$$

where W_i is the weight fraction of the functional group evolved during devolatilization and W_i^0 is the weight fraction of the functional group in the organic part of the raw coal; $k_i = A_i \exp(-E_i/RT)$, and A_i and E_i are determined from time-dependent functional-group composition data during devolatilization. Additional details and constraints involved in this model scheme are discussed
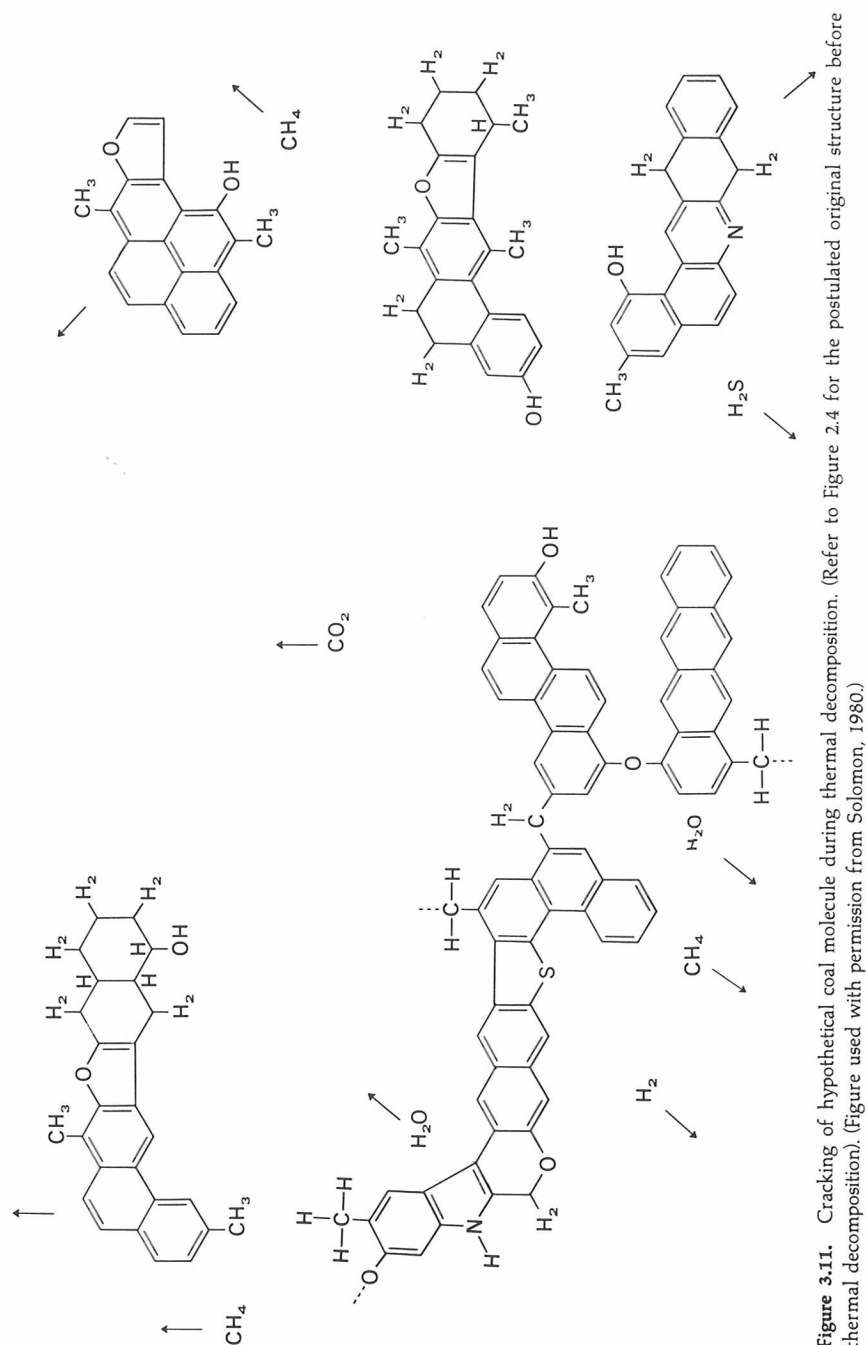
Figure 3.11. Cracking of hypothetical coal molecule during thermal decomposition. (Refer to Figure 2.4 for the postulated original structure before thermal decomposition). (Figure used with permission from Solomon, 1980).
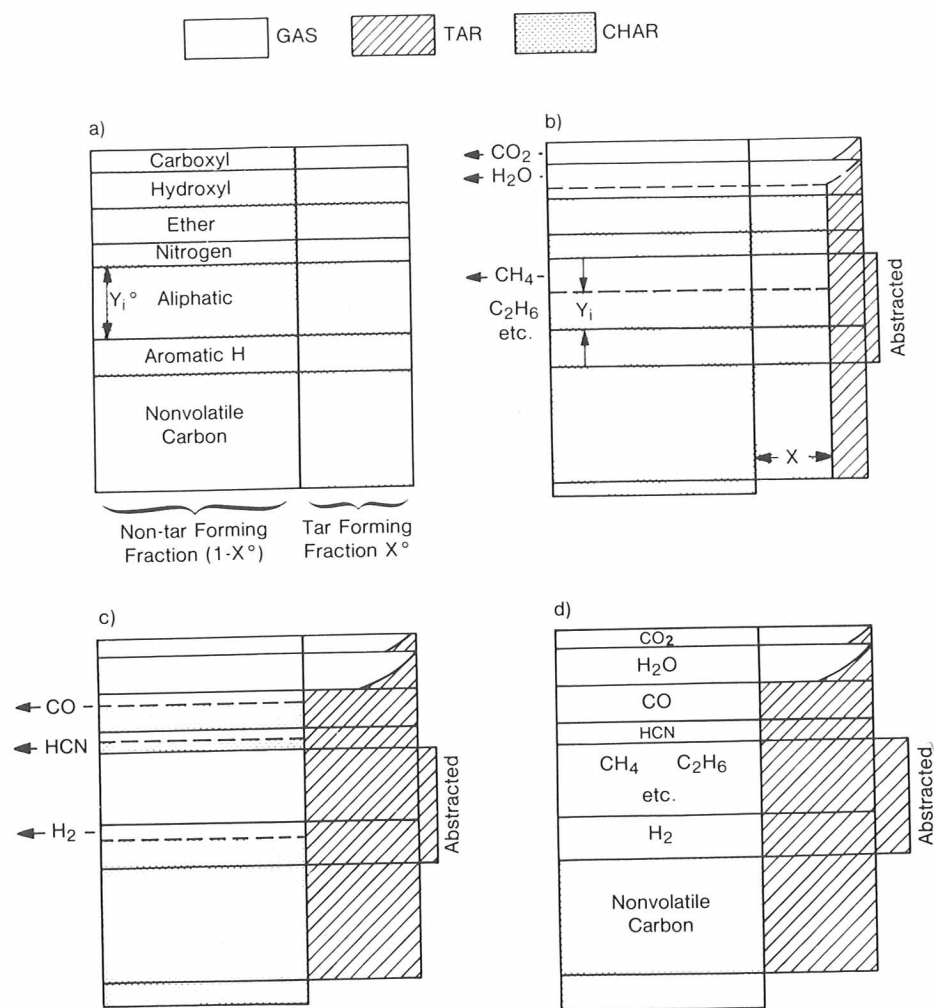
Figure 3.12. Progress of thermal decomposition according to model (a) functional-group composition of coal, (b) initial state of decomposition, (c) later stage of decomposition, (d) completion of decomposition. (Figure used with permission from Solomon, 1980.)

by Solomon (1980), and Howard (1981) where values of kinetic parameters are also presented.

Figure 3.14 shows comparisons of measured and predicted levels of evolved products H_2, tar, and aliphatics, together with residual C, H, and O in the char for a bituminous coal and a lignite for various devolatilization temperatures. Other comparisons for several other coals and other functional groups are
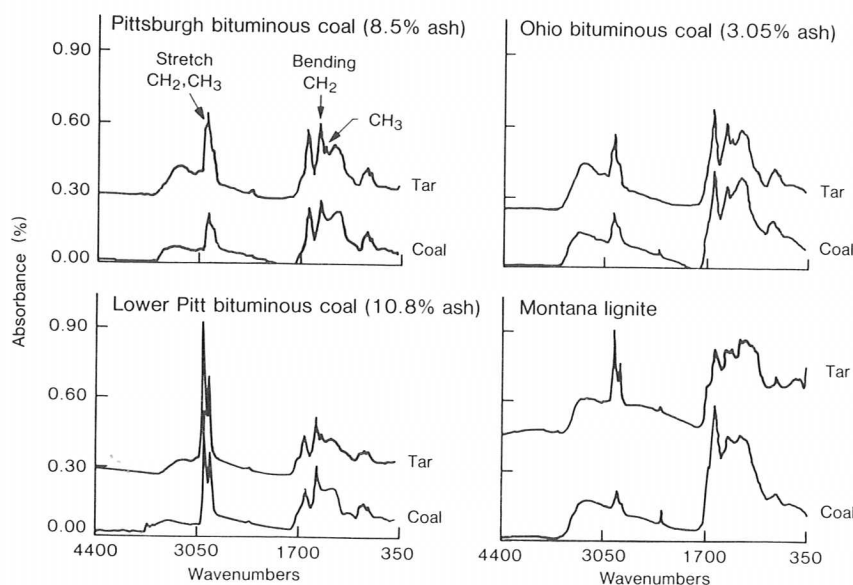
Figure 3.13. Infrared spectra showing comparison of four coals (daf) and the associated tars. (Figure used with permission from Solomon, 1980.)

shown by Solomon (1980). Results are promising; however, the technique still requires further development. For example, kinetic rates for functional groups derived from vacuum thermal decomposition differ from those derived from experiments in other reactors at atmospheric pressure.

3.5c. Effects of High Moisture Content

Specific studies for measurement of devolatilization of coals as a function of moisture level are in progress (Solomon, 1983). This study includes coal–water mixtures and highly cleaned coals. Plans include testing of wet and dry lignite and subbituminous and bituminous coals. It is anticipated that the presence of high moisture levels in coal could have several effects on the devolatilization process, as summarized in Table 3.6. Some insight into the effects of moisture on the devolatilization process could be obtained from a comparison of the bituminous (2.2% H_2O) and lignite coals* (13.6% H_2O) shown in Figure 3.8. However, it is not clear if the raw coals were dried prior to testing. Devolatilization rates for the two very different coals under similar heating conditions were remarkably similar. From this very limited information, if the thermal

*The lignite coal had 28.2% moisture at the time of mining, but apparently only 13.6% H_2O at the time of testing.
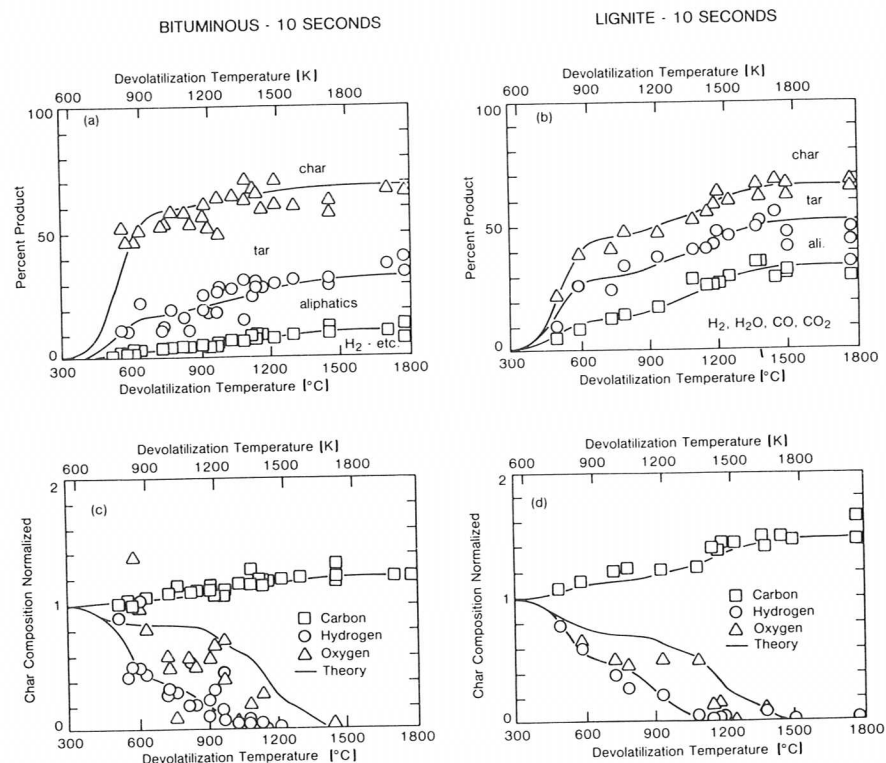

Figure 3.14. Pyrolysis product yields—experiment and theory. The char composition normalized to the composition of the parent coal. (Figure used with permission from Solomon, 1980.)

environment is held near steady, devolatilization rates may not strongly depend on initial moisture content.

3.6. VOLATILES COMBUSTION

3.6a. Background

It was noted above (see Figure 3.9) that a variety of products are produced during devolatilization of coal, including tars and hydrocarbon liquids, hydrocarbon gases, CO_2, CO, H_2, H_2O, HCN, etc. Several hundred hydrocarbon compounds have been identified in the tars produced during devolatilization, mostly aromatic (McNeil, 1981). These products react with oxygen in the vicinity of the char particles, increasing temperature and depleting the oxidizer (e.g., oxygen). This complex reaction process is very important to the control of nitrogen oxides, formation of soot, stability of coal flames, and ignition of char.