

PREDICTING DEVOLATILIZATION AT TYPICAL COAL COMBUSTION  
CONDITIONS WITH THE DISTRIBUTED-ENERGY CHAIN MODEL

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INTRODUCTION

Hypothetical ultimate yields for rapid coal devolatilization arose from the historical notions that a well-defined amount of volatile precursors are present in coal, and that their rate of release is directly proportional to a decaying reactant concentration. However, as reviewed elsewhere(1,2), wet chemical and spectroscopic analyses of coal structure from the past decade suggest a far less direct relationship between the reactive species in coal and the pyrolysis products. According to the aromatic/hydroaromatic model, bituminous coals are composed of aromatic "nuclei" interconnected by various bridges and substituted with smaller functional groups on their periphery. Although there is no well-defined repeating unit, bituminous coal is an extensively crosslinked macromolecular network which swells on solvation and exhibits viscoelasticity(3).

The aromatic/hydroaromatic model suggests three broad classes of chemical reactions: dissociation of bridges, recombination of nuclei, and elimination of peripheral groups. When peripheral groups present initially are converted to light gas, there is a direct correspondence between their initial concentrations and ultimate gas yields. But in contrast, when a bridge breaks, tars do not form at a rate governed by stoichiometric proportions, and furthermore, there is no predetermined concentration of tar precursors, per se, present initially in the coal. In depolymerizations, stoichiometric proportionalities are replaced by probabilities assigned from molecular conformation; i.e., the spatial arrangement of the atoms in a molecule(4). The probabilities relate the fragment size distribution to the concentration of unbroken bridges in the network, independent of the chemical reaction rates. During devolatilization, nuclei disconnect and recombine concurrently, and many fragments never become small enough to vaporize. Tar and char yields are determined by competitive kinetics which depend on complex conformational probabilities as well as chemical reaction rates. Each nucleus can become either tar or char, depending on the transient conditions for the competition. The fate of nuclei is not predetermined, as implied in formulations which include hypothetical ultimate yields for tar and char. Moreover, the disintegrating macromolecular skeleton of coal and the reintegration of intermediates into char are not taken into account in the historical notions mentioned above, nor in any of the available devolatilization rate models.

We formulated the Distributed-Energy Chain Model (DISCHAIN) to account for the conformational aspects of coal depolymerization and char formation in a phenomenological way. The derivation of the model and the qualitative mechanisms for product formation have been described(5). Rate parameters have been specified by correlating transient weight loss from a bituminous coal over a broad range of thermal histories for heating rates to  $10^3$  K/s and temperatures to 1300K(6). In the present study, predictions from DISCHAIN are compared with volatiles yields from very similar bituminous coals for heating rates between  $10^3$  and  $10^5$  K/s and temperatures between

800 and 2100K. No further adjustments of any of the parameters in the model have been made. Nevertheless, predicted yields and reaction times differ significantly among the comparisons, reflecting the influence of the different transient histories in the cases considered.

#### PRODUCT FORMATION FOR VARIOUS HEATING RATES

Chain statistics introduce several novel qualitative features into the formation mechanism for devolatilization products. In DISCHAIN, the monomer formation rate is not directly proportional to either the bridge dissociation or the char formation rate. Limiting cases establish that (1) the conversion of bound aromatic units into monomers accelerates with progressive bridge dissociations, regardless of the chemical reaction rate for bridge dissociation, and (2) the number of char links needed to eliminate all monomers is less than the original number of monomers. Most important, the formation of stable char links is concurrent with the disintegration of bridges during slow heating. This inhibits the subsequent formation of monomers, thereby accounting for reduced yields for lower heating rates.

The mechanistic basis for yield enhancement at faster heating rates in DISCHAIN is not solely the disparity of the activation energies for tar and char formation. Rather, the heating rate dependence is the joint result of the competition between the processes of char and tar formation in conjunction with suppression of monomer generation due to char formation. The activation energy disparity determines the selectivity to tar and char from the common intermediate; i.e., monomer. Independently, chain statistics determine the conversion of the bound aromatic units into the intermediate. Obviously, bound aromatic units which never become monomers are excluded from the competition between char and tar formation.

To further illustrate the role of monomer selectivity, predicted tar yields at four heating rates are shown in Figure 1. In these simulations, the thermal histories are linear temperature ramps at the indicated heating rates to 1900K. The onset of devolatilization moves to higher temperatures for greater heating rates, due to kinetic restraints(7). The devolatilization rate increases in rough proportion to increases in the heating rate. Reaction time constants range from 3 s at  $10^2$ K/s to 5 ms at  $10^5$ K/s. Each transient yield reaches an asymptote while the temperature ramp is being traversed, even at  $10^5$ K/s.

Faster heating tends to preclude char formation, which increases the monomer selectivity, and higher temperatures shifts the selectivity to tar formation. Consequently, ultimate tar yields increase by 70 % over this range of heating rates. Since the mass of aromatic units distributed between char and tar is fixed, char yields are decreasing throughout this range of conditions. Gas yields, which are not shown, are fixed at 8%, although at  $10^5$ K/s, peripheral groups are transported away with tar before they can be eliminated as gases. Product distributions consisting of tars but no light gases have actually been observed during laser pyrolysis at very high heating rates(8).

#### COMPARISONS WITH TRANSIENT CONVERSION MEASUREMENTS

Predictions from DISCHAIN are compared with three sets of data for single-particle, transient devolatilization of high volatile bituminous coals for a broad range of thermal histories. In Bautista's wire grid study of vacuum pyrolysis, thermal histories consist of uniform heating at  $10^3$ K/s to temperatures between 750 and 1200K, followed by sufficiently-long reaction times to observe ultimate yields at each temperature(9). In Kobayashi's entrained-flow study of pyrolysis at atmospheric pressure, the operating conditions encompass heating rates between  $10^4$  and  $10^5$ K/s and temperatures between 1000 and 2100K(1). Time-temperature histories are based on calculations which account for mixing between the dilute coal jet and the preheated coaxial gas stream. In Midkiff et al.'s study of an excessively fuel-rich stabilized coal flame, the nominal heating rate is  $10^5$ K/s and the ultimate temperature is 2000K(11).

The different pressures in these studies may seem objectionable in light of significant reductions in yield for pressures between vacuum and a few atmospheres. Many models invoke competing mass transport and redeposition of tar from the gas phase within and around the particles to rationalize this effect, but this basis is inconsistent with measured tar deposition rates and time scales for volatiles escape. Only a summary explanation is given here, as additional detail is given elsewhere(6).

Vaporization mechanisms determine which heavy compounds leave the condensed phase, depending on the molecular weight, temperature, and pressure. DISCHAIN presumes instantaneous vaporization and escape of all tars formed when monomers dissociate, which is a limiting form for low pressures if volatiles escape by viscous flow. Therefore, the model applies to vacuum pyrolysis regardless of temperature, and to pyrolysis at atmospheric pressure, provided that temperatures are high enough to compensate for the influence of pressure on tar vaporization. Regarding the assumed instantaneous vaporization of tar, the equilibrium vapor pressure of heavy compounds increases rapidly with increasing temperature, so that this assumption is well satisfied throughout the combustion temperatures in both of the selected studies at 1 atm. Based on an equilibrium vapor pressure law for coal liquids(12), the ratio of the vapor pressure and the internal pressure are identical at 1000K and an internal pressure of 1 atm, and at 1250K and an internal pressure of 10 atm.

Predicted product distributions for gas, tar, char, and unreacted coal are compared with measured yields of gas and total weight loss for vacuum pyrolysis in Figure 2. The simulations are based on uniform heating at  $10^3$ K/s to the stated reaction temperature, followed by an isothermal reaction period between 6 and 30 s, depending on reaction temperature. In all cases, ultimate yields were reached before the end of the experimental reaction time. Model predictions were converted to the daf-basis with a reported ash content of 9.2 %.

The relative yields of tar and gas are reliably predicted only beyond 900K, while predicted and measured weight loss differ by several percent at temperatures below 1000K. The predicted temperature dependence is more consistent for tar yields than for gas yields. Predicted yields for unreacted coal and char seem reasonable, but cannot be assessed quantitatively. Unreacted coal persists through 1000K as a result of the broad range of dissociation energies for bridges. The amount of char increases monotonically throughout this temperature range, but exhibits a maximum for higher temperatures and heating rates.

In succeeding comparisons, only weight loss is shown because gas phase chemistry alters the product distribution at high temperatures. The product distributions from DISCHAIN constitute flux conditions for detailed modeling of the rate phenomena in the vicinity of the particles, rather than conditions in the free stream.

The comparison for the atmospheric entrained flow study appears in Figure 3. The simulations are based on thermal histories calculated by Kobayashi which account for mixing effects near the injector(10). These thermal transients are significantly longer than for an individual particle injected into a quiescent gas at the reactor temperature, as expected. Also shown in Figure 3 are correlations from the competing two-step model(10). Kobayashi assigned rate parameters in order to fit these data; in contrast, rate parameters from DISCHAIN were not readjusted from the values assigned from data at much slower heating rates and lower temperatures.

Predicted weight loss is within the experimental error at both the extremes in temperature, but several percent too high at 1510K and 1260K (not shown). Predicted reaction time scales are as reliable as those from the correlation assigned from this data. Also, the predicted ultimate yield of 62 % at 2100K is substantially greater (15 % daf) than the greatest value in the data set used to assign the parameters in DISCHAIN (47 %  $10^3$ K/s and 1300K). Moreover, it is 22 % daf greater than the measured yield at  $10^2$ K/s and 1300K (12). Since the parameters have not been adjusted, these yield enhancements can be attributed to the influence of heating rate, as described in the previous section.

The final comparison involves a stabilized one-dimensional coal flame(11). Factors beyond devolatilization arise in coal flames, but most complications are absent under excessively fuel-rich conditions. The coal density was 470 mg/l, corresponding to fuel equivalences of 3.30 with respect to the whole coal and 1.34 with respect to the ASTM proximate volatile matter. All oxygen was consumed before one-third of the ultimate volatiles yield was observed, and heterogeneous oxidation was negligible.

Complete transient thermal histories, from the point of injection to the onset of devolatilization, have not yet been measured for any coal flame, including this one. Midkiff, et al. report transient weight loss, gas temperatures, and optically-determined particle temperatures on a time coordinate referenced to the first measurement point, rather than the point of injection. The first reported temperature, 1750K, exceeds the threshold for devolatilization at heating rates as fast as  $10^4$  K/s (DISCHAIN predicts that devolatilization begins at 1250K for a heating rate of  $2 \times 10^5$  K/s; c.f. comparison with Kobayashi's data at 1940K in Figure 3). Therefore, a simulated thermal history, instead of the measured particle temperatures, has been used to obtain the predictions discussed below.

Predicted weight loss is compared to the sum of the measured losses of volatile matter and fixed carbon in Figure 4. The thermal history in the simulations consists of uniform heatup at  $10^5$  K/s to 2000K, the ultimate temperature observed in the experiment. The time coordinate for the predictions and measurements is referenced to the onset of devolatilization. The reaction time scale is adequately described, but the predicted ultimate yield exceeds the measurements by 5 %. However, soot was observed but not separated from the collected char samples, so the measured yields are less than the true values. An upper bound for this influence far exceeds the discrepancy in this comparison, as Nenninger et al. observed soot yields of 22 % from the high temperature pyrolysis of a high volatile bituminous coal(13).

#### CONCLUSIONS

The accuracy of the predicted reaction time scales and yields from DISCHAIN is significant because hypothetical ultimate yields are absent, model parameters were not adjusted, and a wide range of thermal histories was spanned in the comparisons with data. Experimental errors necessarily increase as coal combustor conditions are approached. Nevertheless, this evaluation is more stringent than previous comparisons between devolatilization models and measurements, and provides the basis for the following conclusions:

1. Bridge dissociation concurrent with char formation diminishes the conversion of bound aromatic nuclei in coal into unattached tar precursors, which constitutes a mechanistic basis for enhanced yields for faster heating rates.
2. Predicted yields based on the same parameters ranged from 40 % at  $10^2$  K/s and 1300K to 62 % at  $10^5$  K/s and 2100K, in agreement with measured yields at the respective conditions within the experimental error.
3. Predicted reaction times and yields from DISCHAIN agree quantitatively with transient measurements from high volatile bituminous coals for heating rates between  $10^3$  and  $10^5$  K/s and reaction temperatures between 800 and 2100K.

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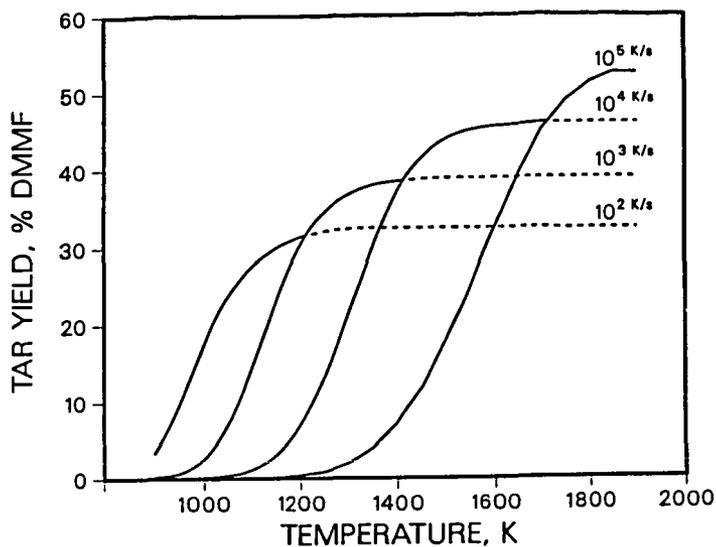


Figure 1. Predicted transient yields for tar during heatup at  $10^2$ ,  $10^3$ ,  $10^4$ , and  $10^5$  K/s along a linear temperature ramp to 1900K.

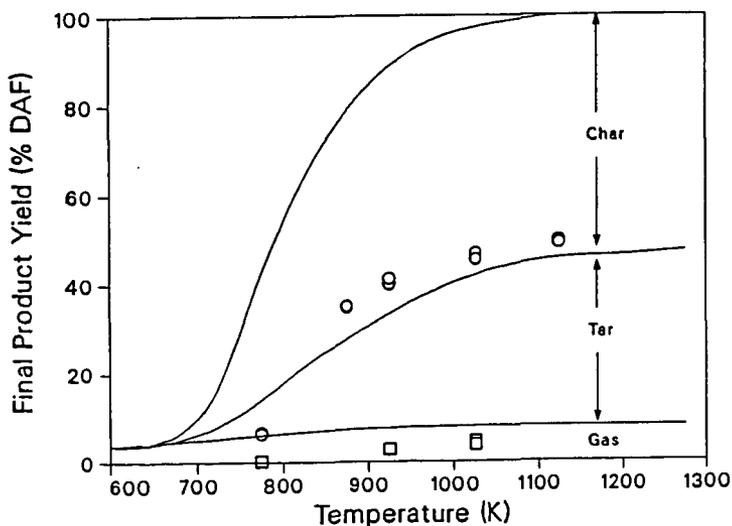


Figure 2. Comparisons between predicted and measured weight loss (O) and gas yields (□) from vacuum pyrolysis of Pittsburgh seam bituminous coal, from Bautista<sup>16</sup>.

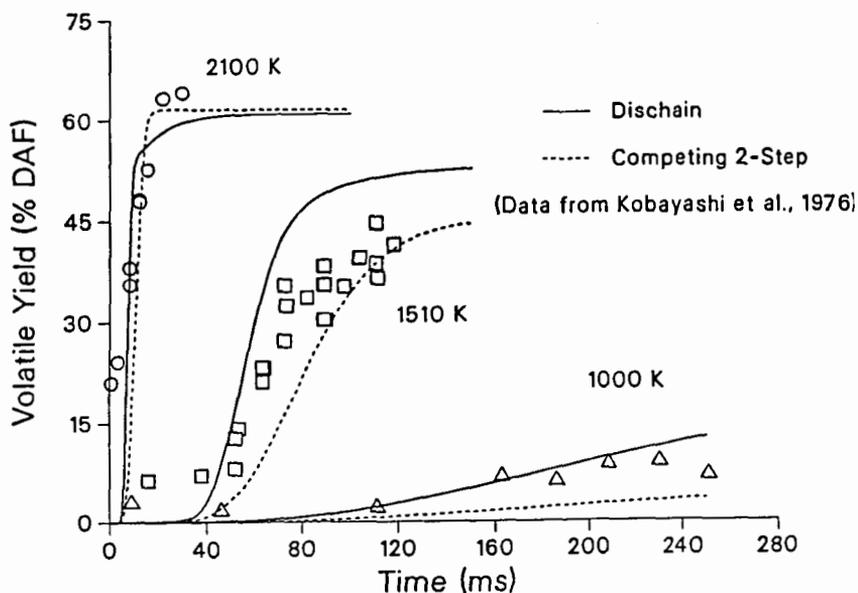


Figure 3. Weight loss observed in an atmospheric entrained flow reactor by Kobayashi<sup>17</sup> compared to predictions from DISCHAIN (solid curves) and from Kobayashi's<sup>6</sup> competing two-step model (dashed curves).

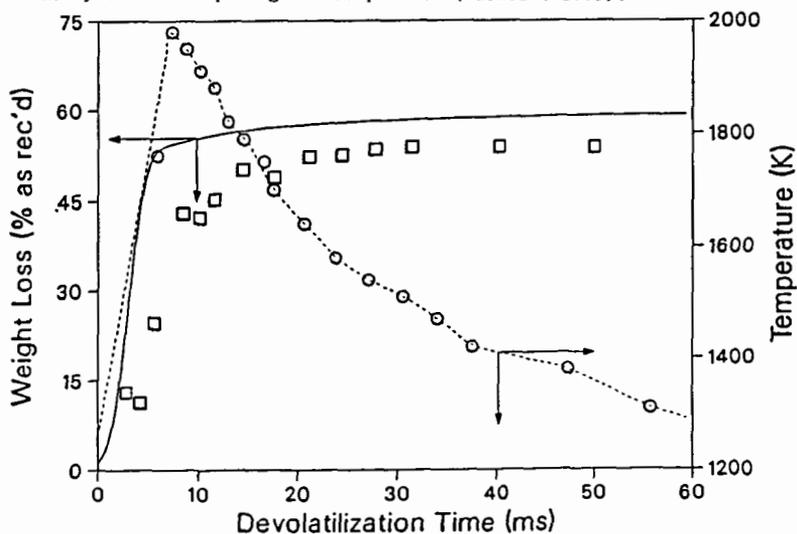


Figure 4. Predicted weight loss (solid line) for uniform heating at  $10^5$  K/s to 2000K compared to the sum of losses of volatile matter and fixed carbon (□) reported by Midkiff, et al.<sup>18</sup>. The simulated temperature profile (dashed line) includes optically-measured particle temperatures (○) during the cooling phase.