

## VERY RAPID COAL PYROLYSIS

Peter R. Solomon, Michael A. Serio, Robert M. Carangelo and James R. Markham

Advanced Fuel Research, Inc., 87 Church St., East Hartford, CT 06108 USA

## INTRODUCTION

Considerable controversy exists concerning the rate of coal pyrolysis. For example, at 800°C, rates reported in the literature (derived assuming a single first order process to define weight loss) vary from a low of around  $1 \text{ sec}^{-1}$  (1-4) to a high near  $100 \text{ sec}^{-1}$  (5-8), with values in between (9,10). The discrepancies cannot be explained by differences in sample composition because experiments in which coal rank alone was varied typically show no more than a factor of 5 variation in rate (11). One problem is that if the higher rate is correct, then any experiment which attempts to obtain isothermal rate data at 800°C must heat the coal in a time short compared with the pyrolysis time, i.e. on the order of  $100,000^\circ\text{C}/\text{sec}$ . At higher temperatures the heating rate to obtain isothermal data must be even faster. But for most experiments at temperatures of 800°C or higher, calculations of heat up rates for pulverized coal suggest that if the higher rate is correct, pyrolysis will typically be occurring during heat up, even assuming zero heats of reaction. Under these circumstances it is necessary to know the coal particle temperature to derive kinetic rates. Coal particle temperatures during rapid pyrolysis have not generally been measured.

In an attempt to resolve this controversy, a new pyrolysis experiment was designed which provided for high heating rates and a geometry which simplified the prediction of particle temperatures (12). It used a small diameter electrically heated tube into which coal and helium carrier gas were injected. The reaction distance was varied by moving the electrode positions. The particle temperatures and the particle residence times were calculated from the measured tube wall temperatures and the gas flow rates, respectively. Even allowing for the uncertainty in these estimated values, the rates measured at asymptotic tube temperatures of 700°C, 800°C and 900°C agreed with the highest reported rates and were inconsistent with the low rates.

These heated tube experiments therefore, lent support to the high rate advocates but suffered in conclusiveness as did the other experiments in this temperature range in not having a direct measure of particle temperature (2-10,12) and reaction time (2,5,7-9,12). The tube reactor experiment was modified to eliminate these drawbacks. Temperatures of the solids were determined at the tube exit using FT-IR emission and transmission spectroscopy (13,14) and the transit time for the coal was measured using photo transistors at the top and bottom of the tube. Temperature measurements were also made inside and outside the tube with a thermocouple.

Measurements were made of the amount and composition of the tar, char and gases evolved as a function of the measured reaction time and temperature. We focus on primary pyrolysis, during which the initial rapid weight loss, the evolution of tar and lighter hydrocarbons, and the disappearance of the aliphatic (or hydroaromatic hydrogen) in the coal/char all happen at similar rates. For a 200 x 325 mesh fraction of a dry North Dakota lignite in a 115 cm long tube having an asymptotic tube temperature of 800°C, primary pyrolysis was completed in a period of 14 milliseconds based on the mean particle residence times. The extent of axial dispersion was small. During this period, the maximum coal temperature was increasing from 600 to 740°C. These data, as well as data obtained at equilibrium tube temperatures of 700°C and 935°C, are in agreement with the high pyrolysis rate originally reported (12).

This paper describes the experimental apparatus and measurement technique, and presents the results for a lignite at temperatures between 600°C and 935°C. The results are compared to the predictions of a pyrolysis model and to the literature data. Reasons for the discrepancies are discussed.

### EXPERIMENTAL

The reactor is illustrated in Fig. 1. It consists of a 0.2" i.d. Inconel 702 tube which is heated electrically. Coal entrained in cold carrier gas is injected at the top of the tube. The coal is fed using a previously described entrainment system (7,8). The coal-gas mixture enters the heated section of tube and heats rapidly. The heat transfer rate is large because of the small tube diameter, the high thermal conductivity of the helium carrier gas, and the fact that the particles collide with the hot walls of the tube. After a variable residence time, the reacting stream is quenched in a water cooled section of tube. The product collection train consists of a cyclone to separate the char followed by a collection bag to collect the gas, tar and soot. The gas from the bag is analyzed by FT-IR and the solids and liquids are collected on the bag surface and in a filter.

#### Temperature Measurements

The temperature of the gas-coal mixture and outside tube temperature has been measured with a thermocouple. At constant current, the tube will reach an equilibrium temperature such that the external power loss by radiation and convection is equal to the electrical power input. With gas and coal flowing in the tube, the tube is initially cooler than the equilibrium temperature, since heat is used to raise the temperature of the gas and coal. The heat absorbed by the coal and gas can be calculated from the measured tube temperature. When the reactants reach the equilibrium temperature, the outside of the tube reaches a constant temperature.

The results for one set of measurements with coal present are presented in Fig. 2. The measurements include: a) thermocouple measurements inside and outside the tube; b) FT-IR measurements at the center of the gas/solid stream 0.75 cm below the end of the hot tube; c) thermocouple measurements at the position of the FT-IR measurement; and d) thermocouple measurements inside a water cooled tube attached to the hot tube to measure the quenching rate.

Heat transfer calculations suggest that inside the tube the thermocouple reads 10-20°C higher than the gas due to radiation from the wall. The bead temperatures at the FT-IR focal point was calculated to be lower by approximately the same amount outside the tube. The measurements of the external tube wall temperature are low due to heat loss from the thermocouple bead to the surroundings. However, the maximum effect of this error can be determined by comparing the asymptotic values of the external wall temperature and the internal gas temperature, which come to thermal equilibrium for sufficiently long distances. The knowledge of this temperature difference along with the apparent wall temperature can be used to determine the error at each measured wall temperature, which gets lower as the tube gets cooler. For example, in the 800°C experiment, the corrections ranged from +35°C at 800°C to +10°C at 500°C when using a 0.002" diameter thermocouple bead. The corrections scaled with bead diameter, as expected. The wall profile shown in Fig. 2 has been corrected for radiation errors. The temperature difference between the outside and the inside of the tube was calculated to be negligible.

Measurements of coal particle temperatures were made using FT-IR emission and transmission spectroscopy. As described in a previous publication (13), the transmittance measurement is used to determine the total emitting surface of the coal particles so that a normalized emission, (emission/(1-transmittance)) can be compared

in both shape and amplitude to a theoretical black-body. The FT-IR measurement can provide a direct measurement of the coal particle temperature during heat up. A simple case is illustrated in the insert of Fig. 2. For this case sufficient time was allowed for the coal to reach the asymptotic tube temperature of 935°C (1208 K) and for pyrolysis to have occurred. For a grey-body (such as shown here for char) the shape of the normalized emission spectrum gives the temperature and the amplitude gives the emittance. The normalized emission spectrum is in good agreement with a theoretical black-body at 1190 K with an amplitude corresponding to an emissivity of 0.9. The measured temperature is in excellent agreement with the tube temperature as a 10°C drop in temperature is expected between the end of the tube, and the measuring point at 0.75 cm below the end. The measurement of temperature before and during pyrolysis is not as simple, since for the size of coal particles used here only specific bands (corresponding to the absorbing bands in coal) provide sufficient absorbance for the spectral emittance to reach 0.9. Then, only these regions can be used to compare to the black-body. The measurement technique, the problems encountered, their solutions and the results are discussed in another paper at this meeting (14). The results at 800°C are presented as the triangles in Fig. 2.

Calculations of the temperature of the gas, the thermocouple bead, and the coal particles were performed given the tube wall temperature as a boundary condition. The calculations assume the temperature dependent heat capacity for coal derived by Merrick (15) which agrees with the measurements of Lee (16), an average spectral emittance of 0.5 for the 200 x 325 mesh particles of coals in agreement with recent FT-IR measurements (14) and zero heat of reaction. The calculations assume convective heat transfer between the tube wall and gas and between the gas and coal particle or thermocouple bead and radiative heat transfer between the wall and the coal particle or thermocouple bead. The heat transfer coefficient between the wall and the gas, which was determined from the Sieder-Tate equation (17), was validated by equating the electric power input to the power radiated and convected outside the tube (determined from the tube temperature and emissivity) plus the heat transfer to the gas inside the tube.

In order to match the measured particle temperatures in the early part of the tube (e.g., < 50 cm at 800°C) it was necessary to include a term to account for heat transfer due to collisions of relatively cold particles with the hot walls. This phenomenon, known as wall-contact heat transfer, has been described by Boothroyd (18). A heat transfer coefficient was defined by analogy to a conventional convective coefficient, i.e.  $Q_{wc} = h_{wc} (T_{wall} - T_{coal})$ .

The predicted results (lines in Fig. 2) are in good agreement with the measured temperatures. The agreement between the actual thermocouple measurements and the predicted values is a good indication that the corrected wall temperature profile is accurate. The measured particle temperatures are slightly below the predicted values in agreement with a 10°C drop from the tube end to the measuring point. Possible values for the heat of reaction were considered. A value of 250 K cal/gram of total volatile material results in a predicted temperature which is too low although the shape of the temperature vs distance curve matched the FT-IR data better than the zero heat of reaction case. Additional data are needed to determine the possible values for the heat of reaction and the chemical reactions to which it applies (e.g. tar loss, overall weight loss, etc.).

#### Particle Residence Time

The heated tube reactor was modified for particle velocity measurements. The passage of a pulse of coal through the system was measured for each electrode position by recording signals from photo transistors mounted on glass sections at the top and bottom of the reactor tube on a dual channel oscilloscope. Photographs of the oscilloscope traces allow an assessment of the mean particle residence time and the extent of axial dispersion.

A technique was developed where short, well-defined pulses could be introduced by using an electrically activated solenoid to inject the contents of a tube containing the coal charge and gas at 10 psig. In addition, the reactor was set up over the FT-IR bench in preparation for hot tests with temperature measurements. This configuration has the added advantage of using a laser from the FT-IR beam as the light source for the lower photo transistor, which improved the signal to noise significantly. It also eliminated the lower glass tube which tended to be obscured with tar after a few hot runs. The only problem was a slight spreading of the particle stream as it emerged from the tube, which meant that the measured dispersion was in excess of what actually occurred in the tube.

The photographs enabled an assessment of the particle residence time and of the particle dispersion, which impacts on the kinetic analysis. Some representative traces from cold and hot tests are shown in Fig. 3. Figure 3a indicates a transit time of approximately 60 milliseconds for the coal in the cold tube. The average transit time in the cold experiments was determined from a number of measurements to be 56 milliseconds. The particles, therefore, travel at about 80% of the gas velocity of 28 m/sec. Figures 3b-3d show the transit time when the tube is heated over increasing distances (75, 100 and 115 cm). The transit time is reduced to about 32 milliseconds when 115 cm is heated (Fig. 3d).

The extent of axial dispersion was small and was typically almost symmetrical, which would lead to a slight (approximately 10%) underestimation of the rate constant. It was neglected in the analysis of results for this paper.

Data are presented in Fig. 4 for the mean particle transit times for hot experiments. The hot data are adjusted so that the transit time in the cold part of the tube is not included. This was done by subtracting the heated length from the distance between the detectors (125 cm) and using the cold data to determine the transit time which should be subtracted from the observed transit time for the hot experiment. The adjusted data then reflect the amount of time it takes to traverse the hot zone.

The particle residence time data definitely indicate that the particles are accelerating in the hot experiments at close to the same rate as the gas except for a slowdown in the region where pyrolysis begins (~50 cm). This is reasonable in light of the small value of the characteristic drag time, 1.5 milliseconds, (which indicates the relaxation time for a particle for a step change in gas velocity) for the size fraction used in the hot experiments (-200, +325 mesh) (17). The data were fit by a model which assumes the particles are moving at 80% of the average gas velocity until primary pyrolysis is 1% complete, at 40% of the gas velocity between 1% and 75% pyrolysis, and back to 80% of the gas velocity after pyrolysis is 75% completed. The reason for the slow down during pyrolysis is not yet clear but is probably associated with evolution of gas from the coal or swelling which has been observed for this lignite under these extremely high heating rates.

Additional confirmation of the particle velocities was obtained from comparing the particle feed rate with the density of particles exiting the tube determined by FT-IR transmittance measurements, where the density of particles in the focus is inversely proportional to their velocity.

## RESULTS

The results are shown in Fig. 5 for isothermal tube temperatures of 700°C, 800°C, and 935°C. Figures 5a-c present the weight % char, tar, and gas (the sum of measured individual gas species) as a function of the reaction distance. The mass balance was between 96.5 and 101%.

The measured and calculated particle temperatures and times as functions of distance are shown in Figs. 5d-f. The calculated particle temperatures match FT-IR temperature data obtained at 800°C and 935°C and the particle times match transit time data obtained at 800°C. Confidence can be placed in the calculated temperature at 700°C because the calculations use the same heat transfer coefficients which give the validated calculations at 800°C and 930°C. The time calculations at 700°C and 935°C employ the same relative velocity between gas and particles that was measured at 800°C. For all three temperatures, pyrolysis occurs during particle heat up, even though heating rates are in excess of 40,000°C/sec.

The solid lines in Figs. 5a-5c are generated using a previously presented pyrolysis theory (8) which calculates the evolution of individual species using a distributed activation energy of the form introduced by Anthony et al. (1) for each species. The rates for tar and hydrocarbon gases are shown in Fig. 6. The gas rate is five times higher than the rate for the same species in Ref. 8. This is to account for the factor of 5 higher rates observed for lignites compared to bituminous coals, discussed in (11). An error was discovered in the calculation of tar evolution in Ref. 8. The rate in Fig. 6 is for the corrected calculation. As a further comparison, the reciprocals of the times required to achieve 63% tar yield are plotted (solid circles) in Fig. 6 as a function of the reciprocal of the average absolute temperature during this period. A single pyrolysis experiment at 600°C gave a rate constant of 6.3 sec<sup>-1</sup>. These data fall close to the line defining the tar rate.

The theory is in excellent agreement with the data. At all three temperatures the observed weight loss is a result of rapid evolution of tar and slower evolution of the gases. The increase in total weight loss with increasing final temperature is the result of gas evolution (primarily CO and H<sub>2</sub>O) due to loss of tightly bound functional groups.

For comparison with previous weight loss data, a single first order weight loss has been calculated (dashed lines) using a rate  $k = 4.28 \times 10^{14} \exp(-55,400/RT) \text{ sec}^{-1}$ . This is one half  $k_{\text{tar}}$  (see Fig. 6) and represents a compromise between the rapid evolution of tar and the slower rate for gas evolution. The single first order rate does not fit the data as well. It gives a steeper weight loss than is observed and the yield does not increase with temperature. Given these limitations inherent in a single first order model, the theory is in good agreement with the data.

#### DISCUSSION

The measured rate for primary pyrolysis weight loss is therefore higher than the high rates originally measured by Badzioch and Hawskley (5). The activation energy of 55 kcal is what is expected from thermochemical kinetics for ethylene bridges between aromatic rings and agrees with pyrolysis rates for model compounds and polymers where these bonds are the weak links (19). The rate is also in agreement with data obtained at much lower temperature (~450°C) at a heating rate of 30°C/sec.

What are the reasons for the discrepancies between these rates and rates reported by many other investigators (1-4,9,10,20-22)? There are two reasons for the discrepancies, interpretation of the rate and knowledge of the particle temperatures. Consider first the grid experiments. The data and analysis by Anthony et al. (1) illustrates the first reason. They presented two kinetic interpretations for their data, a single first order process and a set of parallel processes with a Gaussian distribution of activation energies. Both interpretations fit the data using Arrhenius expressions for kinetic rates. The single first order process which uses an activation energy of 11 kcal/mole requires two parameters, while the distributed rated model which uses a mean activation energy of 56 kcal/mole requires a third parameter to describe the spread in rates. Niksa et al. (3) used a single first

order model with its low activation energy. Suuberg et al. (6) rejected the low activation of the two parameter fit as being chemically unreasonable, and settled for a less accurate fit but with appropriate activation energies. The problem is that a variety of interpretations may provide good fits to the data over a limited range of temperature and heating rates. The grid experiments do not provide sufficient information to choose between the possibilities, some of which lead to highly inaccurate extrapolations. It is only by performing additional experiments at higher heating rates and therefore higher pyrolysis temperatures that the ambiguities can be eliminated. The data presented in this paper indicate that the distributed activation energy model was the better choice to produce  $k \approx 100 \text{ sec}^{-1}$  at  $800^\circ\text{C}$ . Additional discrepancies are probably due to inaccurate assumptions regarding particle temperatures which have not been measured in the grid experiments.

If the high activation energy rate is the better choice, what about the data of Kobayashi et al. (2) which give a rate on the order of  $1 \text{ sec}^{-1}$  at  $800^\circ\text{C}$  and only  $100 \text{ sec}^{-1}$  at  $1700^\circ\text{C}$ ? There was no direct measurement or confirmation of the particle temperature in these experiments. Instead, an assumption was made that the particles were at the gas temperatures at the longest residence time (200 milliseconds) for a nominal furnace temperature of 1260 K where a weight loss of 26 wt. % was observed. It was assumed that the 26 wt.% point was always reached at a temperature of 1260 K in the higher temperature experiments. These assumptions were used to determine a parameter,  $\theta$ , defined as the ratio of the momentum shape factor to the energy shape factor. The particle temperature calculations were performed assuming: a value of  $\theta = 3$ , although a value closer to unity would be more likely; a smaller value of particle heat capacity than is now believed (15,16); a higher value for the absorption of radiation than recent data would indicate for small coal particles (13) and zero heat of pyrolysis. The resulting calculation gives a heatup time of approximately 18 milliseconds at 1260 K, in conflict with the observation that no weight loss has occurred at 70 milliseconds. Furthermore, the initial assumption is in conflict with the data presented in this paper which suggest that had the coal been at 1260 K for even 10 milliseconds, substantially more than 26% weight loss would have occurred. We believe that the particle temperatures at which pyrolysis was occurring were significantly overestimated by Kobayashi et al. (2), leading to underestimation of the kinetic rates.

There are other data which do not agree with our rates and where two color temperature measurements were made (20-22). These measurements suggest a high solids temperature. But these measurements may indicate the temperature of a hot cloud of soot surrounding the particle or hot spots on the particle surface and not reflect the temperature in the region of the particle where pyrolysis is occurring. It is also true that the assumption of constant emissivity used in interpretation of two-color data can be erroneous in some cases (13,14).

#### CONCLUSION

An experiment has been performed to determine pyrolysis rates for a lignite in which both the transit time and temperature of particles have been measured. The measured rate for weight loss is greater than  $100 \text{ sec}^{-1}$  at  $800^\circ\text{C}$ . The results suggest a reinterpretation of heated grid data which have given rates much lower than this at comparable temperatures. The results also suggest that lower rates obtained in entrained flow reactors were due to heat transfer limitations.

#### ACKNOWLEDGEMENT

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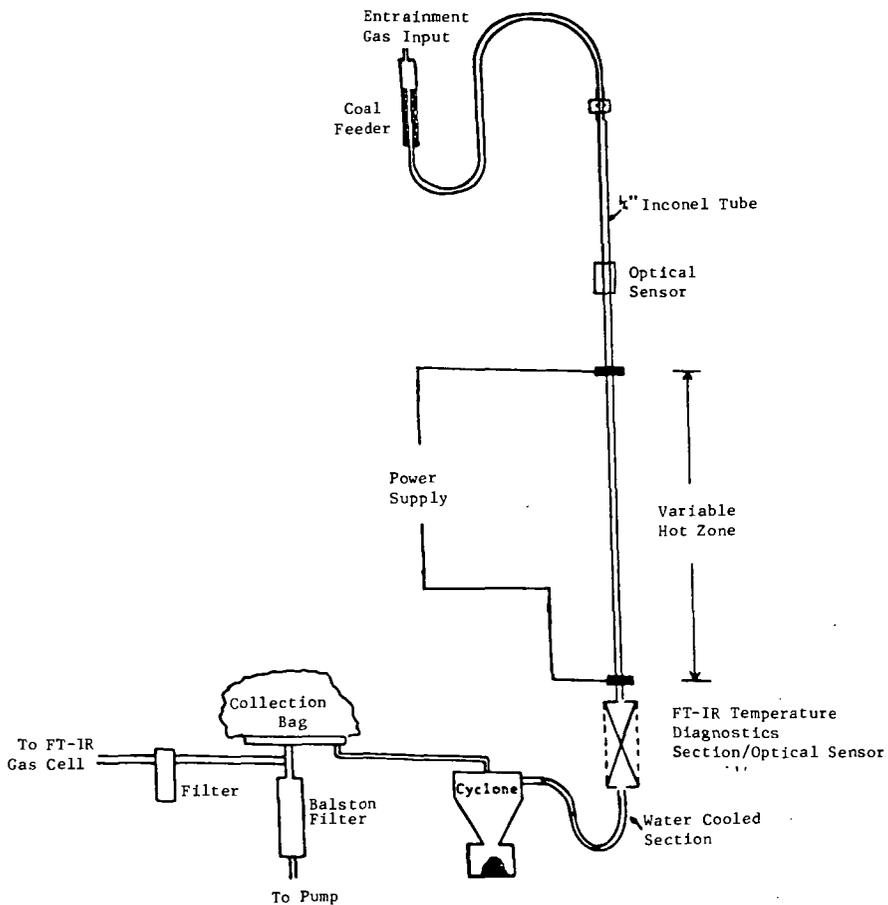


Figure 1. Schematic of Heated Tube Reactor.

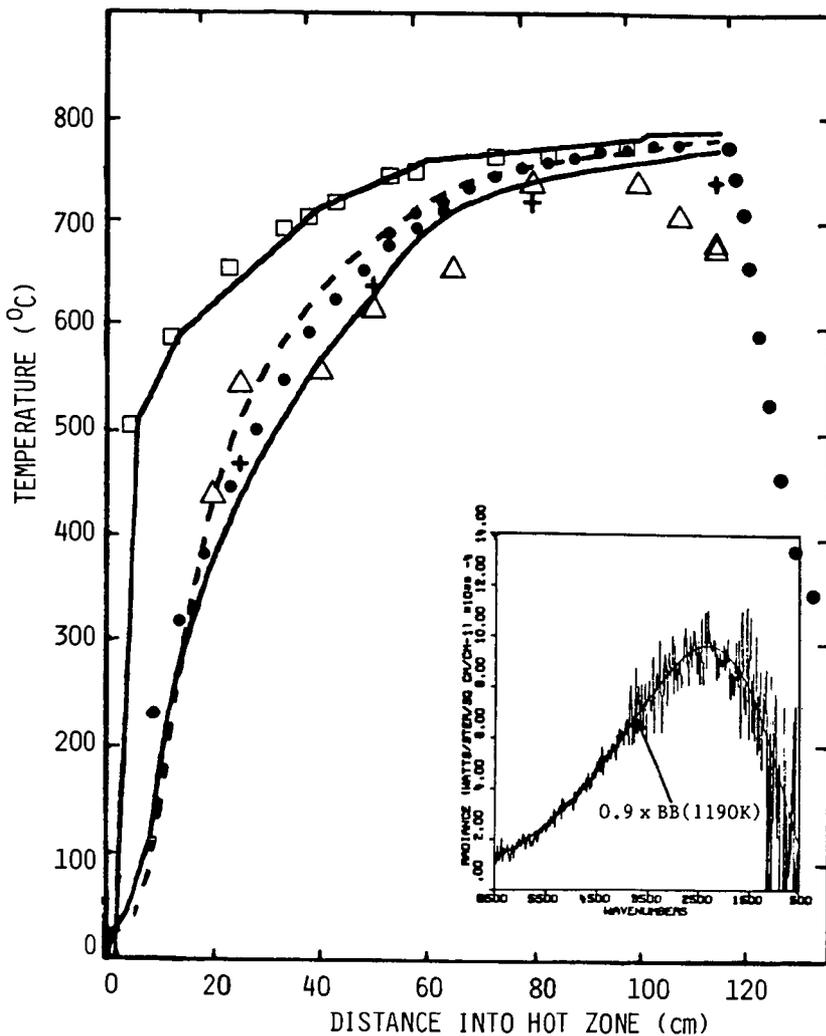


Figure 2. Measured and Calculated Temperatures in the Tube Reactor with Coal and Helium.  $\square$  Outside Tube Temperature Corrected for Heat Loss.  $\bullet$  Thermocouple Temperature Inside the Tube.  $+$  Thermocouple Temperature at FT-IR Focal Point.  $\triangle$  FT-IR Temperature of Coal Particles. Upper Line is the Wall Temperature used as Input. Lower Line is the Calculated Coal Particle Temperature. Dashed Line is the Calculated Thermocouple Temperature. Insert is a Comparison of an FT-IR Normalized Emission Spectrum with a Theoretical Black-body Assuming  $\epsilon = 0.9$ .

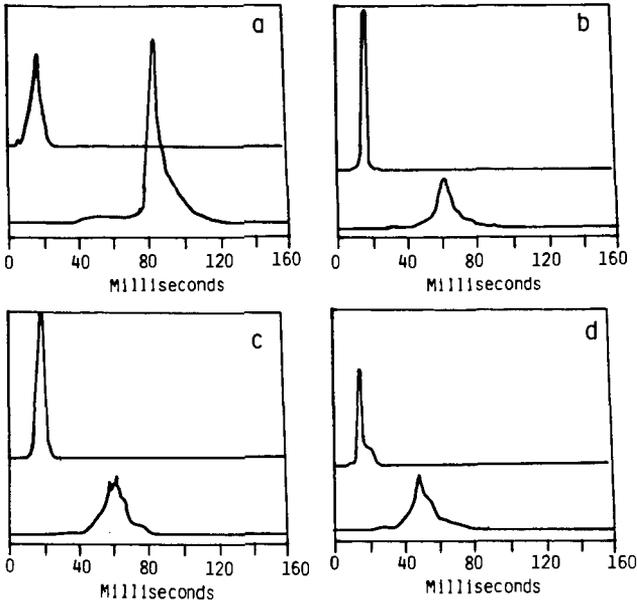


Figure 3. Phototransistor Signals Indicating Coal Particle Transit Times for 4 Electrode Positions. a) 125 cm Cold, b) 50 cm Cold, 75 cm Hot, c) 25 cm Cold, 100 cm Hot, and d) 10 cm Cold, 115 cm Hot.

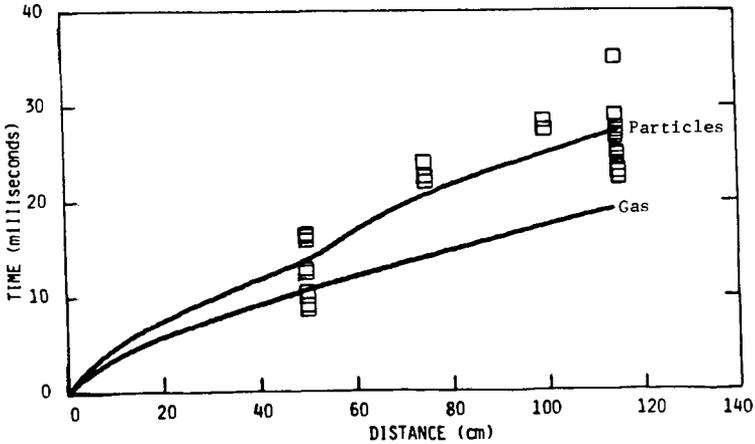


Figure 4. Measured and Calculated Particle Residence Time and Calculated Gas Residence Time in the Heated Tube Reactor. The Calculation Assumes the the Particles are at 80% of the Gas Velocity before and after Primary Pyrolysis and at 40% between 1% and 75% Weight Loss.

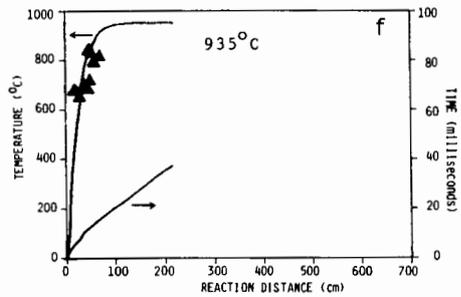
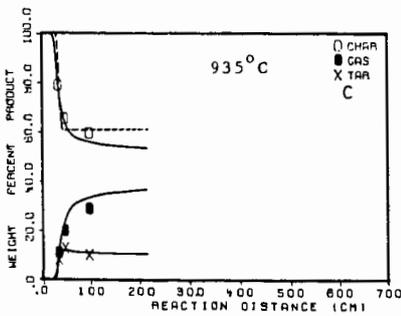
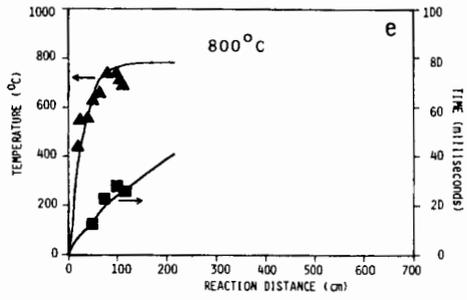
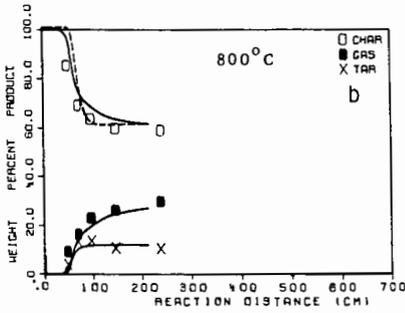
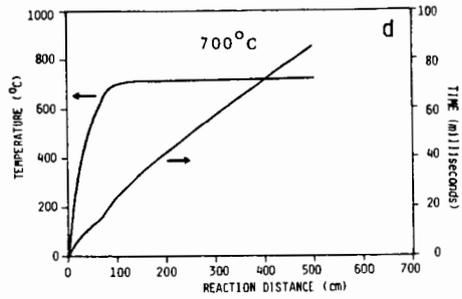
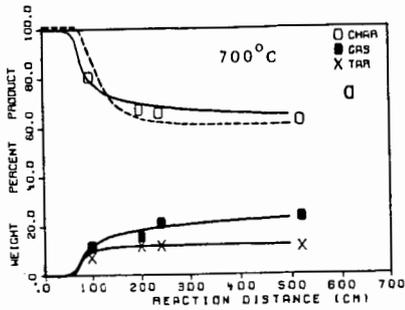


Figure 5. Pyrolysis Results Comparing the Theory and Data for Yields and Particle Time Temperature Histories. Symbols are Data, Solid Lines in a-c are from the Functional Group Model (8). The Dashed Lines are a Single Rate First Order Model. Lines in d-f are from a Heat Transfer Model.

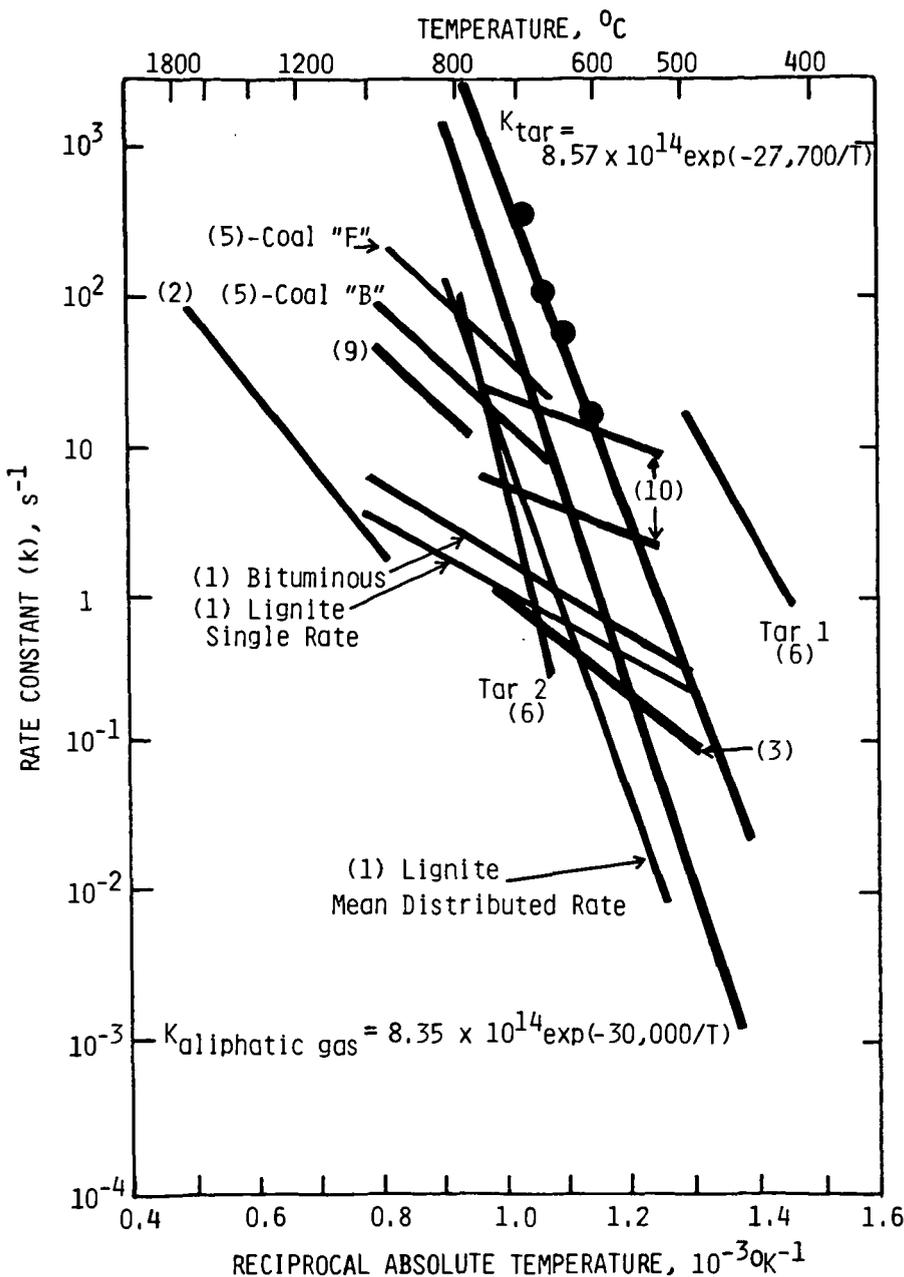


Figure 6. Comparison of Kinetic Rates for Weight Loss (or Tar Loss) from Several Investigations. The Numbers in Parentheses Indicate the Reference from which the Rates were Obtained. The Upper Lines for Reference 10 was for 53-106  $\mu$ m dia. Particles, the Lower Lines was for 850-1000  $\mu$ m dia. Particles. The Rates for Tar and Aliphatic Gas are those used in the Theoretical Calculation. Note that the Number in the Exponent is Roughly 1/2 the Activation Energy.