

AN ENTRAINED FLOW REACTOR WITH IN SITU FTIR ANALYSIS*

Peter R. Solomon and David G. Hamblen

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

INTRODUCTION

A key element in predicting coal gasification behavior is pyrolysis. This is the initial step in gasification, the step which controls the amount and physical structure of the char and the step which is most dependent on the properties of the coal. Recent reviews of coal pyrolysis (1,2,3) conclude that the pyrolysis product distribution and apparent kinetic rates vary widely with the experimental measurement. It is clear that to establish a true predictive capability additional work is needed to understand pyrolysis reactions and define usable rates.

Among the experiments which have been useful in investigating pyrolysis have been the captive sample heated grid devices which have achieved good mass and elemental balances and have provided data on individual species evolution (4-16). However, the heating of the coal is slower than in practical devices so that the kinetic data is of limited value.

Entrained flow reactors which provide more realistic particle heating have been employed to study pyrolysis weight loss but have not provided much species evolution data (17-23). New visual data on pyrolysis behavior have been obtained in reactors with optical access (24, 25). These reactors employ flat flame burners into which coal may be injected.

This paper reports on a new apparatus which has been designed to combine the advantages of the reactors described above. The new reactor: 1) injects coal into a preheated gas stream in a hot furnace to provide rapid particle heating, 2) provides for optical access, 3) employs an FTIR for species concentration measurements, both in-situ and in an external cell and 4) has provisions for obtaining mass balances. The reactor will be used in a program to study pyrolysis and secondary reactions of interest in gasification. The results will be used to test the conclusions of a previously developed pyrolysis model (11-15, 26-29) and fill in needed kinetic data. The paper describes the reactor, reports preliminary results obtained with four coals at furnace temperatures from 700°C to 1200°C and assesses how these results compare to data obtained in other experiments.

EXPERIMENTAL

The reactor has been designed to study coal behavior under conditions of temperature and heating rate encountered in an entrained flow gasifier. The schematic of the experiment is presented in Fig. 1. A gas stream of predetermined composition is heated during transit through a bed of alumina chips maintained at furnace temperature. (Prior to heating, the gas composition can be analyzed by routing the stream through an infrared cell). The gas stream then enters a test section, maintained at the furnace temperature, where coal is introduced through a water cooled injector. The coal is fed using a modification of a MIT entrainment system (30). In the modified system, the feeder tube, which extends up through the coal bed, is slowly lowered as the entrainment gas (injected above the bed) exits through the tube. When the tube feeder entrance is at the level of the bed, coal is entrained in the gas and enters the tube. The rate for coal feeding is controlled by the rate at which the tube is lowered.

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After a variable residence time, the reacting stream passes optical access ports and immediately downstream is quenched in a water cooled collector. There are five optical access ports, two of which are presently employed for the FTIR beam. The other three ports are available for additional diagnostics. The quenched stream of char, tar and gases enters a cyclone designed to separate particles larger than 4 microns (31) and then enters a series of filters to remove and sample the tar and soot. The clean gas stream then enters the room temperature FTIR cell which provides a longer path length for higher sensitivity analysis. The particle residence time can be varied from 0 to 700 msec and the furnace has been designed to operate up to 1650°C.

The FTIR can quantitatively determine many gas species observed in coal pyrolysis including CO, CO₂, H₂O, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₈, C₆H₆, NH₃, HCN, SO₂, COS, CS₂ and heavy paraffins and olefins. The instrument can take spectra every 80 msec to follow rapid changes in the reactor or co-add spectra for long periods of steady state flow to increase signal to noise. FTIR is well suited to in-situ furnace experiments since the FTIR system operates by coding the infrared source with an amplitude modulation which is unique to each infrared frequency. The detector is sensitive to the modulated radiation so that unmodulated stray radiation is eliminated from the experiment.

In the work described below, experiments were run for the four coals listed in Table I. The coals were sieved to produce a -200, +325 mesh size cut. The coal was fed at 2.4 grams/min. Helium was used for both the preheated gas and the entrainment gas. The preheated gas was fed at rates between 40 and 25 l/min depending on temperature to provide a gas velocity of 1 m/sec within the furnace. The entrainment gas was fed at 1.2 l/min. Infrared spectra were obtained with a Nicolet model 7199 FTIR using a globar source and a mercury-cadmium telluride detector. For obtaining the spectra within the furnace and within the cell, 100 scans at 0.5 wavenumber resolutions were accumulated in 140 seconds and transformed in under 2 minutes.

TABLE I
COALS USED IN THE ENTRAINMENT FLOW REACTOR STUDY

COAL	TYPE	WT% (DAF)					ASH (Dry)
		C	H	N	S	O	
Savage	Montana Lignite	71.2	4.6	1.1	1.3	21.8	10.6
Jacobs Ranch	Wyom. Subbituminous	74.3	5.2	1.1	.6	18.8	7.8
Illinois #6	Bituminous	73.9	5.1	1.4	4.2	15.4	11.0
Pittsburgh #8	Bituminous	83.5	5.5	1.6	3.3	6.1	9.2

Gas Analysis in the Furnace

Figure 2 shows the in-situ gas analysis. There is an acceptable noise level and no drastic effects from the particle scattering. The analyses are for the coal injector at positions from 5 to 66 cm above the optical port. The species which can easily be seen are CO, CO₂, H₂O, CH₄, C₂H₂, C₂H₄, and heavy paraffins. Additional species could be observed through the use of software signal enhancement techniques which can be used to detect species whose absorption lines are smaller than the noise (32). These techniques consider all of the absorption lines for a species, rather than a single line.

FTIR spectra obtained directly within the hot furnace allows the observation of heavy products such as tar which don't appear in the gas phase at room temperature and provide a means to determine whether reactions occur during the quenching and sampling of the gas stream. The in-situ observation also permits gas temperatures to be measured as described below.

Temperature Measurements by FTIR

It appears possible to use the ratios of lines from a given species to determine gas temperatures in the furnace. As the temperature of a gas changes, the populations in its higher energy levels increases. In terms of its absorption spectrum, this generally means that more absorption lines are visible. The effect is illustrated in Fig. 3 which compares CO spectra at a number of temperatures. The energy is clearly shifted from the central lines toward the wings as the temperature increases. Lines at 2250 and 2000 cm^{-1} which are too small to be observed at room temperature are clearly visible at the higher temperatures. The ratio of these lines to the lines at the center of the distribution can be used to determine temperature.

Gas Analysis in a Cell

Figure 4 shows the gas analysis from the room temperature cell. This cell was filled with the effluent gas stream from the furnace after passing through the cyclone and filter. The cell provides higher sensitivity detection because the path length is about 12 times longer than in the furnace. The spectra compare the pyrolysis gases from Jacobs Ranch coal injected at 66 cm above the optical port at furnace temperatures of 800 and 1200°C. Important differences in the product mix at these two temperatures can be observed. The top pair of spectra show the region between 3500 and 2800 cm^{-1} . At 1200°C there is HCN, C_2H_2 and CH_4 . At 800°C there is less methane and little HCN or C_2H_2 , but significant amounts of ethane and heavy paraffins (indicated by the broad background). This observation is consistent with the cracking of paraffins to form olefins, acetylene and soot which has been discussed previously (12,14). The region between 2600 and 1900 cm^{-1} shows the CO_2 and CO. The CO_2 increases by 50% but the CO increases by a factor of 3 in going from 800°C to 1200°C. This is consistent with previous observations of low temperature production of CO_2 and high temperature production of CO (11-15). The evolution of CO_2 and CO may be related to the early disappearance of carboxyl groups and the refetion of ether linkages observed in the infrared spectra of chars discussed below. The region between 1800 and 1200 cm^{-1} shows water and methane. The region between 1200 and 500 cm^{-1} shows olefins, acetylene, HCN and CO_2 . The ethylene and heavier olefins are lower and acetylene is higher at the higher temperature (consistent with cracking of olefins to form acetylene and soot).

A comparison of the pyrolysis gas composition from different coals is presented in Fig. 5. The coals were all injected at 66 cm above the optical window at a furnace temperature of 800°C. The spectra show the kind of variation with rank which has been discussed previously (11-15). The low rank coals, which are high in the oxygen functional groups, produce pyrolysis gases which are high in the oxygen containing species, CO, CO_2 and H_2O . The higher rank coals, which are higher in aliphatic functional groups, yield higher concentrations of hydrocarbons.

Data of the kind illustrated above were collected at several reaction distances at 800°C. Curves of concentration vs reaction distance differed among the species. On a normalized basis, however, these curves were similar for the various coals even though the concentration varied from coal to coal. This result is also in agreement with earlier work (11-15).

Changes in Char Chemistry

The infrared spectra of chars provide a convenient means of monitoring the chemical changes occurring during the pyrolysis process. The changes in functional group concentration can be correlated with the appearance of gas species to determine the sources for the species. FTIR spectra of chars from pyrolyzing Jacobs Ranch Coal at 800°C are shown in Fig. 6. The techniques for preparing, drying and making scattering corrections have been discussed previously (13, 33). The aliphatic groups (peak near 2900 cm^{-1}) and carboxyl groups (shoulder near 1650 cm^{-1}) are observed to decrease with reaction distance. The hydroxyl groups (broad peak between 3500 and 2500 cm^{-1}) also decrease although not as rapidly. As the residence distance (and time) is increased, the char aromatic hydrogen peaks near 800 and 3100 cm^{-1} are observed to increase. The O-C bond concentration (peak near 1200 cm^{-1}) shows little change. These changes in the functional group concentrations during pyrolysis are in agreement with results from earlier experiments (14, 15, 21). The changes in char chemistry will be correlated with evolution of gas species and compared with the pyrolysis model predictions.

Conclusions

Preliminary results have been obtained in a newly constructed Entrained Flow reactor with on-line in-situ analysis by FTIR. These results indicate that:

1. Gas concentration measurements for CO, CO₂, water, methane, acetylene, ethylene and heavy paraffins can be routinely made in a hot furnace with an FTIR.
2. Gas temperature measurements appear feasible using ratios of CO lines.
3. On-line gas analysis in an external gas cell is also extremely effective,

Several observations which have previously been reported for other pyrolysis experiments appear to be supported by the preliminary data. These are:

1. Gas kinetics appear to be relatively insensitive to coal rank.
2. The gas composition varies systematically with the functional group composition of the coal.
3. There is temperature dependent cracking of paraffins to form olefins and acetylene and olefins to form acetylene.
4. Functional groups in the chars disappear in the following order: First aliphatics, then hydroxyl, and then aromatic hydrogen and ether linkages. The present results show that carboxyl groups also disappear quickly.

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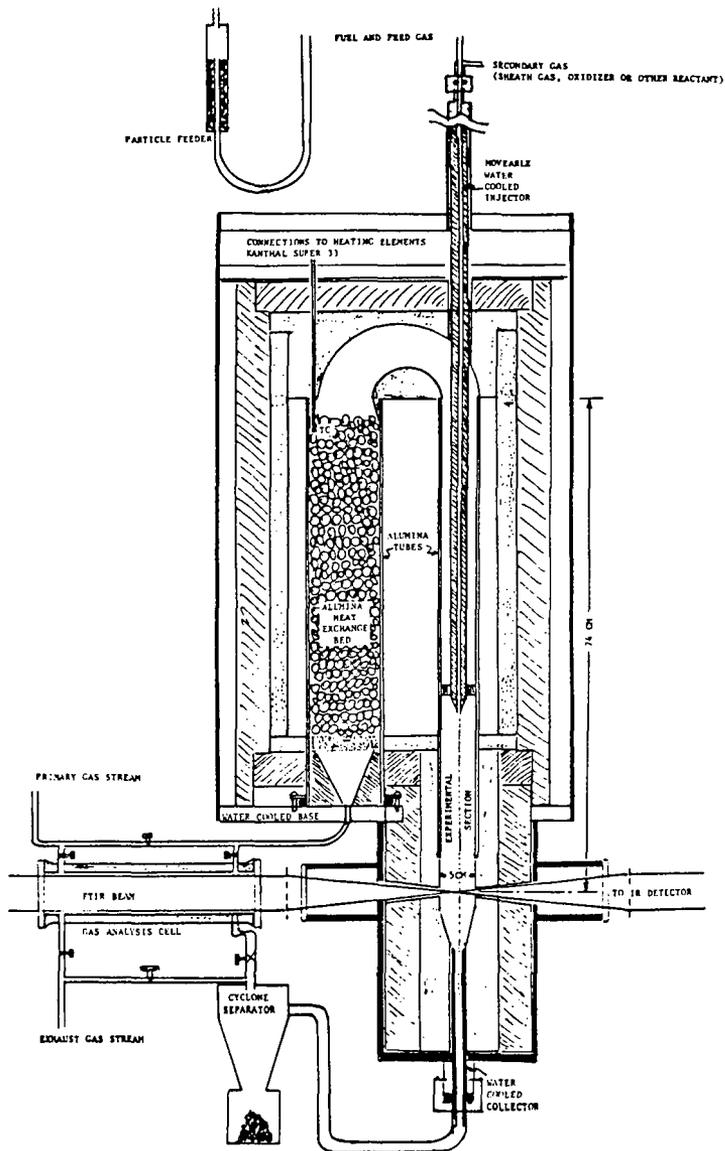


Figure 1. Entrained Flow Reactor.

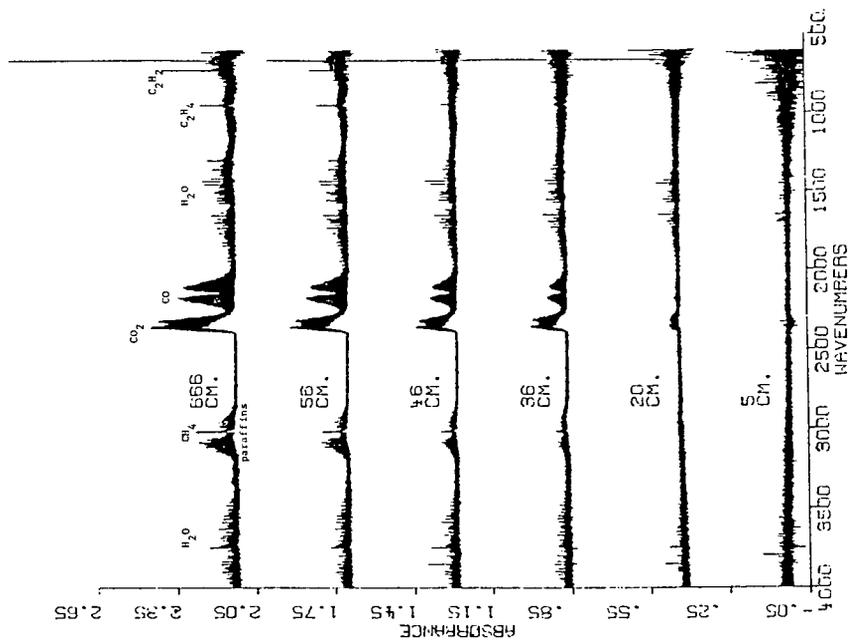


Figure 2. In-Situ FTIR Spectra of Pyrolysis Gases from Jacob's Ranch Coal at 1000°C.

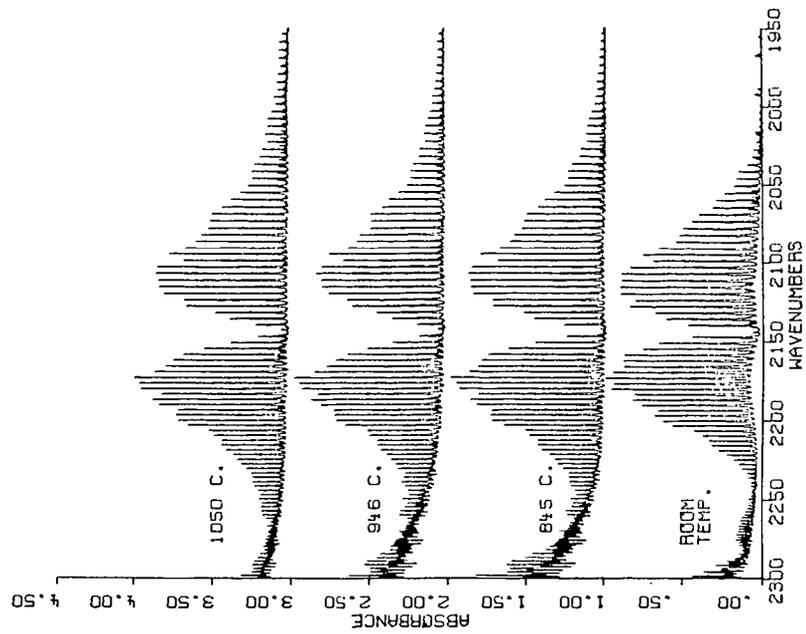


Figure 3. Spectra of CO at Elevated Temperatures.

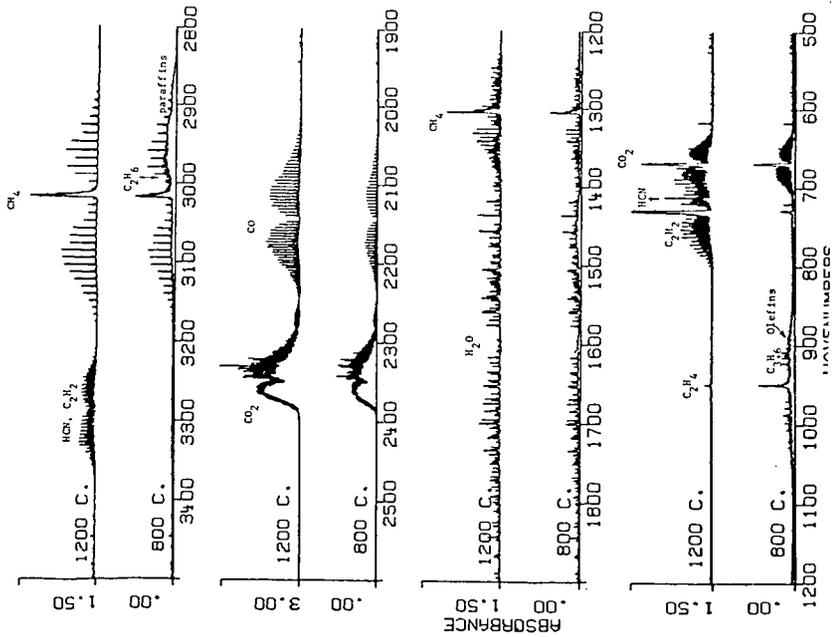


Figure 4. FTIR Spectra of Pyrolysis Gases from Jacob's Ranch Coal at 800°C and 1200°C in Room Temperature Cell. 66cm Residence Distance.

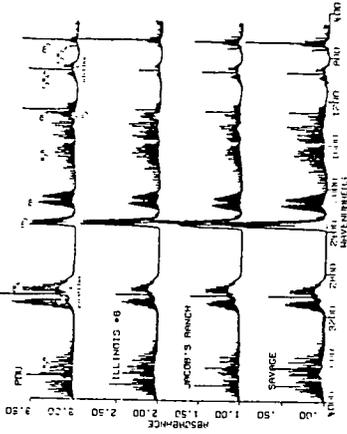


Figure 5. Comparison of FTIR Spectra from 4 Coals Pyrolyzed at 800°C at 66 cm Residence Distance.

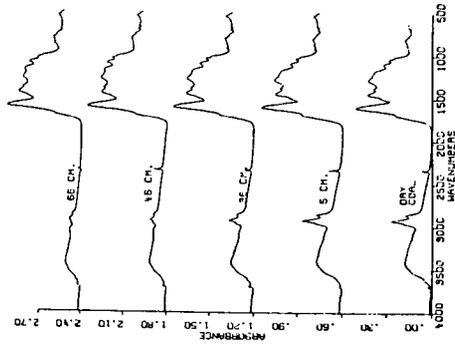


Figure 6. FTIR Spectra of Char from Jacob's Ranch Coal Pyrolyzed at 800°C.