

AN IN SITU STUDY OF RAPID COAL PYROLYSIS USING FTIR*

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INTRODUCTION

Recent investigations of rapid coal pyrolysis have generally been limited to two approaches -- entrained flow techniques and heated grid devices. The entrained flow technique provides a method wherein injected coal samples experience heating rates comparable to those expected in combustion processes. However, the data collected is generally limited to weight loss as a function of apparent residence time in the reactor hot zone (1,2,3). The heated grid techniques provide a more clearly defined time-resolved thermal environment for small particles (60 - 100 μm) and allow determination of the volatile species evolved into a cold environment surrounding the grid (4-8). Due to the mode of heating of the particles in the grid technique one is limited to the particle size ranges that can be employed. Both approaches have provided useful information concerning the nature of rapid devolatilization. It is also clear that other techniques and reactor designs are needed to provide information concerning rapid pyrolysis phenomena for a range of temperatures, particle sizes and reactive atmospheres.

EXPERIMENTAL DESIGN

A reactor has been constructed in which small samples of coal (20 - 60 mg) are rapidly injected (~ 25 msec) into a preheated environment. The injection device allows one to deliver particles as small as 100 μm or as large as several millimeters in diameter. Injection of the small samples into a preheated zone insures that the particles experience initial heating rates comparable to those expected in coal combustors. The gases produced by the thermal decomposition process are monitored in situ by use of a Nicolet FTIR Spectrometer operated in the rapid scan mode. A schematic of the pyrolysis system is shown in Fig. 1.

PYROLYSIS GAS SPECTRA

Figure 2 displays a portion of the time-resolved spectra obtained from the devolatilization of a Pittsburgh bituminous coal (PSOC 170). Figure 3 displays the same spectral window obtained from the rapid scan FTIR data collected from the devolatilization of a Montana lignite. The difference in characteristics of the gaseous yields are apparent. The bituminous coal yielded the greater ratio of hydrocarbon species to carbon oxide species. The same trend is noted in the high resolution scans taken at the completion of the rapid scans (See Figs. 4 and 5). These trends

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were to be expected on the basis of work previously performed by use of a heated grid to devolatilize the coal. That is, the relative yields of the light gases reflect the functional group characteristics of the parent coal (8).

APPARENT FIRST ORDER ARRHENIUS RATE CONSTANTS

The rise times of the various gaseous species were used to extract apparent first order rate constants from the time-resolved FTIR data. For the sake of comparison, the method of extracting the rate constants was the same as that previously employed using the heated-grid apparatus. Figure 6 shows the results obtained for the Pittsburgh bituminous coal and the Montana lignite. Obviously, there is a significant difference in the apparent rate constants obtained by devolatilization in each of the two reactors. It is believed that the variation in rate constants reflect the variations in the thermal flux experienced by the coal particles within each reactor. The initial heating rate of 100 μm coal particles in the heated grid apparatus employed was determined by thermocouple measurements to be of the order of 10^2 to 10^3 °C/sec. In the isothermal furnace the initial heating rates are estimated to be of the order of 10^4 °C/sec and greater (9). The rate constants obtained in the furnace experiments are about a factor of ten higher than those obtained from the heated grid. It is believed that the non-isothermal nature of the pyrolysis process in the furnace is responsible for the apparent lack of temperature sensitivity in the rate constant values.

APPARENT FIRST ORDER RATE CONSTANTS AND COAL TYPE

Inspection of Fig. 6 indicates that, within the resolution of the experiment, the coal type does not have a significant effect upon the apparent first order rate constant for a particular gaseous species evolved. The reactor type has a much greater effect on apparent rates than does the coal type.

The independence of apparent rate constant with coal type is in agreement with results obtained by use of the heated grid that indicated that the amount of a particular gaseous species evolved to be highly dependent on coal type but the rate of evolution to be independent of coal type.

APPARENT RATE AND PARTICLE SIZE

As shown in Fig. 6 there is a decrease in rate with particle size if the particle size range of the sample is changed from -100 mesh to -40 mesh. There does not appear to be any significant difference in the yield structure of the light gases evolved. For the small sample sizes employed, the yield structure of the light gases appeared to vary more with the particular sample employed than with the particle size chosen.

FINAL REMARKS

As indicated by the comments above, the current pyrolysis configuration has been useful in determining the validity of hypotheses formulated by studies performed with the heated grid apparatus. However, in its current configuration it is not without

its disadvantages: calibration of the reactor is extremely difficult; the alumina walls tend to provide active sites for the transformation of sulfur-containing gases; the tar-soot mist formed at higher operating temperatures and by use of smaller particle sizes tends to interfere with the IR signal.

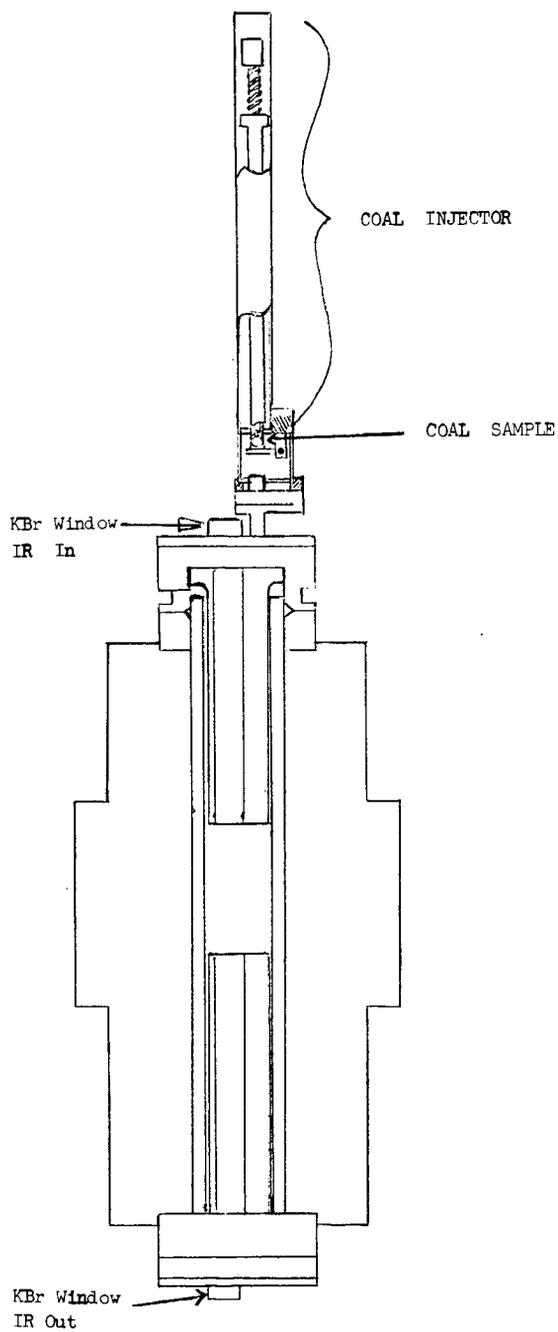
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FIG. 1: PYROLYSIS SYSTEM



TIME-RESOLVED SPECTRA OF PITTSBURG BITUMINOUS COAL
(TIME RESOLUTION BETWEEN SPECTRA 0.2 SEC)

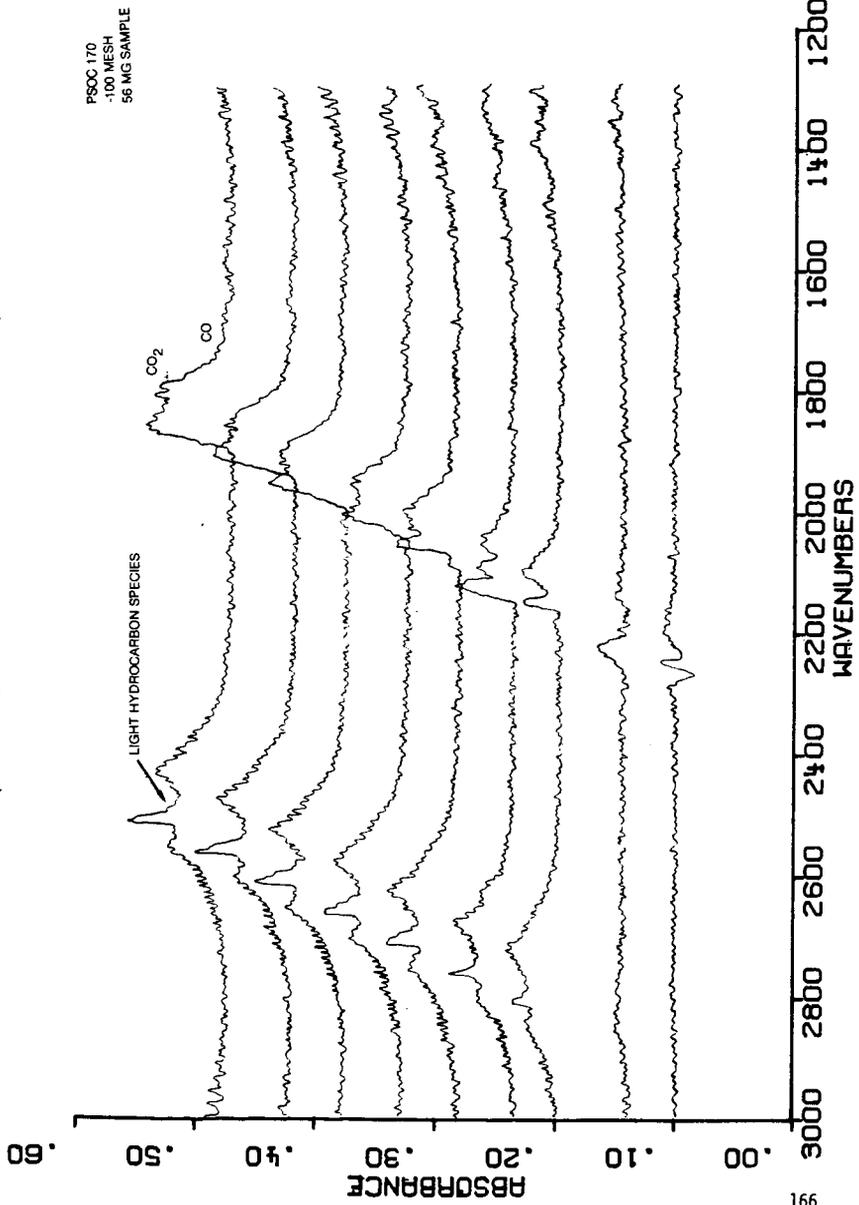
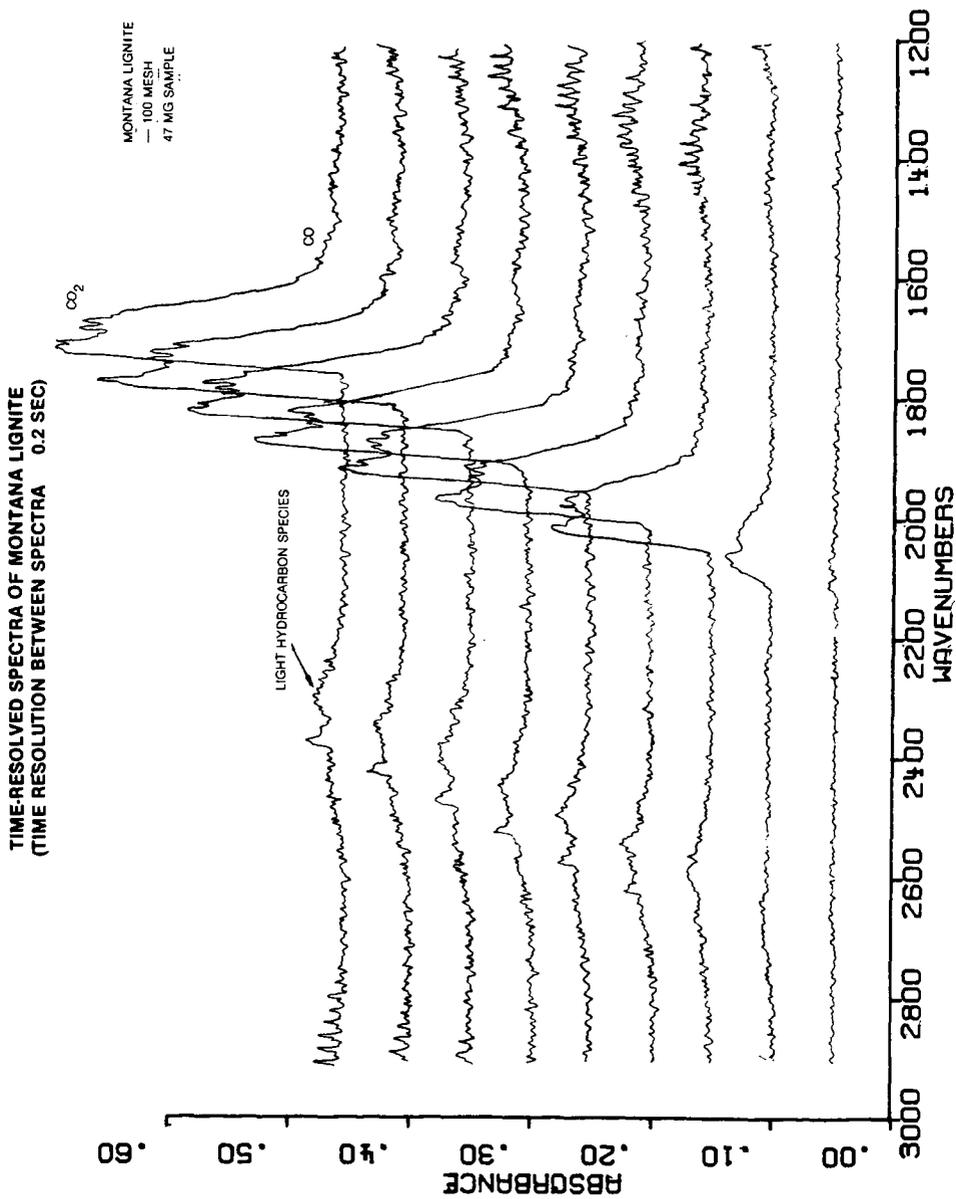
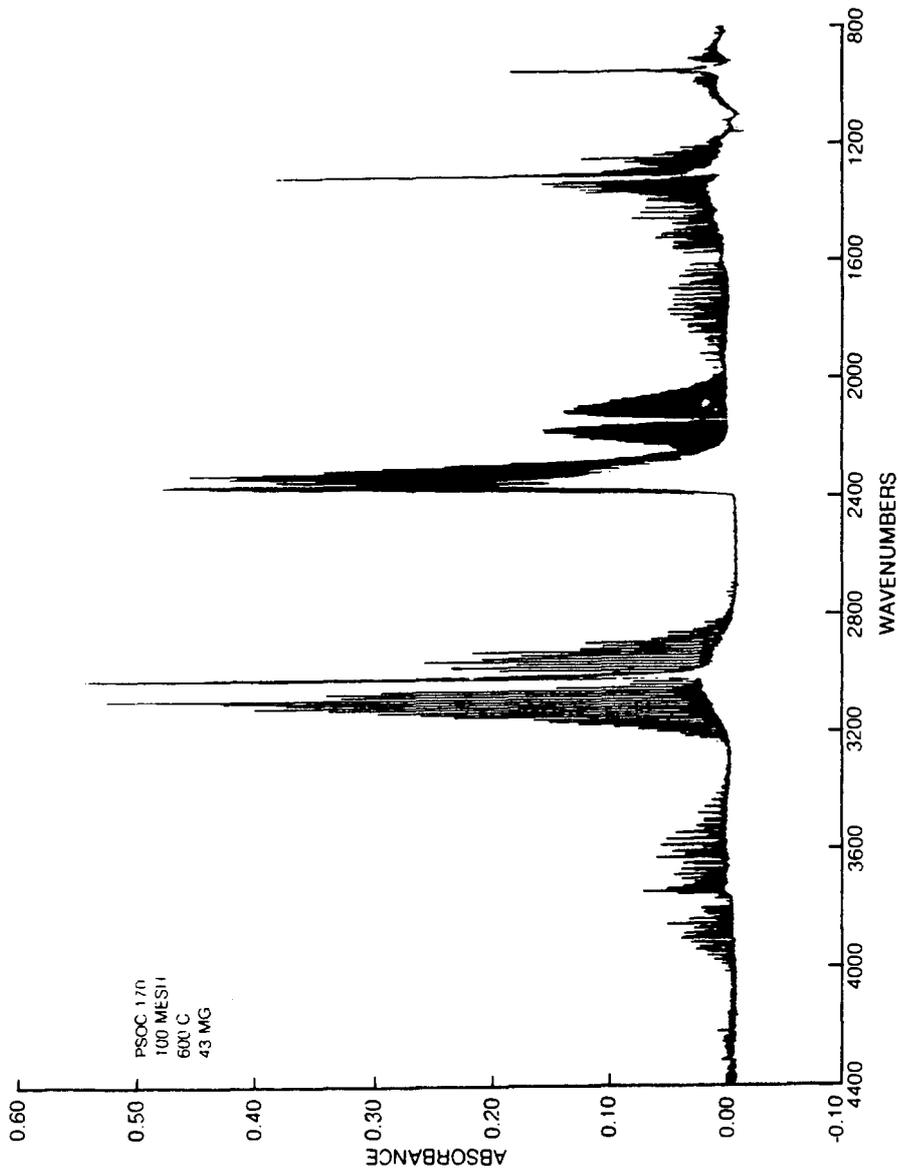


FIG. 2

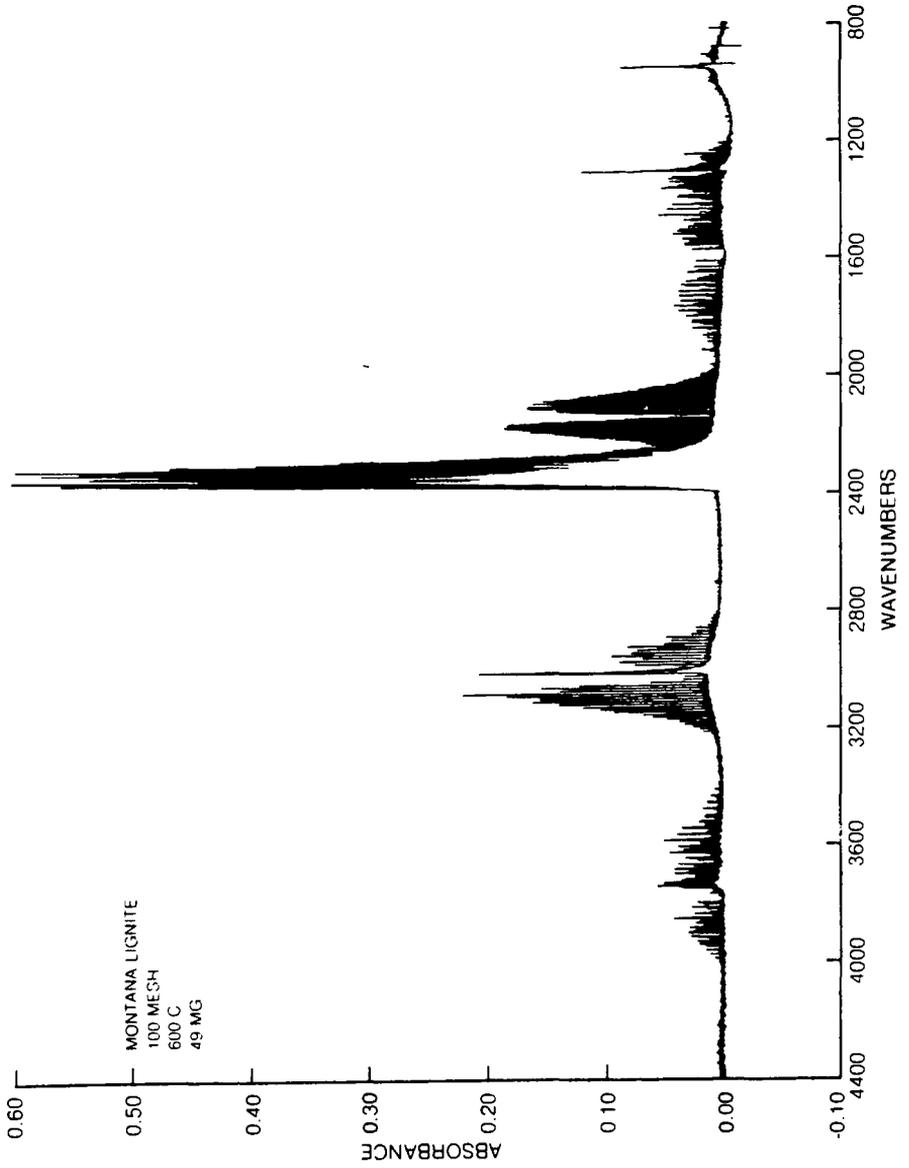
FIG. 3



PYROLYSIS GAS — HIGH RESOLUTION SCAN



PYROLYSIS GAS — HIGH RESOLUTION SCAN



RATE CONSTANT FOR METHANE EVOLUTION

