PYROLYSIS STUDIES OF ILLINOIS #6 AND ITS TAR USING MATRIX ISOLATION FTIR SPECTROSCOPY

C. Judith Chu, Leif Fredin, Robert H. Hauge and John L. Margrave

Department of Chemistry, Rice University, Houston, Texas 77251

INTRODUCTION

The various experiments in this study are performed with the objective of better understanding the initial reaction steps in coal gasification. Emphasis is placed on clarifying and understanding the structure of coal and its tars through pyrolysis studies designed to enhance formation of reactive gas phase intermediate species. Our main concern is centered on the characterization of unknown intermediates and better understanding the mechanism of tar formation. The experiments are designed such that reactive gas phase intermediates can exit the reaction zone rapidly and be trapped with inert matrix gas on a cold (12°K) matrix surface. Identification of these species and possibly free radicals are performed in a newly designed Rice University multisurface matrix isolation FTIR-MS apparatus[1].

EXPERIMENTAL

The Rice University multisurface matrix isolation FTIR-MS apparatus was used in the slow pyrolysis studies of Illinois #6 and flash pyrolysis of its tars. The multisurface MI-FTIR apparatus possesses a large number (60) of deposition surfaces which are useful for pyrolysis studies over a wide range of temperatures. This large number of surfaces is very valuable in detecting small changes occuring as a result of variations in reaction temperature or other reactor conditions. The system is integrated to a high resolution Fourier transform i. r. spectrometer covering a spectral range from the far i. r. to the near i. r. A detailed schematic diagram of the MI-FTIR apparatus is shown in Figures 1a and 1b.

The reactor used in our slow pyrolysis experiments is shown in Figure 2. It consists of a water cooled radiation shield; a hot furnace resistively heated through a cylindrically shaped thin tantalum foil (.001 inches) which has been spot wielded to an outer cylinder of a thicker tantalum tube (.020 inches); and a graphite sample cell. Finely divided powders of coal, between 20-100 mg. of <500 mesh particle size, are place into the graphite cell inside the reactor. After evacuation, the sample is slowly heated from room temperature to approximately 1450°C. The gaseous pyrolysis products are then immediately directed over the very cold depostion surface (12°K) which quenches reactions and traps the species in an inert matrix gas of either argon or nitrogen. In general, one depostion surface is used for each 60-100°C increment rise in temperature over a 10 minute trapping period. The frozen transient products are later analyzed off-line with the FTIR spectrometer.

Figure 3 presents the reactor used in the flash pyrolysis studies of coal tar. The reactor is essentially the same as described for the slow

pyrolysis studies with the exception of the sample cell. Since tar evolves at relatively low temperatures (~100-300°C), it became essential to maintain the coal within this low temperature range to ensure generation of tar. The evolved tar should then pass through a hot zone of ~1200°C for pyrolysis to occur. These requrirements have been achieved by the design of a copper sample cell cooled by flowing either nitrogen or helium gas through small stainless steel tubing (1/16") silver soldered to the back of the copper cell (see details in Figure 3). A piece of 4 mm quartz tubing is attached to the front of the copper cell. This is the hot reactor zone where the flash pyrolysis occurs. When assembled and placed into the furnace, the relatively non-conducting quartz tube becomes positioned at the front of the furnace, in the hot zone, and the copper cell containing the coal sample becomes positioned at the relatively cool back section of the furnace. By varying the flow of the cooling gas from 30 to 0 psi, the temperature of the copper cell can be successfully maintained in the tar evolution range (between room temperature to ~321°C) when the temperature of the quartz tube reaches ~1180°C. Under these conditions, evolution of tar is easily controlled. During the experiment, the temperature of the coal powder was closely monitored with a Chromel-Alumel thermocouple in direct contact with the copper cell. Tar molecules are pyrolyzed as they pass through the hot quartz tube through surface heating. The transient pyrolysis products are trapped onto the 12°K deposition surface along with the inert matrix gas to be analyzed later by FTIR spectroscopy.

RESULTS

1. Slow Pyrolysis of Illinois #6

Slow pyrolysis studies are performed as a basis for characterizing coal and for comparison to other heating techniques. Approximately 28 mg. of Illinois #6 (<500 mesh) coal powder is placed in the graphite cell (see Figure 2) and slowly heated. Gaseous products obtained at different temperatures are trapped in 10 minute intervals with nitrogen onto the 12°K matrix isolation surface and subsequently examined. The resulting MI-FTIR spectra are presented in Figure 4. Variations in gaseous pyrolysis products are easily followed in the three-dimensional plot. As can be seen from the plots, coal devolatilization is characterized by: the immediate evolution of CO_2, H_2O and SO_2 as well as traces of small carbonyls such as acetone, formaldehyde[2], formic acid[3] and acetic acid[4] at low temperatures; evolution of tar at 150-400°C with simultaneous evolution of CH_4, C_2H_4, C_2H_6, C_3H_6 and COS; coupled evolution of CO_2, CO, H_2O, HCN and CH_4 from 400-850°C; and higher temperature evolution of CS_2, CO, H_2O and C_2H_2 as well as nitric oxide[5] and other as yet unidentified species. The interesting observation that carbon monoixide reaches maximum yield at two different temperatures, first at ~800°C and then at ~1350°C indicate two

different sources of CO in the parent coal. This has also been observed by Soloman and co-workers[6].

Tar formation with simultaneous evolution of CH_4, C_2H_4, C_2H_6 and C_3H_6 suggests aliphatic linkage groups in the parent coal. Our studies also indicate the evolution of tar as discrete molecules (perhaps in the form of free radicals) which re-polymerize to give a structure similar to the parent coal. Characteristic tar absorptions in matices are broad absorptions in the C-H stretching region of 3100-2800 cm^{-1}, C-H bending region of 1500-1400 cm^{-1} and C-O stretching regions of ~1100 cm^{-1}. More detailed tar spectra and their variations with temperature are shown in Figure 5.

Sulfur in Illinois #6 coal is evolved in the form of SO_2 and COS at low temperatures and CS_2 at higher temperatures. Traces of H_2S and NH_3 are also observed at low temperatures.

2. Pyrolysis of Illinois #6 Tar

Pyrolysis studies of Illinois #6 tar were carried out to gain a better understanding of its structure and of how it differs from the parent coal. Approximately 100 mg. of Illinois#6 powder (< 500 mesh) is placed in the copper cell (see Figure 3). After assembling the reactor and attaching it to the matrix isolation apparatus, the system is slowly evacuated to 10^{-6} torr. The front furnace is then immediately heated to and maintained at 1180°C throughout the length of the experiment. A constant flow of helium gas is passed through the stainless steel cooling tube at a starting pressure of 30 psi to keep the copper tube at a low temperature. With gradually decreasing helium flow, the temperature of the coal can be raised slowly to induce tar evolution. The tar then passes through the hot quartz tube, becomes pyrolyzed and gaseous intermediates are trapped in 10 minute intervals with nitrogen onto the 12°K deposition surface. The temperature range studied was from room temperature to 321°C. The evolution of tar was found to be a continuous process starting from 120°C and reaching maximum yield between 206-238°C. The resulting MI-FTIR spectra of tar pyrolysis products are shown in Figure 6. It can be seen clearly that the characteristic broad tar absorptions have disappeared indicating pyrolysis of tar. The appearance of several new species as well as increased absorptions of several existing species are observed in place of tar. They are: increased yeilds of CO, C_2H_4 and C_2H_6; appearance of HCN, CS_2, benzene[7] and the methyl radical[8], CH_3; approximately the same yields of CO_2, H_2O, CH_4, C_3H_6, SO_2, COS and the carbonyls (acetone, acetic acid, formaldehyde, formic acid). Traces of NH_3 and H_2S are also observed. The presence of acetylene as one of pyrolysis products is inconclusive since C_2H_2 has the same absorptions as HCN in nitrogen matrices[7,9].

In summary, pyrolysis of Illinois #6 tar was found to produce CO, C_2H_4, C_2H_6, HCN, CS_2, C_6H_6 and the methyl radical CH_3. The formation of C_2H_4, C_2H_6 and benzene as pyrolysis products points to the presence of aromatic hydrocarbons in the tar structure since pyrolysis of other aromatic hydrocarbons are known to produce similar results[10]. CO, HCN and CS_2 indicate presence of oxygen, nitrogen and sulfur in tar. Finally the formation of methyl radicals indicate that the design of our reactor favors and promotes the formation of free radicals which can rapidly exit the reactor chamber without secondary reactions with other species. By varying the diameter of the quartz tube, we hope to further enhance the chances of observing other free radicals.

3. Slow Pyrolysis of Oxidized Illinois #6

Effects of oxidation on Illinois #6 powder were studied. Illinois #6 powder (< 500 mesh) was oxidized by heating the coal in an oven at ~180°C for 4 hours. Formation of carbonyl functional groups in the oxidized coal was observed along with a reduction in aliphatic C-H groups. Results of slow pyrolysis studies of the oxidized coal using the same experimental procedures as described for the unoxidized coal are shown in Figure 7. When compared with results of the unoxidized coal (Figure 4), a clear increase in CO_2 absorption is observed. Oxidation also appears to increase the carbon monoxide absorptions at the lower temperatures (r. t. to 850°C) while CO at higher temperatures remain uneffected. Oxidation also retards formation of tar. Only traces of tar are observed during slow pyrolysis of the oxidized sample.

DISCUSSION

At the present time our work has shown that our pyrolysis technique can be developed as a valuable tool in characterizing different ranks of coal. It is also a highly sophiscated tool for identifying unknown intermediates. As of yet our limited library of refernce data has prevented the identification of all pyrolysis intermediates and products. We will be making numerous additions to this library in the near furture.

ACKNOWLEDGEMENT

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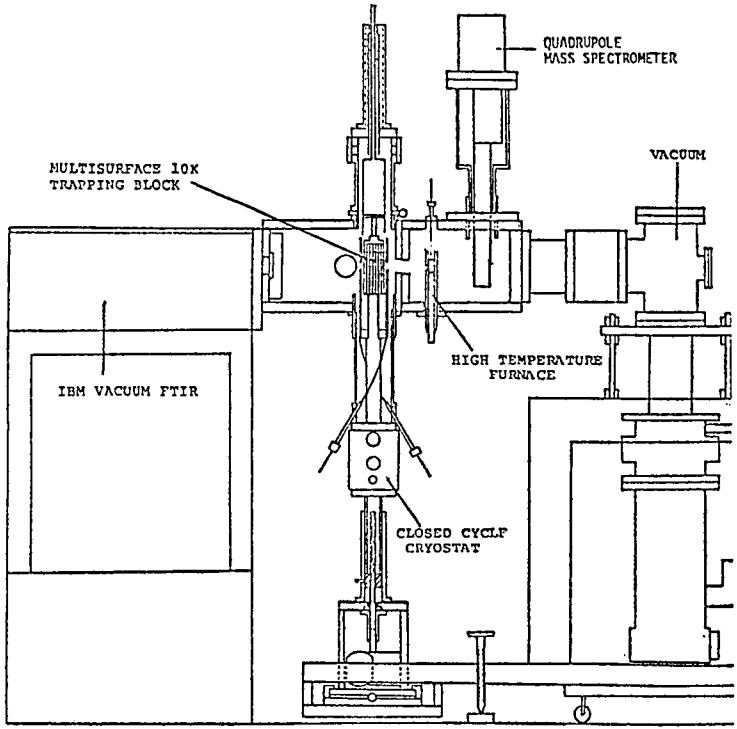
REFERENCES

1. R.H. Hauge, L. Fredin, J. Chu and J.L. Margrave, "The Identification and Chemistry of Species Resulting from the Rapid Pyrolysis of Small Coal Particles in Vacuum and in the Presence of

Reactive Gases", American Chemical Society, Division of Fuel Chemistry, Preprints, 28, 1, 35, (1983).
2. K.B. Harvey and J.F. Ogilvie, Canadian Journal of Chemistry, 40, 85, (1962).
3. R.C. Millikan and K.S. Pitzer, J. Amer. Chem. Soc., 80, 3515, (1958).
4. C.V. Berney, R.L. Redington and K.C. Lin, J. Chem. Phys., 53, 1713, (1970).
5. W.A. Guillory and C.E. Hunter, J. Chem. Phys., 50, 3516, (1969).
6. P.R. Solomon, "The Evolution of Pollutants During Rapid Devolatilization of Coal", Rep. R76-952588-2, United Technologies Research Center, East Hartford Conn. 1977, Rep. NSF/Ra-770422, NTISPB, 278496/AS, 1977.
7. M.M. Rochkind, in "Spectrometry of Fuels, ed. R.A. Friedel, p. 280, Plenum Press, 1970.
8. D.E. Milligan and M.E. Jacox, J. Chem. Phys., 47, 5146, (1967)..
9. C.M. King and E.R. Nixon, J. Chem. Phys., 48, 1685, (1968).
10. Adv. in Chem. Series, 183, "Thermal Hydrocarbon Chemistry", ed. A. G. Oblad, H. G. Davis, R. T. Eddinger, ACS., (1979).

Fig. 1a. Matrix Isolation - FTIR Mass Spectrometer - Side View



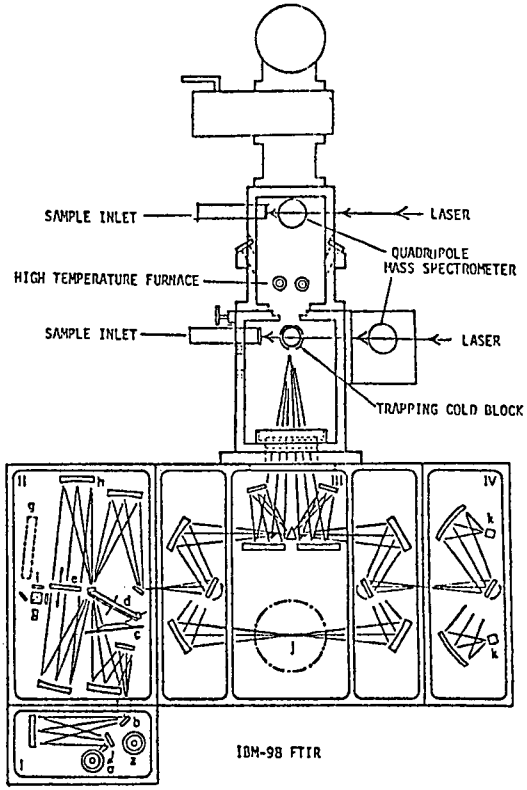


Fig. 1b. Matrix Isolation -FTIR Mass Spectrometer - Top View

Fig. 2 Slow Pyrolysis Reactor

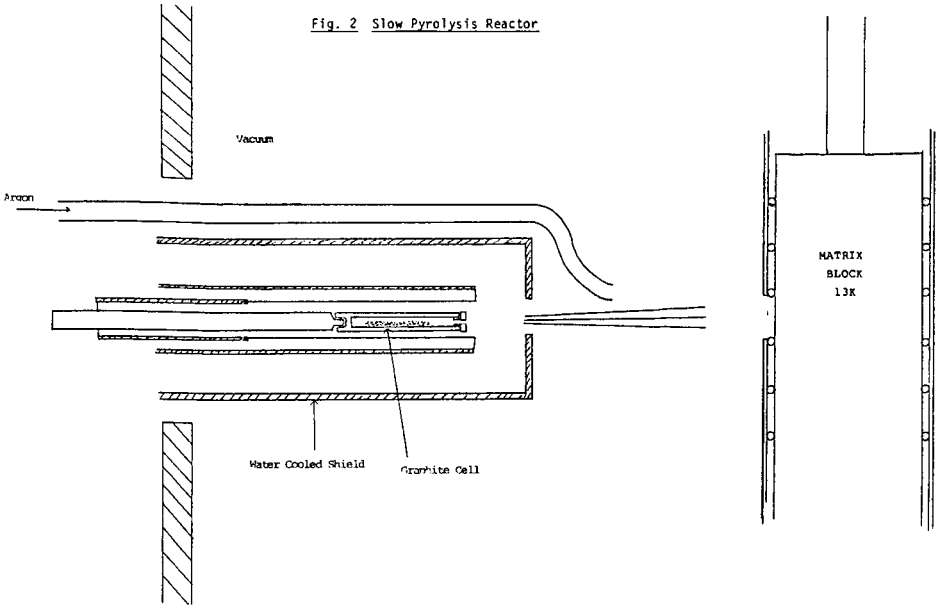


Fig. 3 Reactor for Pyrolysis of Tar

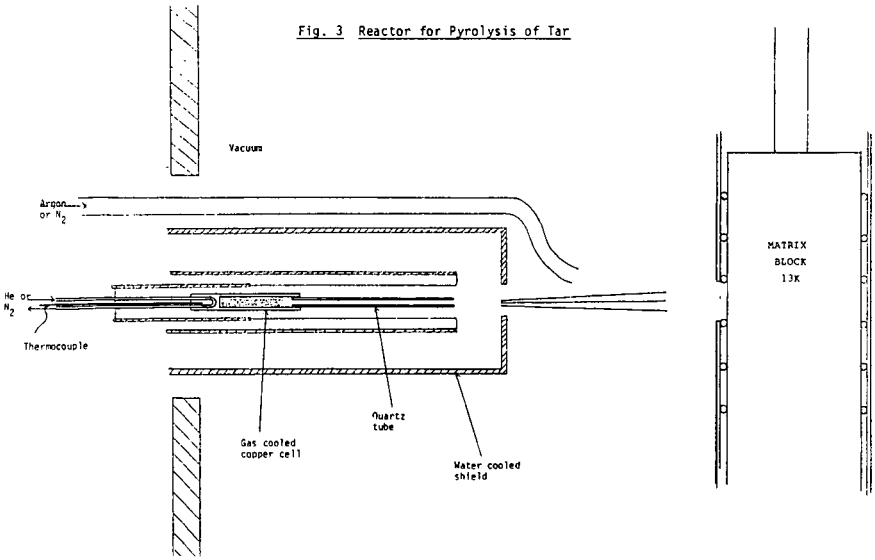


Fig. 4 Slow Pyrolysis of Illinois #6 (500 mesh) from RT to 1489°C in N_2 Matrix (12°K)

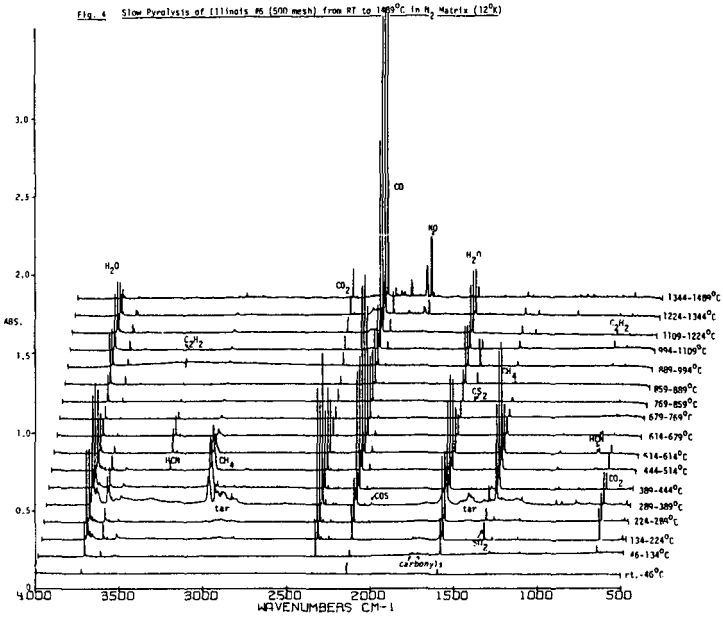


Fig. 5 Slow Pyrolysis of Illinois #6 (500 mesh) in Nitrogen Matrix (12°K)

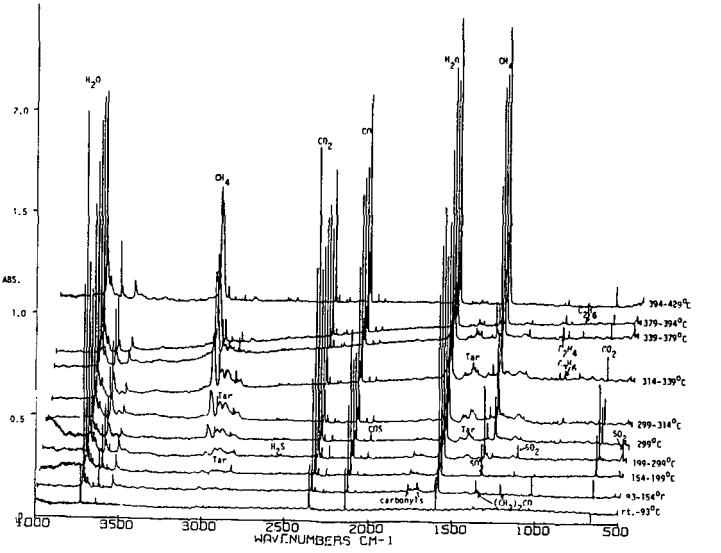


Fig. 6 Pyrolysis of Illinois #6 Tar at 1184°F in Nitrogen Matrix (12°K)

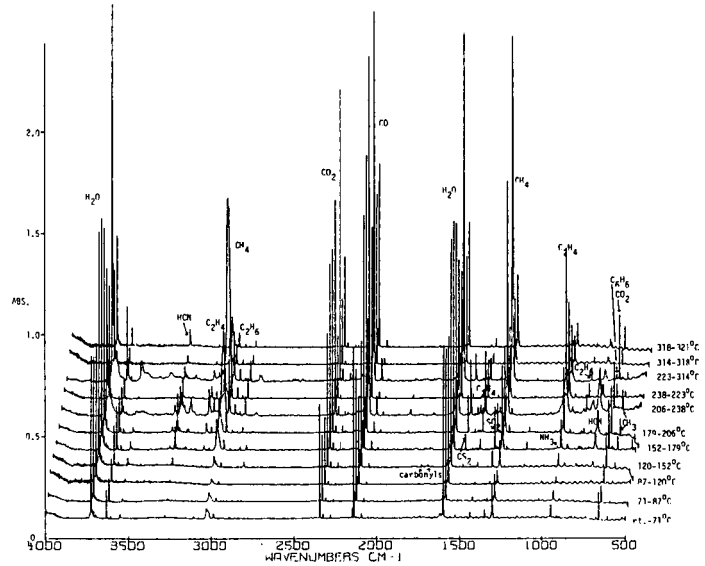
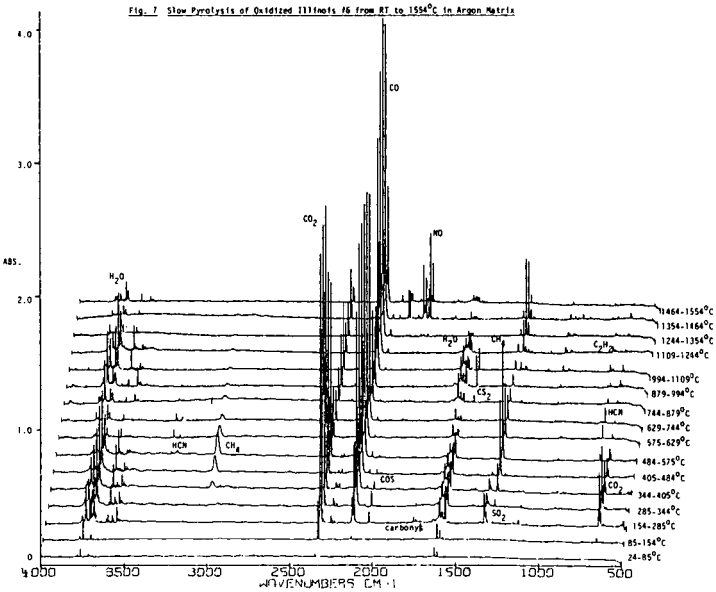



Fig. 7 Slow Pyrolysis of Oxidized Illinois #6 from RT to 1554°C in Argon Matrix