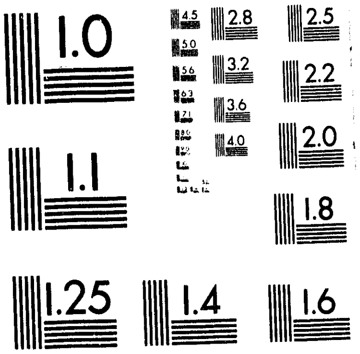
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FUNDAMENTAL STUDIES OF COAL LIQUEFACTION

David S. Ross
Chemistry Laboratory

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U. S. Department of Energy
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Pittsburgh, PA 15236

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Approved:

David M. Golden
Vice President
Physical Sciences Division

MASTER

333 Ravenswood Avenue • Menlo Park, CA 94025-3493 • (415) 326-6200 • FAX: (415) 326-5512 • Telex: 334486

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INTRODUCTION AND BACKGROUND

In our last report we discussed the effects of water, tetralin, and argon as media during the heating of Illinois No. 6 coal. In studies in which the temperature was ramped from ambient to 460°Cat 30°C/min we observed particles to shrink in case of both water and tetralin, and first swell and then collapse back to particles with their starting shapes in the case of argon.

The result with tetralin was expected, but that for water was not. Similarly, the results in argon were not in accord with some models of coal pyrolysis which suggest that coals fully liquefy when heated (Solomon, et al., 1992).

The work described here includes discussion of additional work with Illinois No. 6 coal with argon and water, and new work with *n*-undecane as medium.

CURRENT RESULTS

The earlier analyses of the particle areas were carried out on printed images of the particles captured from the video tape with Adobe Photoshop. We are now begun determining the areas directly with Color Image,* an image processing and analysis software that provides areas promptly by direct pixel count. The values obtained are more reliable, and we expect to use this procedure in the future. In fact at this point with our considerable experience both in the use of the cell and in the manipulation of our image data, the operation is more or less routine. Our present results are reliable, and are preferred in cases where they are in conflict with our earlier data.

Over the past period additional work was conducted with argon and with water, new studies were conducted with *n*-undecane. All of the runs are conducted at constant pressure, 7 atm in the case of argon and 200 atm for both water and undecane, and with a temperature ramp of 30°C/min. The results are shown in Figure 1.

The upper plot presents the results for argon, showing results for three different particles. As discussed last time, the particles begin to swell at about 300°C, and attain their greatest size at near 400°C. They then rapidly decrease in size, returning for the most part to the starting size and shape. The figure shows that the three particles behave similarly, and a smooth curve has been sketched to suggest the behavior in general.

Our discussion last time proposed that this behavior was like that of a balloon, with the thermal generation of gases and other volatiles inflating a skin, which then collapsed around a core

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* Wayne Rasband, NIH, Research Service Branch.

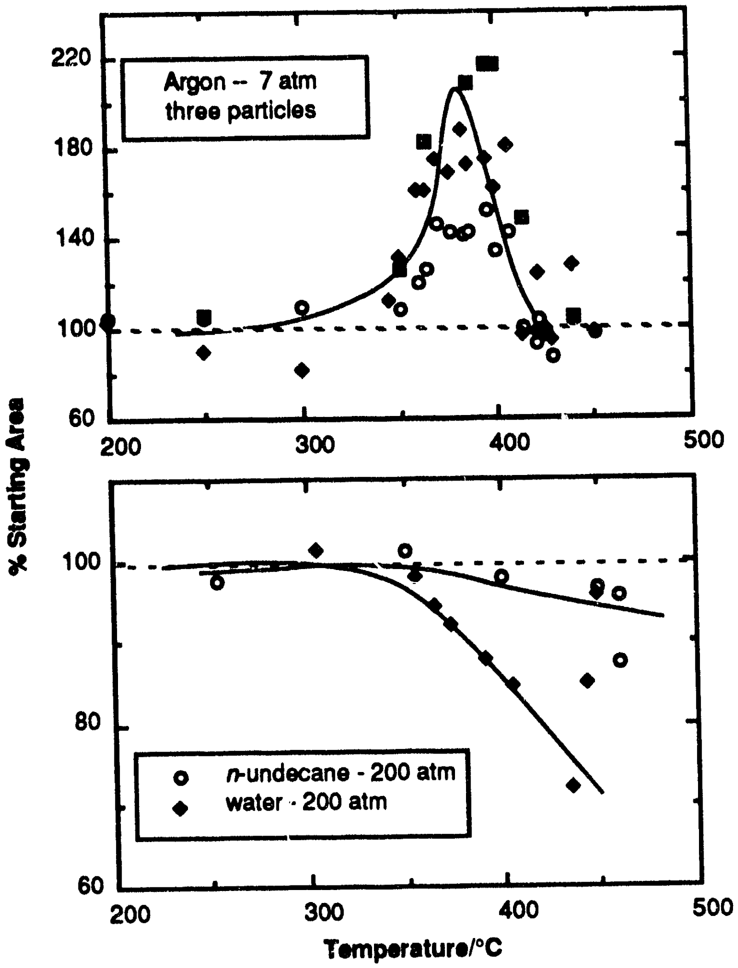


Figure 1. Changes in particle area vs temperature for Illinois No. 6 coal in the presence of various media.

that had retained its shape. That view, however, is not supported by our more recent images, which are of better quality. They show many particles that actually appear to melt; their rather abrupt collapse into a molten fluid appears similar to the melting of a pure, crystalline organic compound when viewed under a microscope on a hot stage. Ergun, et al. in their pioneering microscopy work with coal reported the "melting" of exinite concentrates (1959). The majority of the particles in the field developed molten phases more slowly, and the action appeared to be a discharge of fluid material rather than swelling. The fluid settled around a core that could be seen in many cases as a vague shadow within the fluid. Ultimately the melts from individual particles merged and the entire field appeared to contain a single fluid.

At near 400°C the process then appeared to reverse itself quickly. The fluid phase rapidly vanished, probably by evaporation of the fluid phase, exposing the core particles with profiles similar to the starting shapes. The particles were then unchanged with still increasing temperature.

The lower plot in Figure 1 presents results for water and undecane at 200 atm. The alkane has a critical temperature like that of water, and at least for short periods of exposure should not react with the coal. In the case of water the coal particles began to shrink at around 300°C, or at the same point at which the tars began to emerge in the argon runs just discussed, and there would seem to be a link between the two phenomena. There is an apparent abrupt upturn in the area at around 430°C which we ascribed in our last report to the spreading of what we took to be a tar phase. However we are now less certain of that explanation; the particles in our most recent work appear to be less fluid than we had thought, and at present we view the increase in area to be a genuine swelling of the particles at that temperature. The loss of area in this case is smaller than reported last time, a result due to the improved means of area measurement.

The results in undecane are in some contrast to these. In that medium there is virtually no change in the size or shape of the coal particles up to about 470°C.

DISCUSSION

Swelling in Argon and Shrinking in Water

As stated above, the complimentary effects of the two media suggest that the events are related. The data can in addition be considered with our findings in earlier DOE-sponsored studies in which we used field ionization mass spectrometry (FIMS) to probe the effects of the pyrolysis of Illinois No. 6 and Wyodak coal under a variety of conditions (Contract No. DE-AC22-89PC89880, Ross, et al., 1991). The coals were heated at 2.5°C/min to 500°C in the FIMS inlet assembly and the volatiles that developed were then swept into the instrument and analyzed over successive 30°C increments. Other work included pretreating the coals at 350°C for 30 min and 5 hr in various media including a few atm of N_2 and *n*-undecane, and then subsequently pyrolyzing the samples in the FIMS inlet.

In figure 2 we present the argon data from Figure 1 again, and compare them to the generation of catechol ($Ph(OH)_2$, 110 dalton) in the FIMS-heating of untreated Illinois No. 6 coal. $Ph(OH)_2$ and $MePh(OH)_2$ were the most prominent identifiable fragments from the pyrolyses of both the Illinois coal and Wyodak, greater than the signals for phenol and cresol (MePhOH) which

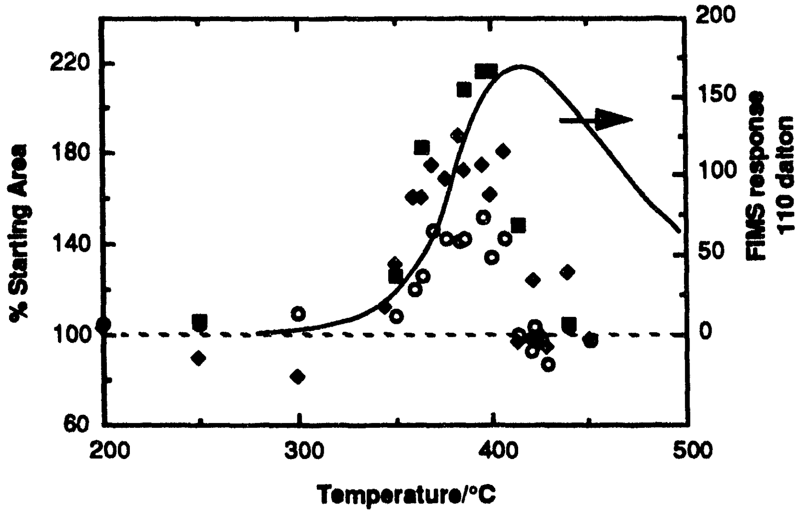


Figure 2. Comparison of the data for the swelling in argon with FIMS-observed liberation of 110 dalton parent peak for Illinois No. 6 coal. (The FIMS work was done at temperature ramping of 2.5°C/min.)

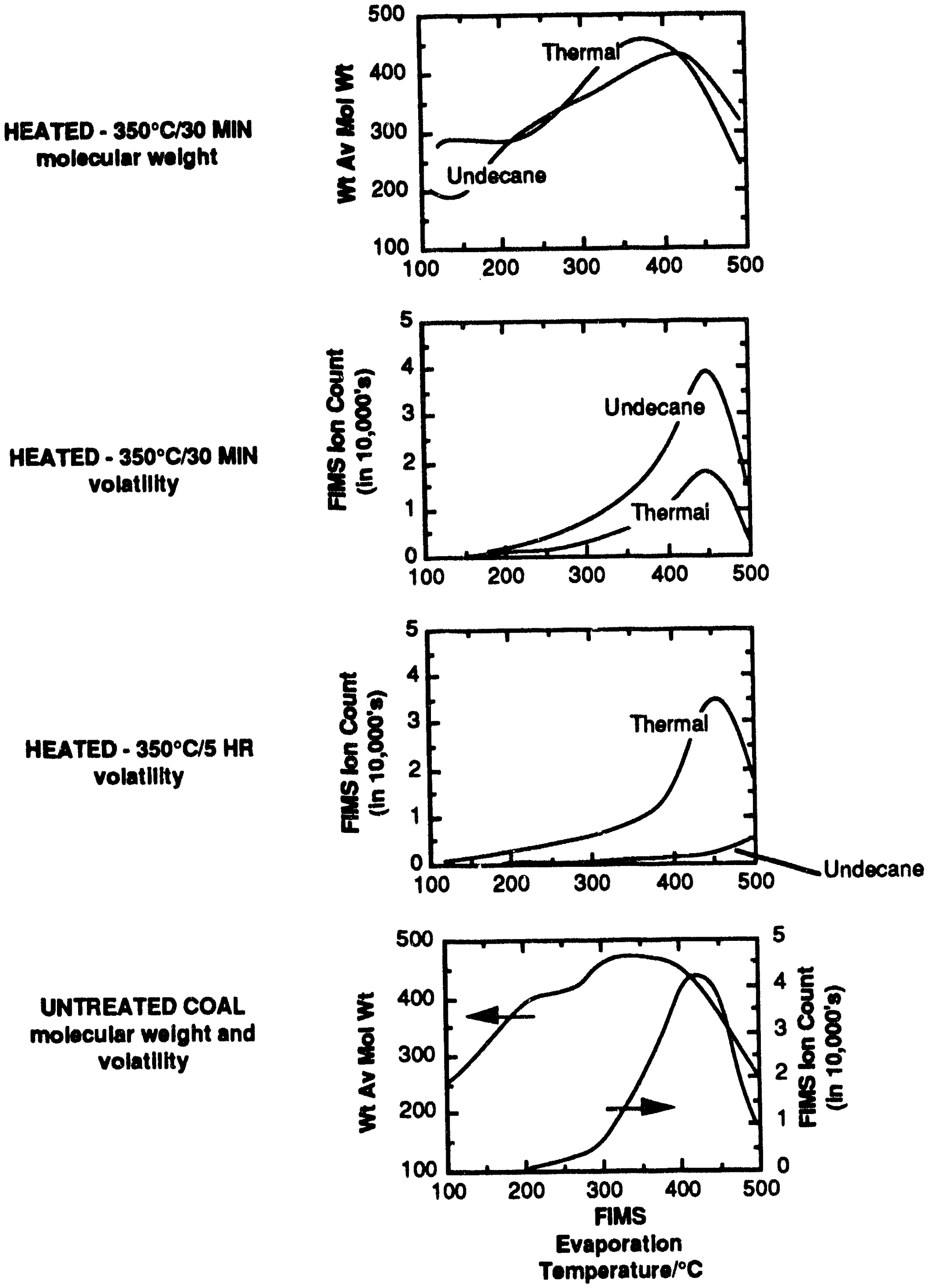
were also prominent. Catechol, methylcatechol, and further methylated derivatives were released with virtually identical profiles.

The figure shows that the swelling and the thermal release of catechol data agree very well, and the fit with the water-induced shrinking of the coal in turn is intriguing. The data suggest that hydrolysis may be significant to coal pyrolysis, even in the absence of added water. This view of pyrolysis is a curious one, and will be considered further in future reports.

For an analysis of the data from the present study with undecane we consider our earlier data once again, in this case in work with Wyodak coal. Figure 3 summarizes the data from the N_2 (designated "Thermal" in the figure) and undecane portion of that work, including both volatility, as indicated by the instantaneous ion count, and weight average molecular weight of the volatiles with increasing inlet temperature. Data for the untreated coal are presented for comparison.

First, it can be noted with attention to the 30-min data that the volatiles from the thermally and undecane-treated coals gave similar molecular weight profiles. Thus there was no evidence of substantial chemical interaction between the alkane medium and the coal. Further, the mass spectra for the undecane-treated material showed no incorporation of the alkane chemically into the coal.

Next, although direct comparisons must be made with caution, after 30 min the quantity of volatiles from the undecane-treated material appears to be somewhat greater than that from the



HEATED - 350°C/30 MIN molecular weight

HEATED - 350°C/30 MIN volatility

HEATED - 350°C/5 HR volatility

UNTREATED COAL molecular weight and volatility

Figure 3. FIMS data for treated and untreated Wyodak coal. The treatment consisted of 30 min or 5 hr heating in undecane or under nitrogen.

thermally treated coal.* These data suggest that the undecane medium slows or eliminates the loss of volatile material during heating. Then, in the subsequent reheating in the FIMS inlet assembly in the absence of undecane, the volatiles, essentially unchanged, escape the coal and enter the instrument.

After 5 hr of treatment, however, it is clear that the undecane-treated coal has virtually no volatiles content. Thus it appears that the volatiles, trapped in the coal during the extended heating, undergo condensation and other polymerization reactions and ultimately become irreversibly incorporated into the bulk coal matrix. Similar lines of reasoning have been employed to explain the marked reduction in volatiles yields with increased applied pressure during coal pyrolysis (Solomon, et al., 1993).

Finally, comparison of the water and undecane results is instructive. In contrast to undecane, water does not block the evolution of the volatile fragments. It is notable moreover that the cross sectional areas of the particles remaining after pyrolysis in argon are about what they were in the starting material. In the case of water, on the other hand, the remaining particles are reduced in size by around 30%, at least to the point where they begin to swell once again. This observation suggests that the water brings about the liberation of more material than does simple pyrolysis.

Water is a reactant in the process, and we are left with the provocative question of what might be added to the water to bring about an even greater conversion and release of material.

REFERENCES

Ergun, S., O'Donnel, H., and Parks, B., 1959. "Microscopic Studies of Rate of Thermal Decomposition of Petrographic Components of Coal," Fuel, 38, 205-210.

Ross, D., Loo, B., Tse, D., and Hirshcon, A., 1991. "Hydrothermal Treatment and the Oxygen Functionalities in Wyodak Coal", Fuel, 70, 289-295.

Solomon, P., Best, P., Yu, Z., and Charpenay, S., 1992. "An Empirical Model for Coal Fluidity Based on a Macromolecular Network Pyrolysis Model," Energy & Fuels., 6, 143-154.

Solomon, P., Fletcher, T., and Pugmiree, R., 1993. "Progress in Coal Pyrolysis," Fuel, 72, 587-597.

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* Differences as here of a factor of two are likely real since the quantities of the samples carefully weighed into the FIMS inlet sample cup were the same within 10%. The day-to-day stability of the instrument was demonstrated in tens of spectra run over several months.

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