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FUNDAMENTAL STUDIES OF COAL LIQUEFACTION

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INTRODUCTION AND EARLIER RESULTS

We are now in a position to operate routinely with our diamond cell, and we report here on new results with Illinois No. 6 coal. Evaluation of our data has been substantially improved by our employing Adobe Photoshop on a Macintosh IIfx, as will be seen in what follows. With the new software we are able to work with the television images, isolating specific particles or groups of particles, and monitoring the changes in their morphology with time and temperature.

(Unfortunately the quality of the images shown here suffers because of the printer used. The resolution and overall quality of the images as they appear on our monitors are superior to those in the figures below, and we are seeking a printer that can provide better quality figures for our reports.)

In our last report we discussed the morphological changes in Illinois No. 6 coal particles under argon or in tetralin, with the changes estimated in those cases from their appearance on our television monitor equipped with an overlaying grid. We found that the individual coal particles contracted in both cases, abruptly at around 440°C in the case of argon, and more gradually, beginning at just under 400°C, for tetralin as the medium. In the latter case the contraction was preceded by what appeared to be a small degree of swelling.

We noted that if the contraction were due to the chemical action of the tetralin reductively cleaving and then dissolving fractions of the coal, then the onset temperature was too low and not consistent with the weak bond cleavage view of tetralin action. This issue is an interesting one, bearing on the fundamentals of the chemistry of coal and coal liquefaction, and discussed again below.

CURRENT RESULTS -- ILLINOIS NO. 6 COAL AND TETRALIN

The heating profile employed in the work is presented in Figure 1. The cell was heated at 25°C/min to 250°C, and the rate then reduced to 10°C/min. The temperature was then held steady at 460°C.

The visual field we are working with is shown in Figure 2. In studies of this kind we must choose specific particles present in the field of view for analysis, and the question of how representative the elected particles are of the bulk material cannot be ignored. It would of course be

Figure 1. Heating profile for the studies described here.

very difficult to assess the changes in all of the particles we capture in our images,* but at present we feel confident our observations satisfactorily represent the coal as a whole. This view is supported by the similarity in behavior in the data here with data from earlier work, as discussed below.

Figures 3, 4, and 5 display images of two adjacent particles chosen for analysis with characteristic dimensions of 50 - 100 μm . Figure 3 shows that there is essentially no change up to 395°C over an 18 min period, but at that point the particle labeled *a* begins to shrink. The action continues in Figure 4 where the particle contracts to about half its initial size over a 45 sec period as the temperature increases from 424°C to 430°C, at which point the contraction stops. The size profile for *a* is presented in Figure 6 and compares very well with the profile generated in an earlier experiment from our last report. As just noted, this agreement suggests that this behavior is representative of at least one class of particle in the sample.

Figure 5 shows that there is a second, higher temperature range of activity, represented by the changes in particle *b*. This particle contracts to about half its size from 450° to 460°C over 1 min. The temperature was held at 460° and there appears to be an additional 7-10% contraction over 10 min at that temperature, although the scatter seen in Figure 6 shows that that change is not outside our error limits. We conclude that the process takes place rapidly and concludes within the initial 1 min period. The remaining portions of the particles we presume to be coke, or thermally

* There is image analysis software available from Automatix that provides that capability, but its cost is prohibitive.

125°C

460°C

Figure 2. Illinois No. 6 coal in tetralin in the cell at 125°C and 460°C. The two particles chosen for analysis are boxed.

225°C

50 μ m

395°C

410°C

420°C

Figure 3. Particles of Illinois No. 6 coal in tetralin at temperatures to 420°C.

424°C

426°C

428°C

430°C

Figure 4. Particles of Illinois No. 6 coal in tetralin at 424°C to 430°C over 45 seconds.

440°C

450°C

460°C

460°C (10 min)

Figure 5. Particles of Illinois No. 6 coal in tetralin at 440°C to 460°C. The second 460°C image is 10 minutes after the first.

condensed organic material similar to that photographed by Eser et al. (1991). The smaller surrounding particles in the images show little change in morphology, and we suppose that these are mineral material.

Figure 6. Size profiles for Illinois No. 6 coal particles in tetralin. The points represent our arbitrary choices of individual "frames" for measurement.

While our data thus far are limited, we can make the following observations. First, we view the shrinking of the particles to reflect the reductive thermolytic conversion of some fraction of the organic phase to material soluble in tetralin. Comparing the two images in Figure 2 we can estimate that 60-70% of the starting coal was solublized by the treatment. Next, it appears that conversion is rapid compared to our rate of temperature ramping, and possibly takes place with two types of coal particles with distinctly different reactivities. Alternatively, given the small number of observations thus far, we might more reasonably conclude that the two curves in Figure 6 define a zone of reactivity. More work with tetralin will allow us to clarify the issue.

The rate of reaction we are observing is in fact surprisingly rapid based upon the common weak bond scission view of liquefaction, as discussed in our last report. In that view weak bonds in the coal, which are typically represented as the central bond in bibenzyl, cleave thermally (eq 1). That reaction is then rapidly followed by capping of the radical products by an H-donor such as tetralin (eq 2). If we consider the behavior of particle *b* at the median temperature in its reactive

interval of 455°C, the rate constant for eq 1 is $3.1 \times 10^{-4} \text{ sec}^{-1}$ (from the work of Stein, et al., 1981). That value dictates that over the 1 min period where the particle exhibits its activity less than 2% of the bibenzyl-like links in the coal would cleave. The case for particle *a* at the lower temperature is even more striking, where well below 1% of the links would cleave in its reactive interval.

On these bases it is difficult to tie a sequence like eqs 1 and 2 to H-donor activity. In work coming up to be done with catalyst impregnated coals supplied by Amoco Oil Company, we expect to be able to develop some additional insights into the liquefaction process.

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