

## A PSEUDOKINETIC STUDY OF COAL LIQUEFACTION

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All approaches to the study of the chemistry of coal liquefaction are handicapped to one degree or another by the inability to accurately measure the detailed structure of the primary reagent -- coal. Recent work at PETC has focused on utilizing quantitative  $^{13}\text{C}$  NMR together with elemental balances to obtain an improved picture of the molecular level chemistry of hydrogen in realistic conversion environments. The method divides total hydrogen incorporated into the organic products into that consumed in hydrogenation, heteroatom removal, and hydrogenolysis. The details of this approach have recently been discussed [1]. To date, the approach has proven useful in describing the influence of reaction temperature [1,2] and catalyst [3] on the utilization of hydrogen. This work describes efforts to determine the relative rates of hydrogen-consuming reactions -- hydrogenolysis, hydrogenation, and heteroatom removal.

#### Experimental

All reactions were done on a shaking microautoclave system, which has the capacity to simultaneously immerse five 40 milliliter microreactors into a preheated fluidized-bed sandbath. This system has a heat-up time of approximately 5 minutes. Prior to reaction the microreactors were charged with 4 g of Illinois No. 6 hvC (River King) bituminous coal and 7 g of a heavy coal-derived distillate (240°C-450°C cut from the SRC-II Process), and pressurized to 1200 psig with hydrogen at ambient temperature. This loading procedure results in a hydrogen pressure of approximately 2000 psig at reaction temperature. Catalytic runs were accomplished by loading the coal with 0.006 g of either molybdenum (as ammonium heptamolybdate) or tin (as  $\text{SnCl}_4$ ). Reactions were run at 0-, 5-, 10-, 20-, 30-, and 60-minute reaction times (time at 380°C).

Following reaction the headspace gas was quantitatively collected and analyzed by gas chromatography. The total reaction product was removed to a Soxhlet thimble and separated via  $\text{CH}_2\text{Cl}_2$  extraction into soluble and insoluble fractions. Both product fractions were analyzed for elemental composition via microanalytical procedures by Huffman Laboratories.

Both  $^{13}\text{C}$  and  $^1\text{H}$  high-resolution NMR spectra were obtained in  $\text{CD}_2\text{Cl}_2$  on the soluble fractions using a Varian XL-100 spectrometer. The  $^{13}\text{C}$  NMR

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spectra of the feed coal and the  $\text{CH}_2\text{Cl}_2$  insolubles were obtained via crossed polarization magic angle spinning, CP/MAS, techniques using a Brücker CXP-100 instrument.

### Results and Discussion

The hydrogen utilization profiling method involves measurement of the  $^{13}\text{C}$  NMR aromaticity change during reaction as a direct quantitative measure of the degree of hydrogenation of the feed slurry. The total hydrogen incorporation is obtained from the elemental analysis, and the amount incorporated in heteroatom removal is estimated from the change in organic heteroatom content. In these low-temperature reactions ( $380^\circ\text{C}$ ), negligible amounts of light hydrocarbon gases were produced. Thus any hydrogenolysis observed must involve cleavage of slurry matrix bonds to yield smaller solid and liquid fragments. It must be remembered that because there is no means of counting bonds, the amount of hydrogen incorporated via hydrogenolysis must be obtained by difference:

$$\text{Total hydrogen} - (\text{hydrogenation} + \text{heteroatom removal}) = \text{hydrogenolysis.}$$

The data in final form are simply the number of hydrogens, per 100 carbons of feed slurry, that are incorporated into organic products via hydrogenation, heteroatom removal, and hydrogenolysis (bond cleavage) reactions.

The results of this study of hydrogen utilization are presented in Figure 1. Figure 1a shows the total net hydrogen incorporation into organic products as a function of time for uncatalyzed and tin- and molybdenum-catalyzed reactions. The catalyzed systems appear to incorporate hydrogen more rapidly than the uncatalyzed reactions (note 20- and 30-minute reaction times), but at the longest reaction time (60 minutes), there is no difference between the total net hydrogen incorporation in catalyzed and uncatalyzed reactions. For the catalyzed reactions the results suggest that product hydrogen content actually decreases from 30 to 60 minutes, whereas in the noncatalyzed reaction, hydrogen is still being incorporated during this time period. This may indicate that retrogressive reactions are important at longer reaction times in the catalyzed reactions. Analysis of headspace gas composition after reaction indicates that this decrease in hydrogen content is not due to hydrogen starvation. The behavior shown in Figure 1 at short reaction times,  $\leq 10$  minutes, is seemingly erratic. However, it does suggest that in general the chemistry is different, either in rate or in the nature of the reactions, from that observed at longer reaction times.

The data in Figure 1b indicate that there is essentially no dependence of heteroatom removal on either catalyst addition or reaction time under these conditions.

The amount of hydrogen incorporated into products via hydrogenation reactions is measured directly by measuring the change in aromaticity during reaction. The data obtained for incorporation of hydrogen by hydrogenation are presented in Figure 1c. It first must be stressed that optimistic error limits on measurement of the change in aromaticity,  $\Delta f_a$ , are  $\pm 0.02$ . This error translates directly into an error of  $\pm 2$  hydrogens per 100 carbons.

With this caution, the data in Figure 1c indicate no significant change in degree of hydrogenation with reaction time. However, it is intriguing to note that all three sets of data -- molybdenum-catalyzed, tin-catalyzed, and uncatalyzed -- show evidence of hydrogenation at 10-minute reaction times and show a drop in the degree of hydrogenation between 10 and 20 minutes. Both catalytic runs also exhibit slightly higher levels of hydrogenation than the noncatalyzed reaction from 20 minutes to 60 minutes of reaction. These small differences are within the limits of error of the method.

The most difficult (and error-prone) mode of hydrogen utilization to measure is the hydrogen incorporated into the system via hydrogenolysis or bond cleavage chemistry. This mode of utilization is determined by difference and incorporates the sum of the errors of the other analyses (total hydrogen, heteroatom removal, and hydrogenation). With this qualification, the data that describe hydrogen incorporation in bond cleavage chemistry are very interesting (see Figure 1d). They indicate that for the first 10 minutes of reaction, there is progressively more net bond formation (condensation). This is followed by a period, 10-30 minutes, during which bond cleavage predominates. Both catalytic systems appear to reach their peak in hydrogenolysis consumption at 30 minutes under these conditions. This maximum is followed by a slight decrease in net hydrogenolysis on going to 60-minute reaction times. The data in Figure 1d suggest the existence of a sequential mechanism for conversion under these conditions. At short reaction times, the apparent internal hydrogen redistribution is based on condensation (bond-making) chemistry, while at longer reaction times, bond cleavage (hydrogenolysis) chemistry appears to predominate.

The hydrogen utilization profile data in Figure 1 can be contrasted with the conversion data shown in Figure 2. The conversion data were obtained on samples generated under conditions identical to those used for generation of Figure 1. Neither of these solubility-based conversion plots seem consistent with the hydrogen utilization data, particularly at short reaction times. The solubility data do not indicate any substantial effect of added catalyst and show no apparent qualitative differences between short reaction times and long reaction times. In particular, the time dependence of conversion based on solubility in the two solvents appears to be substantially different. The THF solubility shows an abrupt change at short reaction time, while cyclohexane solubility is essentially a linear function of reaction time. This lack of correspondence between solubility-based conversion values and hydrogen utilization profiles is probably an indication that the two techniques are measuring different properties of the liquefaction system. It seems likely that solubility, especially in strong solvent systems, might be sensitive to physical changes in the system that are not probed by the chemical methods used in hydrogen utilization profiling. It is possible that the hydrogen utilization profile approach may prove to be more useful in investigations of the detailed chemical mechanism of liquefaction.

### Conclusions

The hydrogen utilization profiles as a function of reaction time indicate that two different time regimes of reactivity may exist under these mild reaction conditions. At short reaction time the data suggest that

hydrogenation and condensation reactions are operative with minimal net hydrogen incorporation. (The possibility exists that the hydrogen generated in condensation during this time period is being shuttled into more reactive regions of the slurry via hydrogenation). After this initial period of hydrogen redistribution, the major chemistry appears to be bond breaking (hydrogenolysis) that results in significant net hydrogen incorporation into the slurry. This description is consistent with a set of two sequential reactions being responsible for liquefaction under these conditions. The data in this study clearly indicate that both tin and molybdenum accelerate the incorporation of hydrogen into the reacting slurry and imply that the major net effect of the catalysts is to make hydrogen more readily available for hydrogenolysis reactions.

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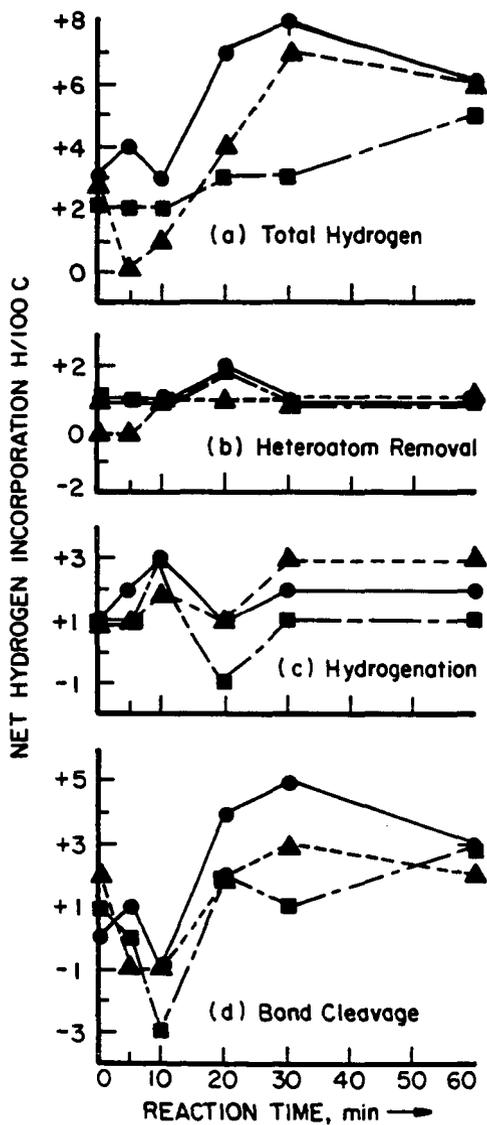


Figure 1 - Hydrogen Utilization as a Function of Reaction Time.

- — Sn Catalyzed
- - - - Mo Catalyzed
- ▲ - - - Uncatalyzed

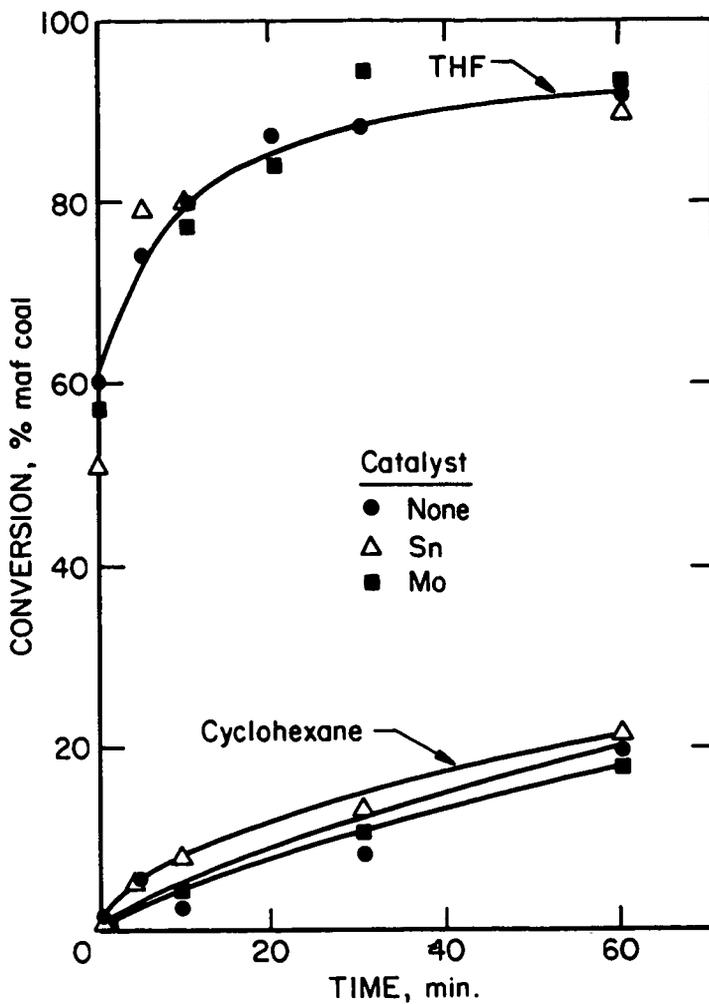


Figure 2 - Conversion of Illinois No. 6 coal at 380°C.