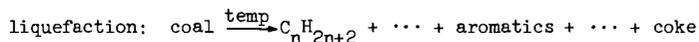
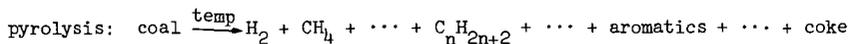


## Hydrogen Consumption in Non-Catalyzed Coal Liquefaction

M. G. Thomas, Barry Granoff, G. T. Noles and P. M. Baca  
Sandia Laboratories  
Albuquerque, New Mexico 87115

### INTRODUCTION

Liquefaction, in general, refers to the thermal reactions experienced by coals at temperature usually above 400°C in suitable solvents. These reactions produce a complex mixture of solubilized (liquefied) and gasified products in high yield over short time intervals (1). The interaction of hydrogen in these reactions is not well understood, but the presence of H<sub>2</sub> has been observed to increase the yields of liquefaction products (2). Hydrogen also provides a reductive pathway to allow for the removal of hetero-atoms as H<sub>2</sub>S, H<sub>2</sub>O and NH<sub>3</sub>. Though the implication of these beneficial uses of hydrogen is net consumption, it has recently been shown that H<sub>2</sub> is also produced in these thermal reactions in non-H<sub>2</sub> atmospheres (3). The thermal reactions of coal in solvent, then, are best represented schematically as a set of two competing reactions (4); i.e.,



where H<sub>2</sub>, the light hydrocarbons and coke are maximized in pyrolysis and minimized in liquefaction. It can be seen then how hydrogen can be produced in the pyrolysis reaction, and how its presence can favor one reaction over the other without being consumed; the H<sub>2</sub> gas may merely inhibit the pyrolysis. Obviously, maximizing the rate of liquefaction/pyrolysis is an important consideration in the efficient use of hydrogen. We will attempt to show how each of these competing reactions respond to changing conditions and some of the effects that the various conditions produce with respect to hydrogen consumption.

### EXPERIMENTAL

Data reported in this presentation have been obtained from analysis of products from 1.) a 1-liter stirred batch autoclave operating between 395°-430°C, and H<sub>2</sub> pressure of 1000-1750 psi measured prior to reaction at 24°C, and 2) a four-stage continuous (non-cycling) reactor operating at 425°C and 4000 psi. In the autoclave experiments, a charge of 50 g daf coal and 115 g #4 cut creosote oil was employed (5). Samples for gas analyses were obtained at ~ 25°C by venting through gas sampling tubes before scrubbing. The GC columns used were 6' x 1/8" O.D., 80-100 mesh poropak Q in teflon lined aluminum. The continuous reactor was packed with glass spheres; each stage was a 10 ft length, .203 inch I.D., void volume ~ 50%. The packing was intended to improve heat transfer and maintain mixing. The reactor was charged with a fixed slurry of #4 cut creosote oil and 30% by weight coal. The coal used in the continuous reactor was -60 mesh West Virginia, Ireland Mine coal. Block diagrams of the autoclave and reactor are shown in Figure 1a and Figure 1b. Analyses of the West Virginia, Ireland Mine coal used for both autoclave and continuous reactor experiments: ultimate (dry)

C 62.83; H 4.45; N 0.90; Cl 0.03; S 6.93; Ash 19.06; O (diff) 0.577; sulfur forms-pyrite 4.55; sulfate 0.25; organic 2.13. A description of the liquid analyses is given in block diagram form, in Figure 2. Data on other coals used in this study can be obtained from Reference 5.

## RESULTS AND DISCUSSION

Comparisons of liquefaction products from different coals are not generally successful because of the variations in composition (of the coals), but can serve to illustrate the nature of the products and the role of hydrogen. Table 1 contains data from six different high volatile bituminous coals and the liquefaction products obtained in each case at 430° and .5 hour reaction times. The amount of reactive macerals varied between 89-95%, but the mineral content changed from 5 to 21%. Although the conversion varies (62-94%), the H/C ratios of the filtered (organic) products are basically the same, about 0.8. Analysis of the gas data certainly show consumption of hydrogen and production of H<sub>2</sub>S and hydrocarbon gases. The H<sub>2</sub> consumption parallels conversion as does the H<sub>2</sub>S produced. However, the production of methane, reflecting the pyrolysis reaction, does not vary in any readily apparent fashion. The H<sub>2</sub> consumed apparently accompanies conversion of the primary liquefaction products to benzene solubles among the several coals, as suggested by Neaval based upon the behavior of one coal in time (6).

Data obtained from the continuous reactor at 425°C shown in Table 2 clearly show two additional features of coal liquefaction 1.) the rapid initial desulfurization followed by a much slower removal of the more resistant organic sulfur; and 2.) accompanying pyrolysis reactions seen here as formation of CH<sub>4</sub>. One conclusion based on these data is that most of the H<sub>2</sub>S (removed sulfur) is produced in the early stages of the reactor (as is the H<sub>2</sub> needed for H<sub>2</sub>S formation). Although organic sulfur is being removed, it is removed in a very specific fashion.

Reactor Stage	Asphaltene %S	Preasphaltene %S
1	1.33	1.68
2	1.24	1.59
3	1.20	1.66
4	1.22	1.68

As shown above, the percentage sulfur in the asphaltenes and the preasphaltenes is not changing significantly in time. The interconversions of the liquefaction products (as preasphaltene → asphaltene + oil) are accompanied by sulfur removal (consistent with H<sub>2</sub> consumption for the conversion to benzene solubles as noted earlier). Thus, sulfur removal does not occur to any significant extent without a concurrent change in solubility properties. This type of reaction is consistent with data published on hetero-atom removal from model aromatic compounds; the molecule is usually saturated with hydrogen, followed by ring opening and then removal of the hetero-atom (7). The resulting products thus, have different structures, solubility characteristics, and molecular weights and are not merely the initial molecule minus a S, N or O atom. For coal derived molecules then, this reductive cracking occurs simultaneously with defunctionalization, and both of these reactions are accompanied by hydrogen consumption.

It is necessary to examine the responses to temperature, time, and pressure to understand the process more fully. Using the same coal as in the continuous reactor, a number of autoclave experiments were performed at residence times between .25 and 1 hour, 395°-430°, and 1000-1750 psi initial pressures (pressure charges measured at 24°C before the heat cycle). Data obtained from these experiments are plotted in Figure 3, and in contrast to the data presented in Table 1, the C/H ratio of the products is changing. In Figure 3a it is seen that as time increases sulfur is removed and the amount of hydrogen in the liquefied product increases, data consistent with results drawn from the reactor runs. Likewise, sulfur decreases and hydrogen in the product increases with higher pressures, Figure 3b. However as temperature increases, the sulfur is lowered but the C/H ratio increases, Figure 3c. Figure 3d shows the amounts of H<sub>2</sub> gas consumed versus temperature. Though a cursory examination of Figure 3d would suggest greater hydrogenation at the higher temperature we know this is not consistent with the liquid analyses, Figure 3c. A more consistent picture is obtained by examination of the quantity of hydrogen in the gas from all sources (H<sub>2</sub>, C<sub>1</sub>-C<sub>4</sub>'s, and H<sub>2</sub>S) at two temperatures:

Gas	Moles Produced at 414°C	Moles Produced at 429°C
CH <sub>4</sub>	.06	.11
C <sub>2</sub> H <sub>6</sub>	.02	.05
H <sub>2</sub> S	.03	.04
H <sub>2</sub> (consumed)	.30	.50

It can be seen that the total hydrogen in the gases produced is greater at higher temperature (approximately twice as large at 429° than at 414°) and indicates that temperature increases favor the pyrolysis reaction (4).

The effects observed in these experiments must not be evaluated without a description of solvent behavior under similar conditions. Table 3 shows both liquid and gas analyses of #4 creosote oil before and after reaction at 407° and 427°C. The H<sub>2</sub> gas consumption and CH<sub>4</sub> production are low compared to data obtained with coals. Also, no desulfurization is observed, though a slight increase in hydrogen content of the oil is observed. The magnitude of the differences observed in the gas data (H<sub>2</sub> consumption, H<sub>2</sub>S and CH<sub>4</sub> formation) between the solvent and the solvents with coal would seem to indicate that the contribution of solvent to these specified (gasification and H<sub>2</sub> consumption) reactions was minimal (8).

#### SUMMARY

The discussion has considered liquefaction as two competing reactions; one which produces solubilized defunctionalized products, and a pyrolysis reaction which consumes hydrogen. Responses of the reactions to the independent variables of pressure, temperature, and time have been described and suggest that hydrogen pressure and time favor the liquefaction reactions (decreases in C/H ratio, decreases in sulfur, and increases in conversion), but that temperature seems to preferentially favor pyrolysis. These conclusions are in general agreement with

literature data. Additionally it has been shown that 1.) sulfur removal occurs concurrent with conversions among the various solvent extraction fractions, 2.) conversion varies with H<sub>2</sub> consumption among a number of similar but different coals and 3.) hydrogen consumption must be evaluated on the basis of a total balance, not just a change in concentration of H<sub>2</sub> gas.

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Table 1. Selected data of several coals and respective liquefaction products.

Coal %S	Reactive Macerals	Mineral Matter	Conv.	OBI	Filtered Product H/C	Mole % H <sub>2</sub> S	Mole % CH <sub>4</sub>	Moles H <sub>2</sub> Consumed
Kent. 11, Fies	93	20.9	93	7.8	.82	6.6	2.87	.57
Kent. 11, Homestead	92	15.7	94	10.3	.83	3.2	2.71	.53
West Va.	91	13.8	88	10.6	.80	2.44	3.70	.41
Ill. 6	95	13.0	87	14.8	.80	1.62	2.16	.40
Pennsylvania	90	5.2	84	16.5	.81	0.38	1.82	.33
Kent. Elkhorn 3	89	5.6	62	22.9	.81	0.36	1.85	.31

Table 2. Reactor products from a run at 425°C, 4000 psi H<sub>2</sub>, 1 lb/hr coal.

Product %S	Benzene Insols	Asphaltene	THF Preasphaltene	% of Total S in THF Insols	Moles CH <sub>4</sub> / lbs. Coal
Reed	30.0	-	-	92.0	-
Stage 1	18.9	11.8	9.9	39.0	.68
Stage 2	15.4	13.1	8.5	40.5	1.47
Stage 3	10.9	15.5	5.3	-	2.18
Stage 4	9.8	13.4	4.8	40.8	3.10

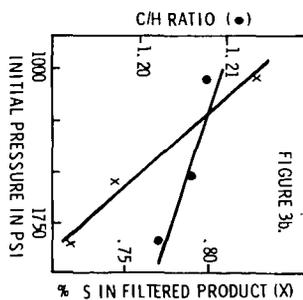
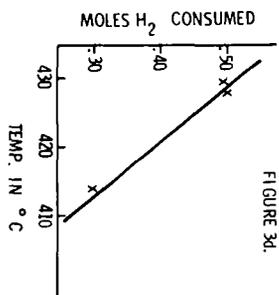
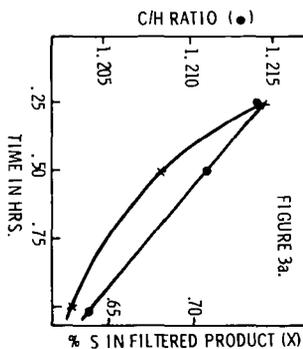
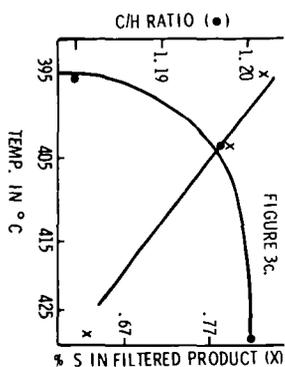


FIGURE 3. a. C/H RATIO AND S vs. TIME (430°C, Initial H<sub>2</sub> Pressure 1500 psi)  
 b. C/H RATIO AND S vs. PRESSURE (405°, time 1 hour)  
 c. C/H RATIO AND S vs. TEMPERATURE (time 1 hour, Initial H<sub>2</sub> Pressure 1500 psi)  
 d. MOLES H<sub>2</sub> CONSUMED vs. TEMPERATURE (time and Pressure as in 3c)

Table 3. Analyses of #4 Cut Creosote Oil

	Initial	1800 psi, .5 hr 407°	1800 psi, .5 hr 427°
Pyridine Insols	0.0	0.0	0.0
Benzene Insols	0.3	1.0	1.6
Asphaltene	7.3	3.9	3.2
Oil	92.7	95.1	95.2
C	90.77	91.03	-
H	5.8	5.93	-
S	.4	.4	.4
Moles CH <sub>4</sub>	-	.0029	.0097
Moles H <sub>2</sub> Consumed	-	.004	.015