COAL LIQUEFACTION IN A FLUOROCARBON MEDIUM. II. KINETICS OF THE 1,2,3,4-TETRAHYDROQUINOLINE REACTION

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Introduction

Many coal liquefaction experiments involve heating coal in a medium which both reacts with the coal and simultaneously dissolves released coal fragments. One problem of this approach is that it is difficult to differentiate between physical interactions which result in solvent power and chemical reactions which disrupt the coal macromolecular network. A secondary problem of such experiments is that accurate measurements of coal conversion require considerable care in collecting all deposits adhering to the reactor walls.

We have reported that coal processed in a perfluorinated liquid medium with small amounts of additives does not dissolve, but in at least one case, that of 1,2,3,4-tetrahydroquinoline (THQ), the processed coal has considerably enhanced solubility.[1] This increased solubility is attributed to a low temperature (200-250°C) reaction between THQ and coal. Since coal is recovered intact in these experiments, coal conversion can be measured by extraction of a fraction of the processed coal, without need for complete recovery of material from the reactor. In the present work, we present kinetic data in order to better understand the mechanism of this interesting coal transformation.

Experimental

These experiments were performed in FC-70 (3M Corp.), a mixture of perfluorinated tertiary aliphatic amines, with average molecular weight of 820 (primarily five-carbon chains), having a boiling point of 215°C. FC-70 has high solubility for gases such as H_2, but very low room temperature solubility for both polar and nonpolar organic molecules. However, at temperatures greater than 200°C, the solubility of THQ in FC-70 exceeds the concentrations employed in the present studies. (FC-70 is not recommended for coal liquefaction experiments at T > 350°C, since at these temperatures the perfluorinated liquid decomposes and polymerizes.) Experiments were performed on three very different coals with carbon contents ranging from 74-84% (MAF). Properties of these coals, as suggested by the Pennsylvania State University Coal Bank, are given in Table 1. In the present work, representative samples of these coals, as obtained from the Coal Bank, are employed without preliminary grinding, washing or sieving. Reactions are carried out in stainless steel tubing bombs (15 cm x 1.3 cm o.d.). Typically the reactor contains 0.5 g of coal, 0.1 g of THQ and 12 g of FC-70. After sweeping out dissolved air, the reactor is pressurized with 8 MPa of H_2 and sealed with a high-pressure valve. The bombs are heated in a fluidized sand bath while being agitated at 300 cpm. Processed coals are compared on the basis of their pyridine solubility.

Table 1. Coal Properties

PSOC Designation	1104	247	1098
Moisture (%)	1.95	30.36	4.19
Ash (% on dry basis)	3.43	11.29	15.86
Volatile Matter (% MAF)	43.83	46.22	41.78
C (% MAF)	84.47	74.44	80.20
H (% MAF)	5.66	4.93	5.73
N (% MAF)	1.46	1.49	1.45
S (% MAF)	1.86	0.53	4.73
O (by difference)	6.48	18.61	7.89

1104 - HVA bituminous coal from Elkhorn #3 Seam
247 - North Dakota lignite A from Noonan Seam
1098 - Illinois #6 coal

After an 8-12 hour Soxhlet extraction with acetone, the processed coals contain only 3-4% retained THQ (from nitrogen analysis). The light color of the acetone extract indicates that very little of the coal is removed in this step. Pyridine extraction was for a miniumum of 8 hours in a micro-Soxhlet apparatus, followed by two-hour extractions with benzene and acetone, a procedure found necessary to remove adhered pyridine from the coal.[1-3] All weighings were done after an 8-hour vacuum drying at 110°C followed by equilibration with $CaSO_4$ in a dessicator.

Results

Coal heated at 250°C in FC-70 with low concentrations of THQ visually appears the same as untreated coal. After the coal particles settle, the FC-70 is transparent and uncolored. It is found, however, that the pyridine solubility of treated coal is increased substantially over its original value. As shown in Figure 1, the conversions of the three very different coals all asymptotically approach 33-35% in long (18 hour) runs, with no evidence of char formation, as indicated by decreased conversion at long time. The pyridine solubilities of the unprocessed coals are included as the t=0 points on these curves. To within the scatter of the data, the plots of log $(C(\infty)) - C(t))$ vs time, shown in Figure 2, are straight lines, in agreement with first-order approach to the ultimate conversions obtainable in these experiments. The least-squares slopes and correlation coefficients of these lines are: $-.62hr^{-1}$, -.98 (1104), $-.77hr^{-1}$, -.99 (247), and $-.57hr^{-1}$, -.95 (1098). These slopes are reasonably close. However, the lignitic coal (247) has very low unprocessed solubility, and undergoes a rapid initial increase in conversion to a value similar to those of the other two coals. If the unprocessed conversion of PSOC 247 coal is not included in the least-squares analysis, the slope of its approach to ultimate solubility is even closer ($-.70hr^{-1}$, -.999) to the slopes for the other two coals.

Discussion

Most coal liquefaction studies emphasize variations in behavior between different coals. In this work we have demonstrated a mode of processing in which three very different coals approach almost identical ultimate conversions

at similar rates. The range of first-order rate constants for the three coals is 30% of their mean value. However, if the unprocessed value (t = 0) is not included in calculating the rate for the lignitic coal (PSOC-247), the range is only 20%. We have previously noted,[1] that it is relatively easy to induce small increases in the conversion of PSOC-247, perhaps because it is initially only 4% soluble in pyridine. For example, unlike a bituminous coal, the conversion of PSOC-247 increased 8% when quinoline rather than THQ is used in our experiment. Thus, it is likely that after an initial very rapid increase in conversion of PSOC-247, its approach to ultimate solubility is at a rate very close to that of the higher rank coals. These kinetics appear to be representative of a chemical reaction rather than of mass transport, since there is very little change in the rate of coal conversion when a fine sieved fraction of the coals is processed. (PSOC-1104, 100-200 μ particles, compared to the as-received coal, which has > 50% of its mass in particles larger than 400 μ.)

There are a number of reasons for preferring a mechanism for these observations that is based on breaking chemical bonds in the coal macromolecular network, rather than one based on physical effects, such as swelling due to relaxation of hydrogen bonds. First, physical effects are generally reversible,[4] and we measure coal conversion after almost all the THQ is removed by 12-hour acetone extraction and the acetone is removed by drying at 110°C, a procedure which should allow reformation of hydrogen bonds. Second, when shorter acetone washes are employed, leaving ca. twice as much THQ on the coal, very similar results are obtained,[1] whereas additional hydrogen-bond rupture would be anticipated with more adsorbed THQ. Third, using the strong bases triethylamine and ethylenediamine in place of THQ produces less than 5% increase in conversion (bituminous coals for 4½ hours). Ethylenediamine is a particularly good low-temperature solvent for coal,[5,6] and would be expected to be effective in a purely physical mechanism. Last, NMR spectra of the evaporated acetone wash show considerable conversion of THQ to quinoline in these experiments. Without H_2 for reformation of THQ, conversions are somewhat reduced.[1] Although probably only a small fraction of the hydrogen transferred from THQ breaks bonds in the coal macromolecule, observation of THQ conversion is consistent with the chemical reaction mechanism. These four points provide a strong argument for a low temperature reaction between THQ and the macromolecular network of a variety of coals and offer an explanation for the unique efficacy of THQ as a coal liquefaction medium.

Although dehydrogenation of THQ is observed in this work, tetralin, another potent hydrogen donor, does not increase coal solubility in similar experiments. Thus, neither basicity nor hydrogen donor ability alone is sufficient for the liquefaction reaction, and it appears that the proximity of a lone pair of electrons to a labile hydrogen is necessary. There are model compounds, such as diphenyl disulfide, which are related to weak bonds in proposed coal structures,[7] and react with THQ at 250°C. It is not yet known, however, which of these reactions satisfy the other criteria (kinetics, selectivity against tetralin, etc.) necessary to explain the results of our experiments. Experiments are continuing to further explore the parameters of this process and to find a mechanism to describe it.

Acknowledgment

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Figure 1. Coal Conversion with THQ in FC-70

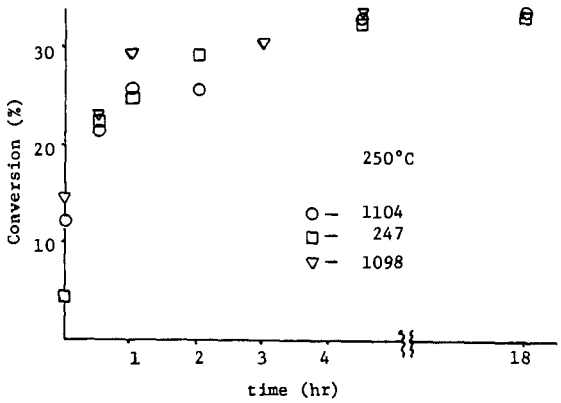
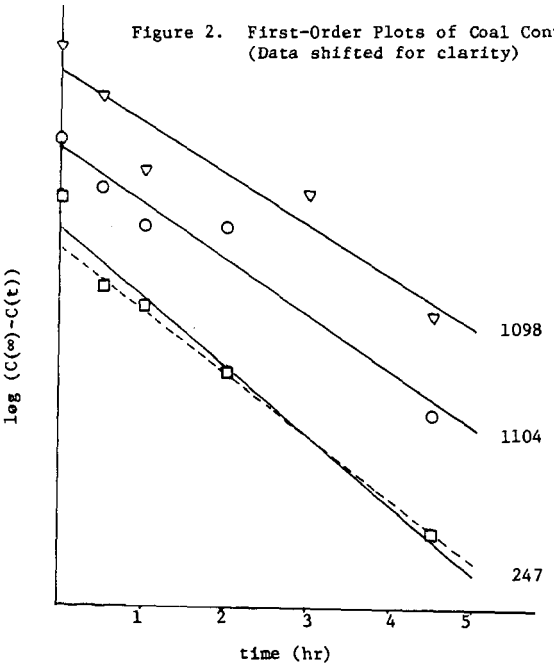
Figure 2. First-Order Plots of Coal Conversion
(Data shifted for clarity)