

ELUCIDATION OF CHEMICAL PROCESSES IN COAL LIQUEFACTION: EFFECT OF RADICAL QUENCHERS

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INTRODUCTION

The thermal liquefaction of coal is a complex, heterogeneous process involving two mutually interactive phenomena: chemical transformation of the organic material and mass transfer between solid, liquid, and gaseous phases (1,2). Thermally generated free radicals play a key role in these conversions; and their subsequent interactions with other species, e.g. hydrogen donors, determine the course of the liquefaction process and the final product mixture (3,4). In functional terms, the organic portion of coal can be described as a two component system: a cross-linked macromolecular network constituting an insoluble, immobile phase; and a low molecular weight, soluble bitumen component comprising a mobile phase (5,6).

Since bitumen is already a soluble low molecular weight material, it should not be considered a liquefaction target. The liquefaction objective is chemical unlinking of the macromolecular coal network. From this perspective, it is important to obtain experimental information about the behavior of the insoluble macromolecular portion of coal during liquefaction. Conventional batch mode experimental techniques which confine starting materials, intermediates, and products to the same reaction space throughout the entire course of conversion cannot provide this information.

Bitumen is reactive under liquefaction conditions (7); and its hydrogen donor/shuttler ability is well established (8,9). Thermal chemical reactions involving bitumen are thus apt to obscure the primary liquefaction processes, i.e. disruption of the macromolecular network. In order to isolate the thermal chemical behavior of the macromolecular component, we have sought to minimize contributions due to bitumen by using pyridine extracted coal. To avoid similar screening effects arising from the lingering presence of liquefaction products, we have developed a short residence time, flow mode micro-reactor which rapidly removes solubilized material from the reaction zone. Using this approach, the response of the insoluble coal matrix to various chemical reagents can be evaluated with minimal interference from bitumen or liquefaction products. In the present study, we have investigated the effects of radical quenchers, radical initiators, and chain transfer agents on the thermal solubilization of pyridine extracted Illinois No.6 coal in benzene.

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EXPERIMENTAL

General

Illinois No. 6 coal from the Ames Laboratory Coal Library was used in these studies. Prior to use, the coal was ground and sized to 100-200 mesh under a nitrogen atmosphere and dried overnight at 110 C under vacuum. The ultimate analysis for this coal (dmmf basis) is C : 80.6%; H : 5.6%; N : 1.6%; S : 2.4%; O(diff): 9.8%. Ash (dry basis) and volatile matter (daf basis) contents are 10.0% and 40.4%, respectively. For these solubilization experiments, coal was Soxhlet extracted with pyridine under nitrogen for two days; and the residue was dried overnight at 110C under vacuum. Solvents, solutions of reagents, and effluent samples were handled and stored under nitrogen. HPLC grade solvents were degassed by sonication, distilled under nitrogen, and introduced directly into the reactor system. Chemical reagents were used as received from commercial sources.

Solubilization Procedures

Solubilization experiments were carried out in a 300 μ L rapid heating, flow mode tubular microreactor. The construction and general configuration of the apparatus and reactor unit have been described previously (10). Important features of the reactor system include temperature and pressure programming capability, continuous, "on-line" optical density monitoring of the reactor effluent; real time acquisition of optical density, temperature, and pressure data; and a time resolved product collection system.

In a typical experiment, approximately 200 mg of 100-200 mesh pre-extracted coal was placed in the reactor, fixed in place by 2M stainless steel frits, and a shielded 0.062 inch o.d. chromel-alumel thermocouple was inserted into the coal bed. After connecting the reactor and purging with nitrogen, the reactor was pressurized, filled with benzene or a solution of reagent in benzene, and the flow rate was adjusted to 1.0 mL/minute. Tetrahydrofuran (THF) was then introduced into the reactor effluent immediately after the exit at a flow rate of 1.0 mL/minute. The system was maintained at a constant pressure of 3000 psi throughout the experiment; and, under these conditions, the residence time of the fluid in the reactor was approximately 5 seconds. The temperature profile of the coal bed was controlled from 20 C to 430 C according to a predetermined program.

Typically, ten aliquots were collected from the reactor during a 70 minute experiment. At the end of the experiment, the reactor was quickly cooled to room temperature while purging with nitrogen; and the residue was removed from the reactor and weighed. The reactor effluent was analyzed with a Varian 3700 Gas Chromatograph equipped with a 30 meter OV-101 fused silica capillary column using internal standards for quantitation.

RESULTS AND DISCUSSION

Overall conversions of coal in the thermal solubilization experiments were determined gravimetrically. Conversions were found to be positive or negative depending, presumably, on the balance between loss of solubilized fragments and uptake of reactive species supplied to the reaction zone reagent solutions. Monitoring of the optical density of the solubilization products gave us further insight into the dynamics of the thermal behavior of coal during solubilization. While it is clear that the latter technique mixes qualitative effects (different species) with quantitative ones

(concentrations), we have found the Integrated Absorbance (IA) to correlate significantly with the gravimetrically determined conversions in several solvents (10). Integrated Absorbance thus provides a useful approximation of yields and rates of coal conversions in these systems.

Figure 1 shows an excellent linear regression fit for IA vs Weight Loss for Illinois No. 6 coal. Data for this plot were taken from thermal solubilization experiments at different temperatures and pressures using benzene as the solvent. We have used such optical density profiles to reveal and investigate differences in solubilization rates for coals of different rank (10), and as the basis for collecting effluent fractions during solubilization (11).

Figure 2 depicts typical kinetograms obtained by this method for raw and pyridine pre-extracted Illinois No. 6 coal. It is clear that the first peak in the raw coal profile is due to pyridine soluble material (i.e. bitumen), eluted between 130 and 320°C. In the benzene solubilization of Illinois No. 6 coal, we have previously established that below 300°C the effluent is comprised, almost exclusively, of physically extracted components, while at higher temperatures thermal processes predominate (12). Thus the kinetogram of pyridine extracted coal reasonably represents the thermal chemical behavior of the macromolecular portion of coal. Gravimetric conversions (dry basis) for the raw coal and the extracted coal are 51.6% and 31.8%, respectively; it is interesting to note that the corresponding ratios of the conversions and the integrated absorbances are 1.62 and 1.58.

Effect of Hydrogen Donors

Thermal liquefaction of coal is generally considered to proceed via radical processes initiated by homolytic cleavages of weak covalent bonds, e.g. bibenzyl or benzyl ether linkages (13). From a radical chemistry perspective, the hydrogen donors commonly used in coal liquefaction are simply radical quenchers (14). Therefore, the thermal solubilization behavior of the pyridine pre-extracted coal in the presence of hydrogen donors will provide useful information about radical processes occurring in the coal matrix during thermal liquefaction. **Figure 3** shows the Thermal Solubilization Profile (TSP) of pyridine pre-extracted Illinois No. 6 coal generated in the presence of 5.0 mole percent THN solution compared with the TSP of pure benzene. The gravimetric conversions (dry basis) were 46.4% and 31.8%, respectively.

Comparison of the two curves reveals a relative increase in the optical density of the THN experiment commencing at about 330°C; this is a clear indication of the onset of radical processes. More detailed information about the effects of THN can be gleaned from a plot of the ratio of the absorbances vs temperature, also shown in **Figure 3**. The effectiveness of THN gradually increased between 330 and 400°C followed by a sharp increase in the ratio. The latter increase is coincident with the significant decline in the TSP of the reference run. This probably indicates the onset of retrogressive process, e.g. char formation, in the absence of a hydrogen donor. Furthermore, the distinct inflection of the ratio curve suggests that there are two levels of reactivity in the coal matrix.

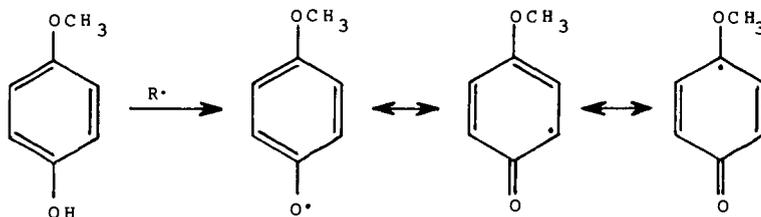
The relative effects of 9,10-dihydroanthracene (DHA) and tetralin on the Thermal Solubilization Profiles of pre-extracted Illinois No. 6 coal are compared in **Figure 4**. In these experiments, 1.0 mole percent solutions of DHA and THN in benzene were used. The TSP generated with pure benzene is provided for comparison. The respective gravimetric conversions for DHA, THN, and benzene are 71.5%; 35.5% and 32.7%. Based on these data, DHA is about 12 times

more efficient than THN. Kamiya, et al. compared the reactivities of these two hydrogen donors in batch mode liquefaction of a Japanese bituminous coal and concluded that DHA is 12.5 to 14.5 times more reactive than THN (15). This close agreement with our results indicates that the reactivities of bitumen, primary liquefaction products, and the macromolecular matrix of coal are all very similar with respect to hydrogen abstraction from hydrogen donors.

Additional information about the thermal behavior of pre-extracted coal can be drawn from the concentration profiles of DHA and anthracene (AN) also shown in Figure 4. The molar concentrations of these species in the reactor effluent were analyzed by GC and corrected for the decomposition of DHA (ca. 6% at 430 C). There is a qualitative similarity between the Thermal Solubilization Profile and the DHA and AN concentration profiles; and this provides additional confirmation that thermal chemical unlinking of the coal matrix is controlled by radical processes. Although it is not clear how accurately these concentration profiles mirror rates of primary liquefaction processes, the slowly decaying AN concentration at later stages of the solubilization (40-70 minutes, 420-430°C) strongly suggests that there is still significant radical activity in the residual matrix.

Effect of the Radical Quencher

In order to further examine the role of the radical processes in the thermal chemical unlinking of pyridine pre-extracted Illinois No.6 coal, a 1 mole percent solution of p-methoxyphenol (PMP) was used to investigate the effects of radical quenchers. PMP is a powerful radical quencher, transconverting reactive radicals to a less reactive resonance stabilized one (16):



The experimental results are shown in Figure 5. The thermal stability of PMP itself was examined in a blank experiment with only a negligible loss of PMP. As in the case of the hydrogen donors, there was significant positive displacement of the Thermal Solubilization Profile compared to the benzene profile. However, the weight loss was only 27.5% compared to 32.7% for the benzene reference experiment; and it appears that PMP may have been incorporated into the coal matrix. This is consistent with the PMP concentration profile also shown in Figure 5. The incorporation appears to be at least partially reversible, with capture occurring in the first 30 minutes and release during the final 30 minutes.

Effect of the Radical Initiator

Diphenyldisulfide (DPDS) was used to investigate the effects of radical initiators on the thermal liquefaction of pyridine pre-extracted coal. The sulfur-sulfur bond in DPDS is known to cleave homolytically at 300°C (17); and, moreover, it is an effective chain

transfer reagent (18). Results of this experiment are summarized in **Figure 6**. From the Thermal Solubilization Profiles it seems clear that DPDS inhibits productive pathways, i.e. formation of soluble products, in the thermal chemical unlinking of the coal matrix. DPDS is converted in a large proportion to benzenethiol as shown in the concentration profiles in **Figure 6**. The only available source of hydrogen, which is necessary for the formation of BT, is coal. Thus, it appears that the primary effect of this radical initiator is hydrogen abstraction from the coal matrix. In addition, the gravimetric results show an 11.1% weight gain indicating trapping of reactive fragments by the coal matrix.

These results are in distinct contrast to those of Stock, et. al. (18). These workers observed substantial acceleration of the thermal dissolution of Illinois No.6 coal by diphenyl disulfide. However, their reactions were conducted in the batch mode on unextracted coal in the presence of excess tetralin so there are several possible explanations. Research is underway to assess the differences in the two systems.

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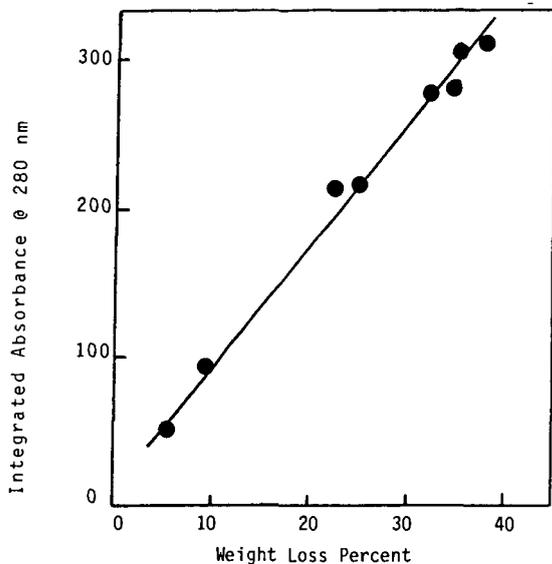


Figure 1. Correlation of Integrated Absorbance with Weight Loss in the Benzene Solubilization of Illinois No.6 Coal.

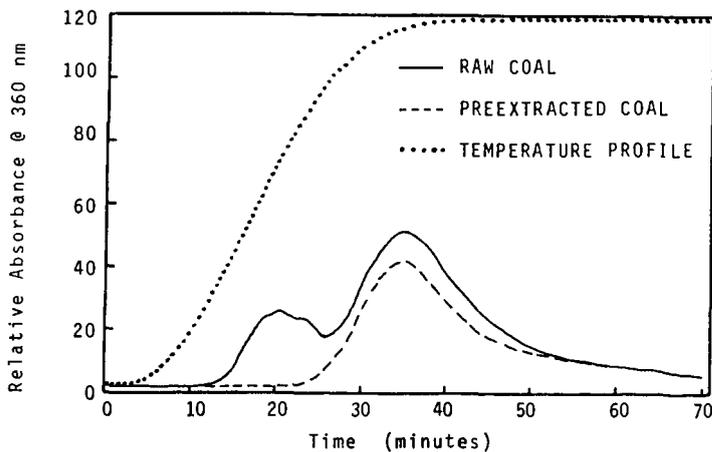


Figure 2. Temperature Programmed Benzene Solubilization Profiles of the Illinois No.6 Coal.

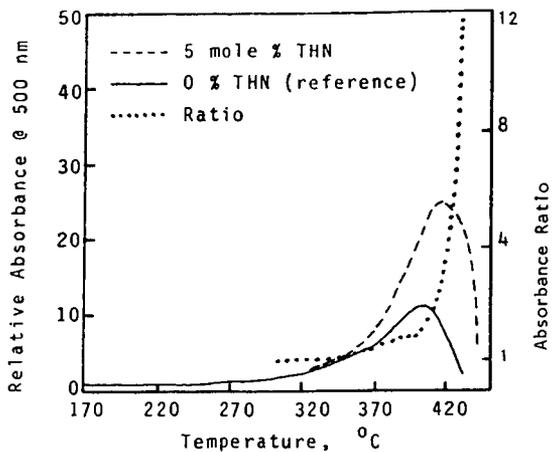


Figure 3. Effect of Tetralin (THN) on the Benzene Solubilization Profile of Pyridine Pre-extracted Illinois No.6 Coal.

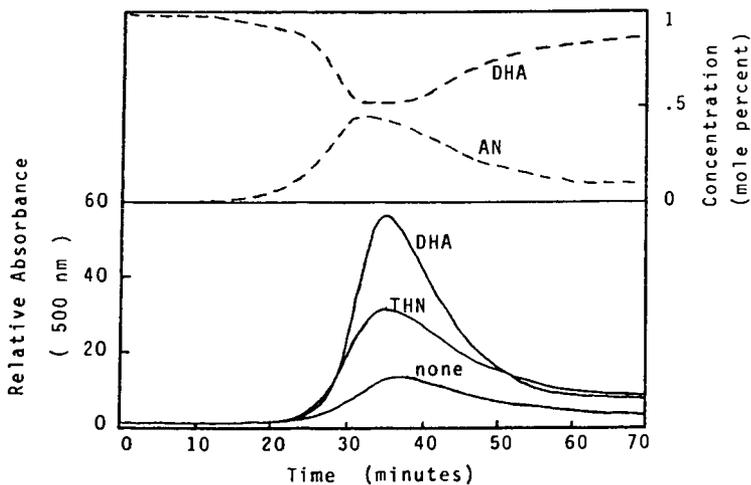


Figure 4. Hydrogen Donor Effects on the Benzene Solubilization Profile of the Pyridine Pre-extracted Illinois No.6 Coal. Top: 9, 10-Dihydroanthracene (DHA) and Anthracene (AN) Effluent Concentration Profiles. Bottom: Thermal Solubilization Profiles.

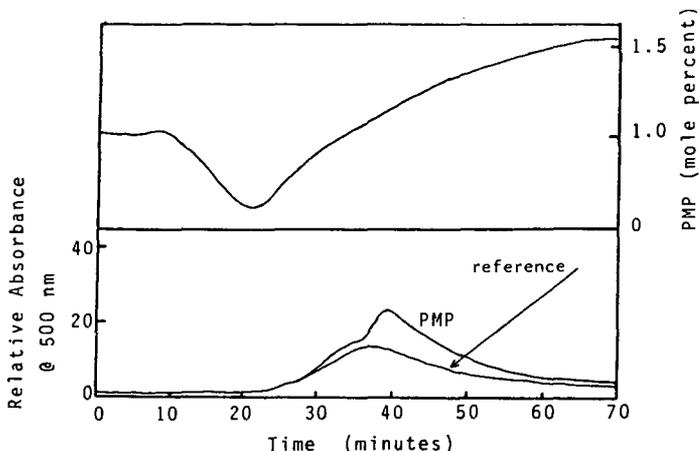


Figure 5. The Radical Scavenger Effect on the Thermal Solubilization Profiles of Pyridine Pre-extracted Illinois No.6 Coal. Top: Para-Methoxyphenol (PMP) Concentration Profile of Effluent. Bottom: PMP Effect on the Thermal Solubilization Profile.

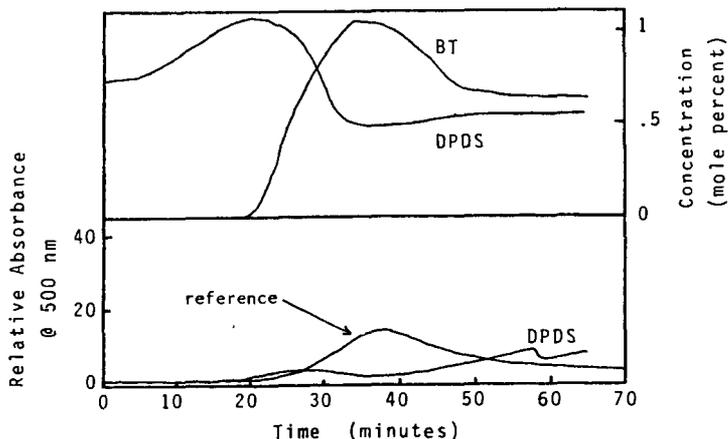


Figure 6. Radical Initiator Effect on the Thermal Solubilization of Pyridine Pre-extracted Illinois No.6 Coal. Top: Diphenyldisulfide (DPDS) and Benzenethiol (BT) Effluent Concentration Profiles. Bottom: DPDS Effect on the Thermal Solubilization Profile.