

AN IN-SITU EXPERIMENTAL OBSERVATION AND
PREDICTIVE MODEL OF FREE RADICAL FORMATION
UNDER LIQUEFACTION REGIME CONDITIONS

By

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Over the past 24 years, there have been many studies of free radicals in coal by electron spin resonance (ESR) techniques directed towards learning something about coal's chemical structure, petrography and geology (1). More recently, some of the more modern and potentially useful magnetic resonance techniques such as ENDOR have been used to probe the structure of coal (2). Beyond providing structural information and being a natural product of coal metamorphosis, the free radicals in coal, especially those formed during the heating of coal, are believed to play a key role in liquefaction and pyrolysis reactions (3). Our goal is to gain a more complete understanding of the effect of liquefaction process variables on the free radicals in coal and try to find what connection free radicals have with liquefaction, i.e. to answer the question: are free radicals the key to coal liquefaction? We have used ESR spectroscopy to study the free radicals in a variety of coals and vacuum pyrolyzed coals (4), free radicals in the various product components from the solvent refined coal (SRC-I) process (5), and the free radicals in a variety of coal solvent slurries reacted under a variety of conditions (6, 7). Coal macerals, or the various organic constituents of coal analogous to minerals in rocks have also been studied by ESR spectroscopy in our laboratory after a variety of pyrolysis (6) and liquefaction treatments (9). All of these experiments were performed as most have been done in the past, i.e. at room temperature after the reactions had taken place. Recently we have developed

a high temperature, high pressure ESR cavity to study the free radicals in coal during liquefaction (10, 11, 12).

We have used this high temperature, high pressure ESR cavity for detailed study of the effects of process variables on the free radicals in Powhatan #5 coal during liquefaction. The procedure used was a 2^5 factorial design involving two levels each of temperature (400 and 460°C), gas (H_2 and N_2), pressure (8.2 and 11 MPa), solvent (tetralin and SRC-II heavy distillate derived from Powhatan #5 coal) and heating time 3 and 15 minutes to reaction temperature. Free radical spectral parameters were monitored continually from about 2 minutes after reaction temperature was reached, up to one hour. After finding, from this work, that temperature and solvent were the two most important variables, we proceeded to study these variables in more detail, using 400, 425, 450, 460 and 480°C and tetralin, naphthalene and SRC-II as liquefaction solvents. The data from the study of process variables effects and the more detailed study of temperature and solvent effects were analyzed with the aid of a regression model.

Free radical measurements on the coal solvent slurries are done under liquefaction conditions, i.e. in-situ, using a high temperature, high pressure ESR cavity. The details of the cavity and its operation have been published previously (11, 12). The cavity system is basically a cylindrical brass TE₀₁₁ X-band cavity with internal modulation coils and internal axial heater inside a water-cooled beryllium copper pressure vessel. Samples are prepared in 4 mm OD, 2.5 mm ID quartz tubes by placing 0.5 g of Powhatan #5 coal in the bottom of the tube and injecting 0.5 g of tetralin or SRC-II heavy distillate (SHD). In the naphthalene experiments, the coal and naphthalene were premixed at 1:1 by weight and then poured into the sample tube. Temperature measurement is by a thermocouple imbedded in the sample. Typically, several spectra are recorded

before heating and then continuously from about 4 minutes after heating was begun up to one hour. Spin concentration measurements are made relative to the signal from a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ reference on the internal wall of the cavity. The calculations for spin concentration and its temperature correction are outlined in detail elsewhere (12, 13). Data are normally displayed as corrected (to 20°C) spin concentration versus time plots.

About 45 experiments were done using Powhatan #5 coal to screen the major process variables, such as solvent, temperature, gas type, pressure, and heating time. The data from these experiments were used to formulate a regression model to sort out the major effects and their interactions (13). Table I summarizes the results of this model. Reaction time alone was found to be insignificant. Temperature was found to be the most significant variable, accounting for about half of the effects present in the model. When solvent and solvent gas interactions are added in with temperature, almost 90% of the variation of the data is accounted for. Heating time, pressure and gas type alone or in combination with temperature have relatively minor effects on the data.

Based on these observations, it was decided that temperature and solvent type warranted further investigation. Experiments at 425, 440, 450 and 480°C were added as well as a complete series of experiments with Powhatan coal using naphthalene as the liquefaction solvent. Heating time was fixed at 3 minutes, pressure at 1600 psig and hydrogen was used in all of the additional experiments. Figure 1 shows the variation of spin concentration as a function of time for the three coal-solvent systems at 400°C . The points are experimental data and the solid lines are the spin concentrations predicted by the regression model. These are not fitted curves. At time 0,

the slurries are unheated. All points at $t > 0$ are at the desired experimental temperature. Note that the spin concentration in the tetralin solvent experiments is essentially the same as the unheated coal and that all the SHD and naphthalene experiments are somewhat higher. Figure 2 is a similar plot of the experimental data and predicted spin concentrations at 480°C . Here the spin concentration of all three Powhatan coal-solvent slurry systems is much higher than that of the unheated slurries. Again, the same ordering of spin concentration among the solvent systems is observed. The relative order of spin concentration in the solvents, tetralin < SHD < naphthalene, is believed to be due to the relative hydrogen donor capabilities of the three solvents. Naphthalene is a pure aromatic and should have no donatable hydrogens. Tetralin has four donatable hydrogens and SRC-II heavy distillate, although highly aromatic, would be expected to have some donatable hydrogen. Figures 3, 4 and 5 are spin concentration versus time plots displaying the data for all six temperatures used for each of the solvents. The naphthalene, Powhatan coal experimental data, shown in Figure 3, shows the general trend to higher spin concentration with increasing temperature. The data at 400 , 425 and 440° fall very close. There is a similar bunching at higher values for the 450 and 460° data. The spin concentration found at 480° is considerably higher than all the other data from the lower temperatures. The SHD Powhatan coal experiments, shown in Figure 4, show a similar ordering of spin concentration among the 6 temperatures, however, the values at the corresponding temperatures are lower than in the previous figure depicting the naphthalene experimental data. Figure 5, showing plots of spin concentration versus time for the tetralin solvent experiments, has a similar trend of increasing spin concentration with temperature, however, the order of the 460 and 480°C data are reversed compared to the other two solvents. From these data and a few data

taken under similar conditions at 470°C, there appears to be a maximum in spin concentration around 460°C in the Powhatan coal tetralin slurry system.

Discussion and Conclusions

1. In general, the coal free radicals are quenched in following the order of naphthalene<SHD<tetralin. This conclusion agrees with our expectations which are based upon the amount of donatable hydrogen present in the three solvents. The rate of free radical formation is assumed to be only temperature dependent. This is based on previous extensive pyrolysis experiments with coals and coal macerals. The observed free radical concentration depends on the competing effects of free radical formation and free radical quenching. The latter, unlike the former, is solvent dependent. The solvent dependency will be determined both by the amount of donatable hydrogen that is available as well as by the ease with which the free radical quenching hydrogen can be transferred to the coal free radicals.

2. The free radical concentration of the liquefaction slurry generally increases with increasing temperature. This is strictly true for the naphthalene and SHD experiments and is followed by the tetralin experiments up to 460°C where an apparent maximum is reached, with the spin concentration decreasing then at higher temperatures. The general increase in spin concentration with temperature is expected due to the greater thermal energy available for bond breaking. From the results of the correlative model, we find that about half of the variation in the spin concentration is due to temperature alone. Temperature and solvent interactions account for 70% of the observed effects.

3. The spin concentration is dependent upon reaction time and this dependence is also influenced by solvent and temperature. At 400°C, the relative slopes of the spin concentration versus time curves, from 0.1 to 1.0 hr., are 15, 5 and 0×10^{18} spins/g per hour for the naphthalene, SHD and tetralin experiments, respectively, demonstrating the solvent dependence. At 480°, the slopes have increased to 40, 35 and 20×10^{18} spins/g per hour for the same three solvents.

4. From the results of the full correlative model, we find that temperature, solvent and residence time and their interactions account for about 90% of the effects noted in the free radical concentration. Gas type has some minor significance as does pressure. Heating time has a negligible effect.

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TABLE I

GENERAL CORRELATION MODEL

<u>Variables Effects*</u>	<u>Sum of Square of Each Term</u>	<u>Fractional Contribution of Each Term</u>	<u>Fractional** Probability of Null Hypothesis (i.e., term not significant)</u>
C ₁ •time•temperature	119455	.480	.0001
C ₃ •time•temperature•solvent	51511	.207	.0001
C ₂ •time•temperature•solvent•gas	52284	.210	.0001
C ₄ •time•pressure	8025	.032	.0001
C ₅ •time•temperature•heating rate	6556	.026	.0001
C ₆ •time•temperature•gas	4739	.019	.0001
C ₇ •time•temperature•pressure•gas	4355	.017	.0001
C ₈ •time•pressure•heating rate	652	.003	.0129
C ₉ •time•temperature•pressure	565	.002	.0205
C ₁₀ •time•heating rate	358	.001	.0649
C ₁₁ •time	256	.001	.1184

Total Number of Points = 773; Total Data Sum of Squares = 328302; Total Model Sum of Squares = 248755; Error = 79548; R-Square (Model SOS/Total SOS) = 0.758

* Corrected Spin Concentration = Intercept + Sum of Terms.

** The lower the number, the higher the probability that the variable effects are real.

SPIN CONCENTRATION VS. ELAPSED TIME
POWHATAN #5 COAL, 1600 psig H₂, 400°C 3 min HT.

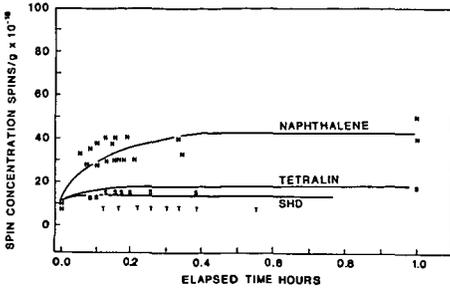


FIGURE 1

SPIN CONCENTRATION VS. ELAPSED TIME
POWHATAN #5 COAL, 1800 psig, 480°C 3 min HT.

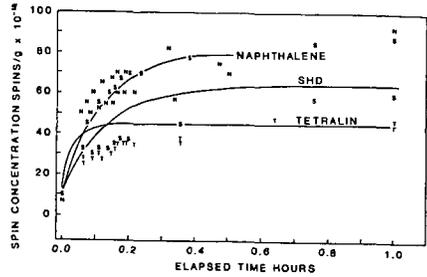


FIGURE 2

SPIN CONCENTRATION VERSUS ELAPSED TIME
POWHATAN #5 COAL AND NAPHTHALENE
1800 psig (11.0 MPa) H₂ 3 min HT
AVERAGE VALUES

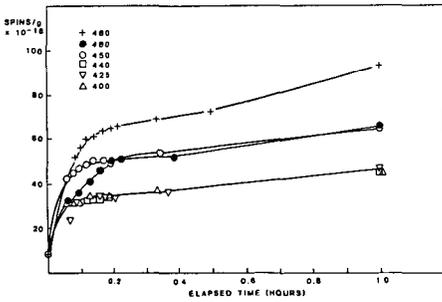


FIGURE 3

SPIN CONCENTRATION VERSUS ELAPSED TIME
POWHATAN #5 COAL AND SRC II HEAVY DISTILLATE
1800 psig (11.0 MPa) H₂ 3 min HT
AVERAGE VALUES

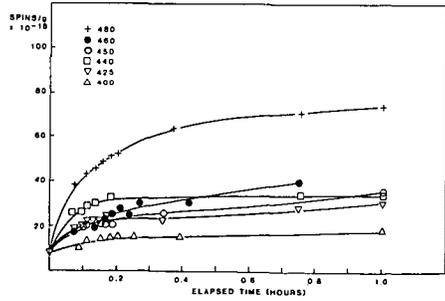


FIGURE 4

SPIN CONCENTRATION VERSUS ELAPSED TIME
POWHATAN #5 COAL AND TETRALIN
1800 psig (11.0 MPa) H₂ 3 min HT
AVERAGE VALUES

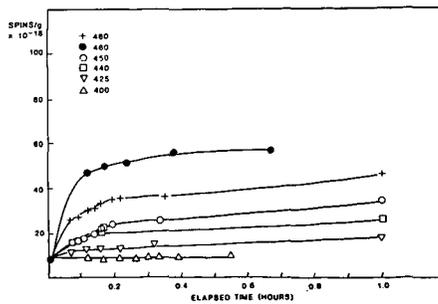


FIGURE 5