

# AN ESR INVESTIGATION OF FREE RADICALS IN COALS AND IN COAL CONVERSIONS

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## I. Introduction

Free radicals in coal are not well understood or characterized despite their apparent great significance in liquefaction (1). The fate of these thermally generated free radicals is believed to determine the type of product obtained and may be associated with problems in coal conversion such as reactor coking and poor yields. This study of free radicals in coals was initiated to gain some insight as to the number and types of free radicals under a number of conditions that might be significant in coal conversion processes. Since the discovery of free radicals in coals by Uebersfeld (2) and Ingram (3), electron spin resonance (ESR) spectroscopy has been used in the study of coal and coal-derived materials by many workers (2-8).

As a technique, ESR is attractive, since radical concentration and chemical information can be obtained with relative ease in a minimal period of time. The spectral parameters of interest are the g-value of the radicals, radical concentration, peak-to-peak linewidth of the first derivative signal, and in some cases, the spectral lineshape.

## II. Experimental

Six coals, ranging in rank from lignite to low volatile bituminous, were examined by ESR after a variety of treatments. The analytical data for these coals are summarized in Table I. Several sample treatments were used. Four coals were treated by evacuation to  $\sim 10^{-4}$  torr with heating for 2 hours in 2 mm I.D. ESR tubes with subsequent sealing under vacuum. Several coals were treated under liquefaction conditions by mixing them with approximately equal weights of either naphthalene or tetralin in ESR tubes and heating them under 1800 psi of  $H_2$  or  $N_2$ . Some samples were prepared without solvent. The effects of different heating rates, solvents, gases, and residence times on the ESR parameters will be discussed. Duplicate samples were prepared in many cases to check reproducibility. All spectra were recorded at room temperature with Varian V-4500 single- and dual-cavity x-band spectrometers. Details of the measurements and peripheral equipment used are described in Ref. 8. The possible effect of many different factors, such as solid state effects, "skin" effects, sample inhomogeneity, and coal particle fractionation, on these measurements was considered and is discussed elsewhere (8).

## III. "Room Temperature" Experiments

The results obtained in the ESR experiments on coals evacuated at  $\sim 100^\circ C$  and at room temperature are essentially in agreement with the results obtained by earlier workers (4). The g-values show a large difference between the lignite and subbituminous coal and the four higher rank coals. (See Table II.) In the case of the higher rank coals, their g-values are typical of  $\pi$ -type aromatic hydrocarbon radicals (9,10). The subbituminous coal and the lignite have higher g-values indicating that atoms other than carbon and hydrogen are important in the electronic structure of the radical.

The spectral linewidth of all samples was measured as run in vacuum. Several samples yielded spectra which consist of a sharp line ( $\sim 1$  gauss) superimposed on a broader signal. As noted by Retcofsky et. al., a small amount of fusain ( $\sim 1\%$ ) in coal can account for the sharp component seen in spectra of evacuated samples (4).

The radical concentrations for the six coals follow the expected increase with rank with two exceptions. The Kentucky #11 coal has an extremely high free radical concentration for its rank. The Lower Dekoven coal is somewhat lower than expected, probably due in part to its extremely high ash content.

The lineshapes of the spectra were estimated in some cases. The lineshape functions considered were the Lorentzian and Gaussian functions. The samples yielded spectra which range from some nearly equal linear combination of the two functions, as is the case with the Wyodak coal, to the very broadly sloping, multi-component spectra sometimes found for the higher rank coals. The lineshapes of coal spectra are probably affected by unresolved hyperfine, anisotropic effects or the large number of somewhat chemically different radicals found in coals.

#### IV. Heat-Treated Coals

Four of the coals, Wyodak, Pocahontas #3, Illinois #6, and Lower Dekoven, were evacuated and heated to temperatures up to 600°C. Radical concentrations, g-values, and linewidths were measured for each sample. The radical concentration of the coals is seen to change dramatically over the temperature range studied. Up to 400°C, only moderate changes in radical concentration occur. Radical concentration increases sharply between 400°C and 500°C and drops substantially on going to 600°C (8). This behavior is qualitatively in agreement with the work of Smidt and Van-Krevelen, among others (6).

Figure 1 shows the change in g-values of the radicals in the coals as a function of temperature. Two of the coals, the Pocahontas #3 coking coal and the Illinois #6 high-volatile bituminous coal, show a minor decrease in g-values from 2.0029 to 2.0027. Such a change in g-value shows a minor change in radical structure, the radical tending to become more hydrocarbon in nature. The Wyodak sub-bituminous coal shows a very large decrease in g-value, from 2.0037 to 2.0027, which occurs below 500°C. One of the bituminous coals, Lower Dekoven, Illinois, shows some interesting changes in g-value when heated. Between 250° and 500°C the g-value decreases to an abnormally low value of 2.0023. There are several possible explanations for this behavior, among these is the appearance of  $\sigma$ -type radicals. Many  $\sigma$  radicals have g-values around 2.0024 and some are known have g-values as low as 2.0008 (11). From the increase in the g-value of the radicals in the Lower Dekoven coal on heating to 600°C and the decline in radical concentration, it is likely that the  $\sigma$ -radicals are involved in recombination reactions.

#### V. Liquefaction Experiments

Several coals were treated using various temperatures, heating rates, solvents, reagent gases, and residence times to determine their effect on the ESR spectral parameters. The Wyodak subbituminous coal was selected to determine experimental conditions to be used on a series of coals. In our initial experiments, this coal was heated at  $\sim 13^\circ\text{C}/\text{min}$  to 440°C in 1800 psig of  $\text{N}_2$  or  $\text{H}_2$  gas and held at that temperature for 2 hours. Examination of these samples at room temperature by ESR showed essentially no difference in g-values (2.0028), or linewidth (5.1 vs 5.5). Some difference in radical concentration between the samples treated with the two gases does occur, the samples treated in  $\text{H}_2$  having somewhat fewer radicals,  $25 \pm 13 \times 10^{18}/\text{g}$  vs  $45 \pm 3 \times 10^{18}/\text{g}$ . The same coal was reacted with tetralin or naphthalene in 1800 psi of  $\text{H}_2$  or  $\text{N}_2$  at the same temperature, heating rate, and for the same length of time. Linewidths and g-values were the same for all combinations, within experimental error, being about 5 gauss and 2.0027 to 2.0028, respectively. Free radical concentration of tetralin-treated Wyodak coal appears to be the same, around  $25\text{-}30 \times 10^{18}$ , whether  $\text{H}_2$  or  $\text{N}_2$  gas is used. Naphthalene-treated coals do show some slight dependence (less than a factor of 2) of the free radical concentration on the gas used, the concentration being lower when  $\text{H}_2$  is used. The difference in radical concentration in this coal in what should be the best donor, tetralin and  $\text{H}_2$ , compared

to the worst donor system, naphthalene and  $N_2$ , is only slightly more than a factor of 2. Using tetralin with  $H_2$  and naphthalene with  $N_2$  as the treatments for the coal samples, the effects of heating rate and residence time were investigated. The radical concentration in samples was reduced in samples heated at a faster rate ( $32^\circ C/min$ ) and held at the maximum temperature for a shorter time (10 min). The tetralin- $H_2$ -treated samples showed a reduction in radical concentration that was much larger. The difference in radical concentration between the treatment schemes is about 5 to 1 for the Wyodak coal, again with the naphthalene- $N_2$ -treated samples having more free radicals remaining. Doubling the residence time from 10 minutes to 20 minutes had no apparent effect on tetralin- $H_2$ -treated samples. Some of the radical concentration data collected for different heating rate-residence time treatments for the two solvent-gas treatment schemes are shown in Figures 2 and 3 for the temperature range  $400^\circ$  to  $500^\circ C$ .

Two other coals, Kentucky #11 and Hagel lignite, were studied by ESR after treatment with the tetralin- $H_2$  and naphthalene- $N_2$  systems. All samples were heated at  $\sim 32^\circ C/min$  under 1800 psig and after they were kept at the desired temperature for 10 minutes, the reactor was cooled rapidly ( $\sim 3$  minutes to RT) by high-pressure air. A plot of the g-values of the Kentucky #11 coal radicals as a function of temperature is shown in Fig. 4. Around  $420^\circ C$  there is a considerable difference in g-values for the samples treated by the donor and non-donor systems. As the temperature is raised to  $\sim 475^\circ C$ , these differences disappear. The differences in g-values cannot be easily interpreted since all of these fall in the range of hydrocarbon radicals, and differences as large as these seen here are found between the anion and cation of the same radical species (9,10). The Hagel lignite runs show no such temperature dependence of g-values in the  $400^\circ$ - $500^\circ C$  range, with most of the samples having very similar g-values, between 2.0027 and 2.0028. Spectral linewidths for these two coals show no dependence upon temperature between 400 and  $500^\circ C$  or the solvent-gas treatment system used. The lignite samples had spectral linewidths generally between 5 and 6 gauss. There was more scatter in the linewidths found for the Kentucky #11 samples, ranging from 4 to 6 gauss. The free radical concentration of the Kentucky #11 samples is shown in Figure 5. Here the differences between the donor and non-donor treatments are apparent, as it was in Fig. 2 for the Wyodak coal. The Hagel lignite shows similar effects due to donor capabilities of the sample treatment; however, there is a generally higher concentration in all cases, the tetralin- $H_2$ -treated samples having radical concentration  $\sim 20 \times 10^{18}$  compared with  $\sim 40 \times 10^{18}$  for the naphthalene- $H_2$ -treated samples. It is believed that the lower radical concentration found for the tetralin- $H_2$ -treated samples is due to hydrogen transfer to the radical sites. A few extraction experiments were attempted on the Wyodak coal samples after the liquefaction treatments to see if a correlation between radical concentration and toluene-insolubles could be made. No significant differences were found, although this may be due to large experimental scatter. Conversions on a toluene soluble, daf basis are from 64 to 77%. Further effort in this area is planned.

#### VI. Solvent-Refined Coal

SRC filter feed, process solvent, and filter wash solvent were obtained from the Pittsburg & Midway Coal Mining Co. SRC pilot plant near Tacoma, Washington. The samples used in most of this work are the dried filter solids, process solvent, filter wash solvent, the filtrate, which is about 50% process solvent and 50% filter-feed with solids removed, and the filter feed as received. A sample of the solid SRC product from the Catalytic, Inc., SRC pilot plant in Wilsonville, Alabama, was also examined. The results of the ESR measurements are shown in Table III. All values are for the organic paramagnetic species present.

#### VII. Conclusions

In general, concentrations of naturally occurring free radicals are of the order of  $5-15 \times 10^{18}/g$ . In coals heated in vacuum, the concentration of radicals is

quite high,  $100-200 \times 10^{18}/g$ , and reaches a maximum between 400 to 500°C, dependent on rank and maceral content. Coals heated to similar temperatures in the presence of a high-pressure (2000 psig) gas have somewhat lower concentrations ( $<100 \times 10^{18}/g$ ). This could result from small molecules or radicals escaping less readily in a high-pressure gas than in vacuum. The gas acts as a solvent. Naphthalene affects free radical concentration in a manner similar to that of the gases by acting as a solvent. Tetralin, as a hydrogen donor solvent, is the most effective treatment among those tried for consuming free radicals. Hydrogen transfer is presumed to occur and in some cases this hydrogen transfer quenches some of the naturally occurring free radicals in coal. The free radical concentration of SRC is similar to that found for other solvent-treated systems.

#### VIII. References

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Table I

#### CHEMICAL ANALYSIS (DAF)

	C	H	O	S	N	ASH(dry)	RANK
Wyodak Gillelte, WY	72.2	5.5	21.0	0.3	1.0	9.2	Subbit C
Hagel-ND*	71.0	4.9	21.8	.72 (total)	1.6	9.7	Lignite
Kentucky #11*	76.4	5.4	10.0	5.7 (total)	2.2	16.0	HVB
Illinois #6	82.0	5.4	9.5	1.0	1.7	6.5	HVB
Lower Dekoven-IL*	80.6	5.8	4.8	7.7	1.8	21.9	HVA
Pocahontas #3-WV	86.4	3.9	6.8	0.9 (total)	1.2	3.3	LV

\*Data supplied by P. Given, Pennsylvania State University.

Table II

ESR PARAMETERS OF COALS  
All samples evacuated 2 hr at 105°C

	<u>g-Value</u>	<u>Linewidth</u>	<u>Radical Concentration per g x 10<sup>-18</sup></u>
Hagel Lignite	2.0040	6.7	4.7
Wyodak Subbit C	2.0037	7.43	5.8
Kentucky #11 HUB	2.0029	1.9	14.1
Illinois #6 HUB	2.0029	1.34 & 6.02	6.8
Lower Dekoven HVA	2.0028	0.86 & 4.14	4.1
Pocahontas #3 LV	2.0029	0.97 & 6.03	15.8

Table III

SRC ESR DATA\*

<u>Sample</u>	<u>g-Value</u>	<u>Linewidth (gauss)</u>	<u>Concentration (spins/g)</u>
SRC Filter Cake Solids	2.0026	2.9	18 x 10 <sup>18</sup>
Filtrate	2.0031	6.4	0.7 x 10 <sup>18</sup>
Filter Feed	2.0027	1.4	3.5 x 10 <sup>18</sup>
Recycle or Process Solvent	2.0029	9.4	0.2 x 10 <sup>18</sup>
Wash Solvent	2.0037	6.8	6 x 10 <sup>15</sup>
Wilsonville SRC Solid Product	2.0028	1.0	15 x 10 <sup>18</sup>

\*All materials are from the P&M SRC pilot plant at Tacoma, Washington,  
except as noted.

Figure 1. g-Value Vs Temperature

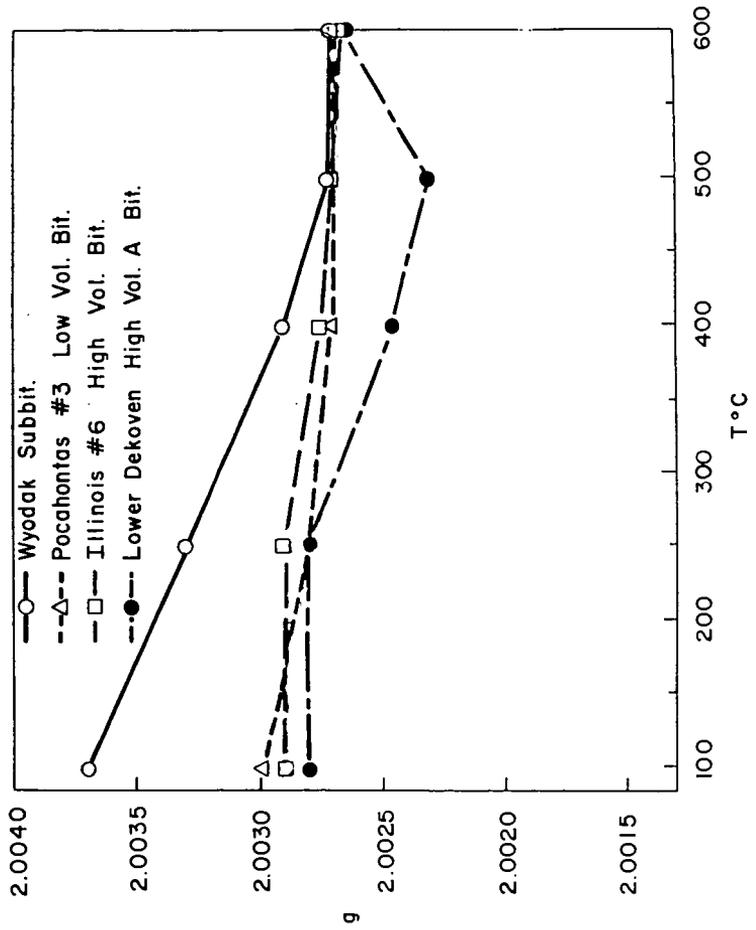


Figure 2. Radical Concentration Vs Temperature

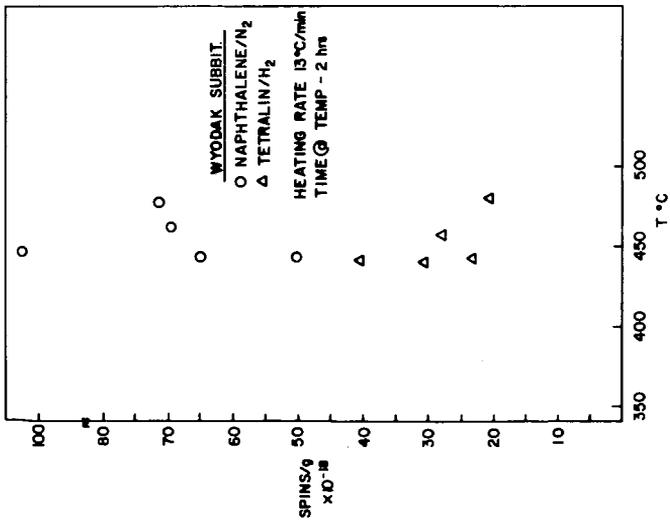


Figure 3. Radical Concentration Vs Temperature

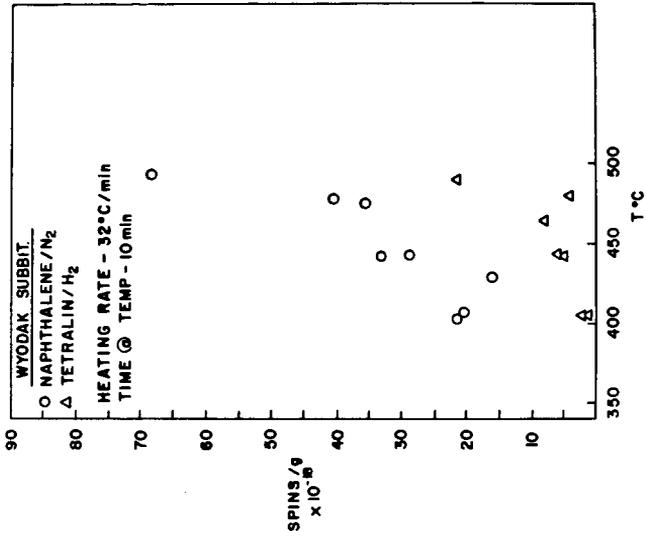


Figure 4. g-Value Vs Temperature

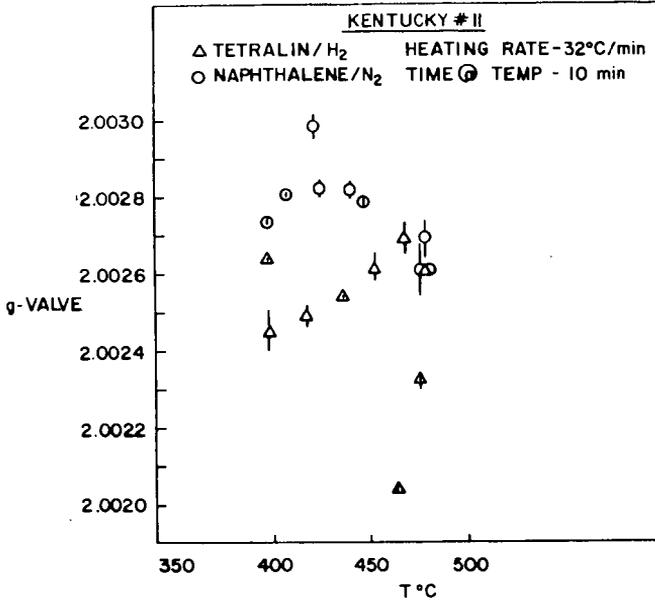


Figure 5. Radical Concentration Vs Temperature

