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FUNDAMENTALS OF COAL DEPOLYMERIZATION: AN EXPERIMENTAL AND STATISTICAL CORRELATIVE MODEL OF THE EFFECTS OF TEMPERATURE AND SOLVENT ON FREE RADICALS IN COAL

A Quarterly Report for the Period October 1—December 31, 1980

By
L. Petrakis
D. W. Grandy
G. L. Jones

January 1981

Work Performed Under Contract No. AC01-79ET14940

Gulf Research & Development Company
Pittsburgh, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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L. Petrakis, Project Manager
D. W. Grandy
G. L. Jones

Gulf Research & Development Company
P. O. Drawer 2038
Pittsburgh, Pennsylvania 15230

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EXECUTIVE SUMMARY

In this project we are attempting to develop information as to the nature and possible role of free radicals in the depolymerization of coal under hydroliquefaction conditions. It is generally assumed that free radical chemistry plays an important role in the liquefaction of coal. Central in our work has been the use of a specially designed high pressure/high temperature electron spin resonance cavity that allows us to quantitatively monitor free radicals in coal 2-4 minutes after the heating cycle is initiated. In previous reports, we have detailed the methodology that is being used as well as work that gave the relative effect of various process variables on the concentration of free radicals from a Powhatan #5 coal. In this report we detail the role of temperature and solvents for the same coal. In addition, a correlative mathematical model has been developed that not only fits the data, but also it can be used to examine the sensitivity of free radical formation to the various process variables. ESR measurements have been made at various temperatures from 400-480°C. The solvents that have been used are tetralin, naphthalene and SRC-II heavy distillate that has been derived from the Powhatan #5 coal. The free radical concentration has been measured quantitatively and repetitively at these various sets of conditions. The heating time has been restricted to three minutes, gas pressure to 1600 psi and the gas used is hydrogen.

The main conclusions from this work include the following. In general, the coal free radicals are quenched in the naphthalene < SRC-II heavy distillate < tetralin. The observed free radical concentration depends on the competing effects of free radical formation and free radical quenching, the latter being both temperature and solvent dependent. The free radical concentration of the liquefaction slurry generally increases with increasing temperature. The rate of quenching of free radicals by SRC-II heavy distillate is closer to that of tetralin at lower temperatures and approaches that of naphthalene at the higher temperature. 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. The correlative model represents the experimental results within the reproducibility of the data. The spin concentration is dependent upon reaction time, and this dependence is also influenced by solvent and temperature. The activation energies for the different solvents quenching the free radicals are distinctly different for the different solvents.

Future work will emphasize the role of mineral matter, components of SRC-II heavy distillate as effective solvents and structural definition of products so that the kinetic and mechanistic implications of the free radical chemistry on product obtained can be pursued.

INTRODUCTION

The mechanism of direct hydroliquefaction is widely believed to proceed by a free radical mechanism.^(1,2) Pyrolysis of coal is assumed to be the first step in which the structure of coal is broken down to smaller fragments by thermal bond rupture. A wide variety of these fragments, which are free radicals or fragments with an unpaired electron, are the initial product in the thermal breakdown or depolymerization of coal. Free radical fragments exist in naturally occurring coal due to the reactions which have taken place over geologic time that are responsible for the change in coal's physical and chemical properties in the metamorphic process. The free radical fragments resulting from thermal bond rupture may then proceed by a variety of reaction pathways to more or less useful products. The control of the reactions which these fragments undergo, by the pressure, gas and type of solvent present, is a key factor in the yield of liquefaction processes. The temperature at which liquefaction (or pyrolysis) occurs should also be very important in that it will determine the number of a given type of bonds that can be broken in a certain time period as well as the type of bonds that can be broken and thus the chemical nature and number of the fragments. Studies of the pyrolysis of model compounds are directed to this end.⁽³⁾ Obviously, the chemical nature of the coal, determined by rank and petrography, will determine the distribution of bond types and structures present in a coal and, hence, the type and number of free radicals produced at a given temperature.

The major variables which affect liquefaction should include, but are not limited to, the type of coal, solvent and gas used in the process as well as the conditions, such as temperature, pressure, reaction time and heating rate. From our previous work on free radicals in coal and coal liquefaction, we have found that the most important variables are the types of coal, temperature, solvent and residence time.^(4,5,6) Heating rate, gas and pressure appear to be less important, at least under the conditions of our experiments which are batch type. In continuous processes where solvent must be regenerated or rehydrogenated, gas and pressure are surely important. The effect of catalysts on liquefaction is not addressed here at all but is known to be important, and will be addressed in a future paper.

In this paper, we address the effect of temperature, solvent and residence time in a detailed fashion. The temperatures used are 400, 425, 440, 450, 460 and 480°C. Solvents studied are tetralin, SRC-II heavy distillate and naphthalene. Tetralin is believed to be an "ideal" solvent and has four donatable hydrogens per molecule; naphthalene should be a poor solvent in that it has no donatable hydrogen. SRC-II heavy distillate, derived from Powhatan No. 5 coal, the coal used in this work, is a "real" solvent and should have a hydrogen donation ability that is in between naphthalene and tetralin; it will be abbreviated as SHD throughout this paper. Under liquefaction conditions, none of these solvent systems will remain unchanged over the course of the reaction. Some "leveling" is going to take place due to the production of coal liquids (similar to SHD but not as uniform in boiling range), the possible hydrogenation of naphthalene to tetralin and the dehydrogenation and rearrangement of tetralin. All of the above events will tend to average the effect of solvent but as will be seen in our results, a solvent effect on the concentration of free radicals certainly exists.

In addition to the experimental results to be discussed that were outlined above, we introduce the methodology and utilization of a correlative model that predicts the response of the free radical concentration to manipulation of the variables and quantifies the importance of the process variables. This model utilizes both the data from our previous paper⁽⁶⁾ which

involves variation of temperature, pressure, solvent and gas type, heating time and reaction time as well as the data from the more detailed study outlined above wherein heating time, gas type and pressure are held at constant values.

EXPERIMENTAL

Free radical measurements on the coal solvent slurries are made at reaction conditions, i.e., in situ, using a special high temperature, high pressure ESR cavity. The details of the cavity and its operation have been published previously.⁽⁷⁾ The spectrometer used is a Varian E-line Century series version of a Varian V-4500. Only the magnet and power supply have been retained from the old unit. Samples are prepared in 4mm OD, 2.5mm ID, 25 cm long quartz tubes by placing ~0.5 grams of Powhatan No. 5 coal in the bottom of the tube and injecting ~0.5 grams of tetralin or SHD as the solvent. In the naphthalene experiments, coal and naphthalene were premixed and placed in the ESR tube. The tube with the sample was then placed in the high pressure, high temperature cavity and a thermocouple for temperature measurement was imbedded in the upper part of the sample well within the heated zone. Closures were tightened, the system was purged repeatedly with hydrogen and the experiment begun. Typically, several spectra were taken before heating and then continuously from about 4 min. after heating was begun. About 3 min. are needed to reach temperatures in the 400° range without overshooting and another minute is required to tune the spectrometer. Six 100 gauss, 1 min. scans were first recorded then several 8 min., 1000 gauss scans were recorded up to one hour at reaction temperature.

The 1000 gauss scans contain both the coal free radical signal and the signal from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in a capillary on the side wall of the cavity used as a spin concentration standard. The calculations for spin concentration and temperature correction of the spin concentration are outlined in detail elsewhere.^(8,9) After entering the data into a computer system, they are normally displayed as corrected spin concentration versus time plots. All spin concentrations were corrected to 20°C for easy comparison to the spin

concentrations of unheated samples and measurements in the literature. The conditions of these experiments are 3 min. heating time to the desired temperature, H₂ gas at 11.0 MPa (1600 psig), reaction times from 4 min. to 1 hr after beginning heating, Powhatan No. 5 coal, temperatures from 400 to 480°C and tetralin, SHD and naphthalene as solvents. Nearly all experiments were repeated at least once to check reproducibility and to prepare enough material for Soxhlet extraction. Table I summarizes the conditions of each of the experiments.

A Predictive Model for Analysis of the Data

The experimentation in this project has been carried out on the basis of a carefully conceived experimental design that would allow a statistical evaluation of the data. In addition, during the course of the experimentation, the data have been entered into a computer data bank so that the eventual analysis could be effected readily. Now that the earlier-identified most significant variables have been tested more thoroughly, we present the development and utilization of a predictive model that treats not only the data summarized here, but those that were presented in a previous paper.⁽⁶⁾

General Model Development

By means of analysis and modeling, we intend to rank the variable effects and interactions and to quantify the contribution of each variable to the overall spin concentration. From the analysis, a correlation model was developed for the corrected spin concentration depending on the principal experimental variables: temperature, solvent type, gas type, pressure and heating time. Table II summarizes the variables and their levels in the data base. Because the measurements are made for a time sequence, time is also included as an independent variable.

The data were analyzed and the correlation model developed by means of the Statistical Analysis System (SAS) described elsewhere.⁽¹⁰⁾ This package of computer routines is used extensively nationwide for data analysis. Initially a model was developed to include all the independent variables in Table II, either standing alone or embedded in an interactive term.

The following considerations entered into the construction of the model. First, the basic time behavior of the spin concentration is one of exponential growth and decay to an asymptote. Thus, each term in the model must contain a normalized time dependent term which decays to unity at infinite time. The initial spin concentration is dependent only on the coal type and is, therefore, constant. Thus, the model consists of an intercept or initial term which depends on the coal and a series of time dependent terms which are zero initially and are independent of time for long times. The form chosen is the following:

$$\text{time term} = 1 - \exp(-kt)$$

where k may depend on the solvent type and t is elapsed time in minutes.

The shape of the corrected spin concentration versus time curves will depend on the value of k . The data show that k has three different values for the three solvents, 0.2 for heavy distillate, 10 for tetralin and 2 for naphthalene. These coefficients, being nonlinear, were chosen by judgment. The model coefficients for each term and the intercept were obtained by standard multiple regression techniques for linear models.

Fundamental kinetic considerations show that the temperature dependence is of the Arrhenius type, i.e., of the form

$$\text{Temperature term} = \exp(-E/\text{temperature})$$

The temperature coefficient, E, should probably depend on the solvent type, but no such dependence was included in this model.

The solvent and gas variables are so-called class or discrete variables as opposed to the continuous variables, time, temperature, pressure and heating time. This means that the terms involving the discrete variables contains a different coefficient to distinguish the type. This coefficient is then multiplied by the value of the continuous variables to obtain the contribution of that term in the model.

The pressure term was also found to follow an exponential dependence of the form

$$\text{pressure term} = \exp(-k \cdot \text{pressure})$$

because increased pressure reduced the spin concentration.

The heating time dependence was a simple linear term.

The expected interactions included in the model were temperature-pressure, temperature-solvent type, temperature-solvent-gas, temperature-pressure-gas, temperature-heating rate. Other interactions were also included to determine unusual effects.

Each model term is the product of two or more sub-terms involving the independent variables and a linear regression coefficient (C's). Each sub-term has the form described in the previous paragraphs. The model is shown in Table III with the terms ranked in order of decreasing order of statistical significance (vide infra). The statistical significance in this case is defined as the fraction of the model sum of squares contributed by each term separately.

In those experiments with duplicated conditions, the measured spin concentration was found to vary typically by $\pm 20\%$. Examples are shown in

Figures 1-6. The two sets of points are the duplicated experimental measurements, and the solid lines are the predictions of the model. The variation appeared to increase with time or with the level of the corrected spin concentration. Variations are small at short time and for low temperatures, and much higher at long times and higher temperatures. However, out of a maximum value of corrected spin concentration from 30 to 70×10^{18} , typically, this variation represents at least $\pm 20\%$.

Simplified Model

To bring about a more consistent pattern, the data base was modified by averaging the corrected spin concentration for adjacent times for each of the duplicated experiments. Additional experimental data were also entered, and the data base was expanded somewhat. The original data base contained 773 observations. The new averaged data base contained 169 observations. The heating time, gas pressure and gas type were fixed at 3 min, 1600 psig and hydrogen, respectively.

The same model terms were used for this data correlation. However, only five terms (four variable terms + intercept) were needed instead of twelve in the more complete model. This could be deleted with no change in the model predictions. The contribution of the fifth term is very small. The form of each sub-term was also the same as in the more complete model. This simple model is summarized in Table IV (vide infra). Note that solvent alone contributes very little to the model sum of squares. However, temperature-solvent interactions are quite important.

RESULTS AND DISCUSSION

The results of more than 30 experiments are shown in Figures 1 through 6.* Each is a plot of spin concentration (corrected to 20°C) versus elapsed time. The points at $t=0$ are spin concentrations of the unheated slurry and have an average value of about 8×10^{18} spins/g based on the weight of the coal. Any points after $t=0$ are at the desired reaction temperature, i.e., no data were taken during heating between ambient temperature and the desired reaction temperature. Figure 1 shows the results of the series of experiments run at 400°C. The letters used in those plots stand for the solvent used in the experiment, e.g., T for tetralin, N for naphthalene and S for SRC-II heavy distillate. The solid line is the value of the spin concentration for each solvent predicted by the regression model of the data (vide infra). At $t=0$, only the values for naphthalene are printed since the computer program employed (SAS) uses an alphabetical hierarchy to handle overprinting.⁽¹⁰⁾ As can be seen in the figure, the tetralin coal slurry spin concentration is essentially unchanged over more than 30 min. at 400°C compared to the unheated spin concentration. The Powhatan coal and SRC-II slurry radical concentration undergoes a slight rise from the unheated level until its value has about doubled at one hour. The experiments in which naphthalene was used as a solvent show a tripling in the spin concentration after heating with a continued rise until a value of 40×10^{18} spins/g is reached at one hour compared to about 8×10^{18} initially. Tetralin apparently is a very effective solvent for quenching the free radicals formed at 400°C since there is no net change from the free radical concentration in the untreated state. One cannot conclude that only the thermal free radicals are quenched since some of our earlier work shows that some pre-existing free radicals may undergo reactions in tetralin giving an overall reduction in the free radical concentration at temperatures somewhat higher than 400°C compared to the unheated or natural free radical concentration.⁽⁵⁾ Thus, while the

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* See appendix for a complete set of spin concentration vs. time plots for each experiment.

free radical concentration may be the same after heating Powhatan No. 5 coal in tetralin at 400°C for more than 30 min., the radicals themselves may not be the same chemically. Variations in g-values in some coals and coal components treated under similar conditions support this.⁽⁵⁾ SRC-II heavy distillate appears to be less effective than tetralin but better than naphthalene for quenching free radicals.

The results of the free radical concentration measurements made during the liquefaction experiments performed with the three solvents at 425°C are shown in Figure 2. The coal samples liquefied with tetralin exhibit the lowest free radical concentration, about 12 to 15×10^{18} spins/g, and a comparatively small dependence of radical concentration on residence time. The runs in which naphthalene and SHD are used as the solvent had high spin concentrations, about 20 and 30×10^{18} spins/g respectively. Both of these solvents also had a slightly greater time dependence of the free radical concentration compared to the tetralin liquefaction runs.

Figure 3 shows the results of the liquefaction experiments done at 440°C. In these experiments, the free radical concentrations of the Powhatan No. 5 and tetralin reaction mixture was similar to that obtained when SHD was the solvent. The naphthalene solvent liquefaction runs are again the highest in spin concentration at 30 to 35×10^{18} spins/g. The time dependence of the spin concentration is significant with all three solvents, particularly with SHD and naphthalene where it is about 25 to 50%.

At 450°C, the separation in spin concentration between naphthalene and the other two solvents becomes more apparent as is illustrated in Figure 4. Within the first 30 minutes, the tetralin and SHD runs have spin concentrations between 15 and 25×10^{18} spins/g compared to 40 to 60×10^{18} spins/g in the naphthalene experiments. Again, the spin concentrations with all these solvents show an increase with reaction time. This could possibly be due to the formation of radicals over an hour's time which are more stable, possibly more delocalized, than those formed in the initial stages of the reaction. Other possibilities are that the radical species are

the same but the solvent used is not as accessible to those radicals formed later in the reaction as they were in the early stages due to coal liquid products coating the coal particles and/or vaporization of the solvent from the original slurry.

The situation at 460°C is somewhat more complicated as shown in Figure 5. The SHD solvent experiments have the lowest spin concentration, about 15 to 30×10^{18} spins/g, with the tetralin and naphthalene experiments having spin concentrations which are considerably higher, ranging from 25 to 60×10^{18} spins/g, and quite scattered.

At 480°C, the results are somewhat similar to those found at the other temperatures with the exception of those at 460°C. As shown in Figure 6, the liquefaction experiments in which tetralin was used as the solvent have the lowest spin concentration, ranging from about 25×10^{18} spins/g at the beginning of the reaction rising to about 40×10^{18} spins/g at one hour. The SHD and naphthalene runs are much higher in spin concentrations going from 45 to about 90×10^{18} spins/g over the one hour reaction time.

In these six figures, which compare the spin concentrations of Powhatan No. 5 coal liquefied in three different solvents over one hour reaction time, two general trends are evident. At nearly every temperature, the tetralin experiments have the lowest spin concentration and those with naphthalene have the highest. The results of the SHD liquefaction runs are usually in between the spin concentration found in the other two solvents although they sometimes overlap the experimental results of one solvent or the other. This result is satisfying from the standpoint of the hydrogen donor capabilities of the three solvents. It is expected that tetralin should be the best solvent for "capping" free radicals, that naphthalene should be the poorest and SHD intermediate. There is, however, something unique at 460°, since the results do not follow the trend observed at the other temperatures. Not enough is known about the free radical chemistry of model compounds at those temperatures to help account for the variations observed. Nevertheless, the time dependence of the radical concentrations suggests that either more radicals are being made over the course of the reaction than the

solvent can effectively "cap" by hydrogen transfer or that the radical formed later in the liquefaction reaction are of a type that is stable with respect to hydrogen transfer or recombination. The former case could be explained by either solvent depletion at the radical sites or a coating of a relatively insoluble coal product forming on the coal particles. If it is the case of a different type of radical species being formed due to different rates of coal bond breakage at each temperature, then the bonds broken at higher temperatures and longer residence times must be of higher energy and the radicals formed must be more stable than those radicals formed early in the reaction or at lower temperatures. This assumes that solvent is in excess and is readily accessible to the radicals. Further experiments now under way, including g value measurements and studies of model systems in our and other laboratories should help explain these interesting observations.

Figures 7A through 9A are composite figures showing the results obtained for the free radical measurements during Powhatan coal liquefaction in each of the solvents at the six temperatures used, i.e., 400 - 480°C. Figure 7A shows the results of the naphthalene liquefaction experiments. The points are an average of the experimental values. An estimate of the reproducibility can be obtained by comparing duplicate experiments in Figures 1 through 6. In the naphthalene experiments, the free radical concentration rises significantly above the value of the unheated coal at all temperatures, by a factor of 3 to 5 initially and by 4 to 9 at one hour. The data appear to cluster into temperature ranges, with 400, 425 and 440°C in one group, 450, 460°C in another group and 480°C by itself. This grouping is not readily explicable, however, the overall ordering appears to be reasonable in that the highest temperature produces the highest spin concentration and the values decrease with decreasing temperature for any given time. At all temperatures, an increase in spin concentration with time is evident with the rate of increase in spin concentration with time or the slope of the line increasing with increasing temperature. This is expected since higher temperatures should break more bonds faster.

Figure 8A shows the results obtained with SHD at the various temperatures. At 400°C, the spin concentration rises only slightly upon the initial heating and slowly rises to about 18×10^{18} spins/g at one hour. The results for the 425, 440, 450 and 480°C runs are very similar with an initial rise to about 20×10^{18} spins/g and a spin concentration at one hour of about 30 to 40×10^{18} spins/g. A much higher initial and one hour spin concentration is found for the liquefaction runs at 480°C. The initial rise is to 40×10^{18} spins/g with a final value of 75×10^{18} spins/g. Although the clustering of data at the various temperatures is somewhat different from that observed with naphthalene, the basic ordering of temperatures is the same. The runs below 480°C all have rates of increase in spin concentration (slope of the spin concentration versus time plot) which are about 1/3 to 1/2 that of the naphthalene data.

The results of the Powhatan No. 5 tetralin liquefaction runs for all of the temperatures used are shown in Figure 9A. There is a distinct separation and ordering of the time series data for the 400° through 450° runs. The 400°C data are essentially flat; no rise over the unheated spin concentration and no increase in spin concentration as a function of time. The 425, 440 and 450°C data show some initial increase in spin concentration with heating but are much flatter in slope than the naphthalene or SHD experimental data. The 460°C data shows a much higher spin concentration than that found at 480°C. Some data at 470°C with tetralin exists and the values for the spin concentration from these runs falls in between the 460 and 480°C run values. This is, the maximum value of the spin concentration of Powhatan No. 5 coal in tetralin appears to be around 460°C, although a few more data must be obtained in the 450 to 470°C range to find, conclusively, the exact temperature of maximum spin concentrations in this system.

Discussion of Model Results

The overall fit of the models to the experimental data is best illustrated by means of parity or so-called scatter plots as shown in Figures 10 and 11. A perfect fit to the data would appear as a straight line

with a slope of 45° and with all points superimposed. One measure of fit is the width of the spread of the points about the center line. In the case of the general model (Figure 10), the spread of the points is about $\pm 15 \times 10^{18}$ spins/g which is less than twice the standard deviation of the measured data of 10×10^{18} spins/g. For the simplified model all the points also occur within 15×10^{18} spin/g while the standard deviation of this data set is about 7×10^{18} spins/g. Clearly, most of the points fall within the typical precision of ESR absolute intensity measurements of $\pm 20\%$.

There is a slight bias to predict values lower than those measured for the general model as shown by the difference in scales in Figure 10. Just the reverse can be said for the predictions of the simpler model. However, there appears to be no serious biases in either model.

Figures 10 and 11 also show that the data are fairly uniformly distributed over the range from 8 to 80×10^{18} spins/g. Figure 10 shows a cluster of values above 100×10^{18} spins/g. These come from runs in naphthalene solvent at low hydrogen gas pressure. However, the model adequately predicts those points as well.

The picture that emerges from the use of the the general model is summarized in Table III. The terms in the model are shown on the left. The C's are the linear regression coefficients. Each term such as time, temperature, etc., has the form described in the previous section.

To the right of each term is the type I sum of squares contribution. Below is the total model sum of squares and the total sum of squares in the data. The sum of squares attributed to error is the difference between these. The second column is the fractional contribution of the sum of squares of each term. One can see that the first three terms involving only time, temperature, solvent type and a solvent-gas interaction contribute most to the

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* Type I sum of squares means the contribution to the model sum of squares when entering each term first.

model predictions and that the effect of the last three variables, gas type, gas pressure and heating time, are small. All terms were found to be statistically significant at greater than 95% probability except the last two terms. The fractional probabilities are shown in the rightmost column. The probabilities shown are for the so-called null hypothesis, i.e., that the term is not significant. Thus, the smaller the number, the larger the probability that the term is different from zero. A completely insignificant term has a theoretical fractional probability of 1. The coefficients in the model are generally weighted by or related to the sum of squares contributions. Thus, the last seven terms could be deleted from the model and only slightly reduce the predictability of the model.

The temperature term alone explains nearly 50% of the variation in the data, as shown by the fraction contribution to the sum of squares of 0.5. The solvent and temperature interaction term explains about 20%, and the solvent temperature-gas interaction term explains another 20%. The gas term alone contributes very little, and the heating rate, pressure, gas interactions even with temperature have essentially negligible effects.

Because three of the variables in the data were found to be much less important, primary emphasis was placed on the effects of solvent and temperature. As mentioned previously, the data base was expanded to include six temperature and three solvent levels. For modeling purposes, the values of duplicate runs were averaged to give a single time series for each condition. Values of heating time, gas pressure and gas type were fixed. These effects are quantified in the simplified model summarized in Table IV. The simple model consists of five terms involving time, temperature and solvent type with each term weighted by the linear regression coefficient. The sum of squares, fractional sum of squares contributions and fractional probabilities are shown. These indicate that temperature and temperature-solvent interactions are of primary importance and that time and solvent type by themselves are much less important.

The coefficients of the temperature-solvent interaction term and the solvent term specific for each solvent are also indicated. These coefficients shown in Table V, indicate the weighting given to each solvent. For example, the coefficient of the solvent term is about 20 for naphthalene and 0 for tetralin while the value for heavy distillate, 2, is close to that for tetralin. This indicates that the solvent effect for heavy distillate is close to that for tetralin while naphthalene gives rise to a higher spin concentration by at least $18-20 \times 10^{18}$ spin/g.

The solvent-temperature interaction coefficients are also weighted heavily for naphthalene and heavy distillate while that for tetralin is 0. In this case, the coefficient for heavy distillate is higher than that for naphthalene indicating a somewhat stronger temperature dependence for this solvent. This effect is discussed later. However, the net effect of the solvent is to place heavy distillate close to tetralin.

Figures 1-6 show the predicted and experimental results at each of the temperature levels for the three solvents. The predictions compare remarkably well with the measured values. These figures show that variations in measured values are typically $\pm 20\%$. They also show that naphthalene always produces the highest spin concentration followed by heavy distillate and then tetralin. The spin concentrations increase with temperature and the increase is greatest with heavy distillate. The only major and unexpected difference between the predicted and measured values is with tetralin at 460°C where there is a marked increase in spin concentration over the levels at 450°C and 480°C . The model predicts an intermediate level at 460°C . There is no explanation for this abrupt increase at this time but the effect is reproducible. These results indicate that tetralin is better at quenching or stabilizing the free radicals by more efficient hydrogen transfer and that SRC-II heavy distillate is close to tetralin in this regard.

Figures 7a and b through 9 a through b show the measured and predicted values for the three solvents at the six temperature levels in each. These figures again show the stronger effect of temperature on heavy distillate. The effect is less for tetralin and least for naphthalene.

The temperature dependence is further illustrated by Figure 12 which shows the plot of the natural log of spin concentration/ 10^{18} versus inverse absolute temperature. The three lines refer to the three solvents. Each line is obtained by averaging the values at each temperature level. The slopes are an indication of the difference in activation energies for the production reaction which increases spin concentration and the quenching reaction which reduces this value. Because the forward reactions are probably not dependent on solvent type but are primarily influenced by the thermal decomposition of the coal, these reactions should have the same temperature dependence or activation energies regardless of solvent. Therefore, the differences shown are probably due to the solvent-dependent quench reactions which show that heavy distillate has a somewhat higher activation energy in this regard. These kinetic effects can best be quantified by means of nonlinear regression analysis and development of fundamental intrinsic kinetics models. These will be addressed in a future paper.

CONCLUSIONS

From the analysis of the data, several conclusions can be made concerning the behavior of the free radical concentration for Powhatan #5 coal during liquefaction in a batch reactor operated under pressure:

1. In general, the coal free radicals are quenched in following the order of naphthalene < SHD < tetralin. The free radical concentration in the coal liquefied in SHD was closer to the tetralin experiments than the naphthalene runs. 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 also. 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. Therefore, the rate of quenching by

SRC heavy distillate is closer to that of tetralin at lower temperature and approaches that of naphthalene at the higher temperature. In future work, it is hoped to quantitatively delineate this behavior.

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 concentrations 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.

5. The correlative model predicts the experimental results within the reproducibility of the data. There are some conditions for which the model does not predict the free radical concentration, however, these data do not follow the general trends in the data noted in the other conclusions above.

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TABLE I
SUMMARY OF EXPERIMENTAL CONDITIONS*

<u>Experiment Number</u>	<u>Solvent</u>	<u>Temperature°C</u>
04-31-1E	Tet	400
05-21-1E	Tet	460
05-28-1E	Tet	460
07-21-1E	Nap	460
07-24-1E	Nap	460
07-28-1E	SHD	460
07-30-1E	SHD	460
08-12-1E	SHD	460
08-14-1E	SHD	400
09-19-1E	Nap	425
09-24-1E	Nap	440
09-26-1E	Nap	480
09-30-1E	Tet	425
10-01-1E	Tet	440
10-15-1E	Nap	425
10-17-1E	Nap	440
10-18-1E	Nap	480
10-22-1E	Tet	425
10-23-1E	Tet	440
10-24-1E	Tet	480
11-07-1E	SHD	450
11-11-1E	SHD	450
11-12-1E	Tet	450
11-14-1E	Tet	450
11-15-1E	Nap	400
11-18-1E	Nap	400
11-19-1E	Nap	450
11-21-1E	Nap	450
12-15-1E	Nap	460
12-16-1E	Nap	460
13-15-1E	SHD	440
13-17-1E	SHD	440
13-20-1E	SHD	480
13-21-1E	SHD	480
14-19-1E	SHD	425
14-19-2E	SHD	425

* 3 min heating time, H₂ gas at 1600 psig for all experiments.

TABLE II.
MODEL VARIABLES

<u>Independent (Continuous)</u>	<u>Range or Level</u>
Time	0-60 minutes
Temperature	400-480°C
Pressure	1200 and 1600 psig
Heating Time	3 and 15 minutes
 Level or Class Variables:	
Solvent	Naphthalene Tetralin SRC-II Heavy Distillate
Gas	Hydrogen Nitrogen
Dependent: Corrected Spin Concentration	8-140 spins/g coal x 10 ¹⁸

TABLE III

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 .007	.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.

TABLE IV

SIMPLIFIED MODEL

<u>Variables Effects*</u>	<u>Sum of Squares</u>	<u>Fractional Contribution</u>	<u>Probability of** Null Hypothesis</u>
C ₁ •time•temperature	22024	.58	.0001
C ₂ •time•temperature solvent	12092	.32	.0001
C ₃ •time•solvent	3783	.10	.0001
C ₄ •time	230	~0	.0503

Total Model Sum of Squares	38130
Total Data Sum of Squares	47737
Error	9606
R ²	.80
Total Number of Data Points	168

* Corrected Spin Concentration = Intercept + Sum of Terms.

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

TABLE V

COEFFICIENTS FOR SIMPLIFIED MODEL

		<u>Coefficient Value</u>
Intercept		10.4
C ₁		3198.1
C ₂	naphthalene	1143.7
	heavy distillate	1769.6
	tetralin	0
C ₃	naphthalene	19.8
	heavy distillate	2.3
	tetralin	0
C ₄		1.85

ACKNOWLEDGMENT

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Figure 1

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

Figure 2

SPIN CONCENTRATION VS. ELAPSED TIME
POWHATAN #5 COAL, 1600 psig H₂, 425 °C 3 min HT.

Figure 3

SPIN CONCENTRATION VS. ELAPSED TIME
POWHATAN #5 COAL, 1600 psig H₂, 440 °C 3 min HT.

Figure 4

SPIN CONCENTRATION VS. ELAPSED TIME
POWHATAN #5 COAL, 1600 psig H₂, 450 °C 3 min HT.

Figure 5

SPIN CONCENTRATION VS. ELAPSED TIME
POWHATAN #5 COAL, 1600 psig, 460 °C 3 min HT.

Figure 6

SPIN CONCENTRATION VS. ELAPSED TIME
POWHATAN #5 COAL, 1600 psig, 480 °C 3 min HT.

SPIN CONCENTRATION VERSUS ELAPSED TIME
POWHATAN #5 COAL AND NAPHTHALENE
1600 psig (11.0 MPa) H₂ 3 min HT
AVERAGE VALUES

Figure 7B

PREDICTED SPIN CONCENTRATION VS. ELAPSED TIME
POWHATAN #5 AND NAPHTHALENE

SPIN CONCENTRATION VERSUS ELAPSED TIME
POWHATAN #5 COAL AND SRC II HEAVY DISTILLATE
1600 psig (11.0 MPa) H₂ 3 min HT
AVERAGE VALUES

Figure 8A

Figure 8B

PREDICTED SPIN CONCENTRATION VS. ELAPSED TIME POWHATAN #5 AND SHD

SPIN CONCENTRATION VERSUS ELAPSED TIME
POWHATAN #5 COAL AND TETRALIN
1600 psig (11.0 MPa) H₂ 3 min HT
AVERAGE VALUES

Figure 9A

Figure 9B

PREDICTED SPIN CONCENTRATION VS. ELAPSED TIME POWHATAN #5 AND TETRALIN

Figure 10

PREDICTED SPIN CONCENTRATION VS. ELAPSED TIME GENERAL MODEL RESULTS

Figure 11

PREDICTED SPIN CONCENTRATION VS. ELAPSED TIME SIMPLIFIED MODEL RESULTS

Figure 12

NATURAL LOG OF SPIN CONCENTRATION VS. INVERSE ABSOLUTE TEMPERATURE

APPENDIX

EXPERIMENTAL PLOTS OF SPIN CONCENTRATION VS ELAPSED TIME

See Table I for Experimental Conditions

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=07-21-1E

65

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=07-24-1E

66

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=09-19-1E

87

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME EXPNUM=09-24-1E

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=09-26-1E

89

NOTE: 3 OBS HIDDEN

NOTE: 3 OBS. HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=10-17-1E

94

ELAPSED TIME HOURS

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=10-18-1E

95

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=11-15-1E

105

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=11-18-1E

106

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=11-19-1E

107

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=11-21-1E

100

NOTE: 2 OBS. HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=12-15-1E

111

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=12-16-1E

112

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=07-28-1E

67

NOTE: 3 ORS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=07-30-1E

68

NOTE: 2 OBS. HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=08-12-1E

71

NOTE: 2.OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=08-14-1E

73

NOTE: 1 OBS HAD MISSING VALUES OR WERE OUT OF RANGE 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=11-07-1E

101

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=11-11-1E

102

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=13-15-1E

114

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=13-17-1E

115

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=13-20-1E

116

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=13-21-1E

117

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=14-19-1E

118

NOTE: 2 ORS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=14-19-2E

119

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=04-31-1E

40

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=05-21-1E

45

NOTE: 4 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=05-28-1E

48

NOTE: 5 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=09-30-1E

90

NOTE: 3 OBS. HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=10-01-1E

91

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=10-02-1E

92

NOTE: 3 OBS HIDDEN

REC165

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=10-22-1E

96

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=10-23-1E

97

NOTE: 2 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=10-24-1E

98

NOTE: 3 OBS HIDDEN

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=11-12-1E

103

CORRECTED SPIN CONCENTRATION VS. ELAPSED TIME
EXPNUM=11-14-1E

104

NOTE: 3 OBS HIDDEN

PREDICTED AND EXPERIMENTAL SPIN CONCENTRATION VS ELAPSED TIME PLOTS

SOLVENTS

- 1 = NAPHTHALENE
- 2 = SHD
- 3 = TETRALIN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=1 REACTION TEMP DEG C=400

9:03 MONDAY, JANUARY 5, 1981 26

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C*CON*ETIME SYMBOL USED IS E

NOTE: 63 OBS HAD MISSING VALUES

STATISTICAL ANALYSIS SYSTEM
SOLVENT=1 REACTION TEMP DEG C=425

9:03 MONDAY, JANUARY 5, 1981 27

PLOT OF PRAD+ETINE SYMBOL USED IS P
PLOT OF CSCON+ETINE SYMBOL USED IS E

NOTE: 51 OBS HAD MISSING VALUES

STATISTICAL ANALYSIS SYSTEM
SOLVENT=1 REACTION TEMP DEG C=440

9:03 MONDAY, JANUARY 5, 1981 28

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C*CON*ETIME SYMBOL USED IS E

NOTE: 53 OBS HAD MISSING VALUES

STATISTICAL ANALYSIS SYSTEM
SOLVENT=1 REACTION TEMP DEG C=450

9:03 MONDAY, JANUARY 5, 1981 29

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C*CON*ETIME SYMBOL USED IS E

NOTE: 53 OBS HAD MISSING VALUES 1 OBS HIDDEN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=1 REACTION TEMP DEG C=460

9:03 MONDAY, JANUARY 5, 1981 30

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C\$CON*ETIME SYMBOL USED IS E

NOTE: 55 OBS HAD MISSING VALUES

1 OBS HIDDEN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=1 REACTION TEMP DEG C=480

9:03 MONDAY, JANUARY 5, 1981 31

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C\$CON*ETIME SYMBOL USED IS E

NOTE: 24 OBS HAD MISSING VALUES 1 OBS HIDDEN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=2 REACTION TEMP DEG C=400

9:03 MONDAY, JANUARY 5, 1981 32

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C\$CON*ETIME SYMBOL USED IS E

NOTE: 57 OBS HAD MISSING VALUES

STATISTICAL ANALYSIS SYSTEM
SOLVENT=2 REACTION TEMP DEG C=425

9:03 MONDAY, JANUARY 6, 1981 33

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C*CON*ETIME SYMBOL USED IS E

STATISTICAL ANALYSIS SYSTEM
SOLVENT=2 REACTION TEMP DEG C=440

9:03 MONDAY, JANUARY 6, 1981 34

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C*CON*ETIME SYMBOL USED IS E

NOTE: 51 OBS HAD MISSING VALUES

STATISTICAL ANALYSIS SYSTEM
SOLVENT=2 REACTION TEMP DEG C=450

9:03 MONDAY, JANUARY 5, 1981 35

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C\$CON*ETIME SYMBOL USED IS E

NOTE: 55 OBS HAD MISSING VALUES 3 OBS HIDDEN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=2 REACTION TEMP DEG C=460

9:03 MONDAY, JANUARY 5, 1981 36

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C\$CON*ETIME SYMBOL USED IS E

NOTE: 17 OBS HAD MISSING VALUES

STATISTICAL ANALYSIS SYSTEM
SOLVENT=2 REACTION TEMP DEG C=480

9:03 MONDAY, JANUARY 5, 1981 37

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C*CON*ETIME SYMBOL USED IS E

NOTE: 54 OBS HAD MISSING VALUES

9:03 MONDAY, JANUARY 5, 1981 38

9:03 MONDAY, JANUARY 5, 1981 38

NOTE: 25 OBS HAD MISSING VALUES

STATISTICAL ANALYSIS SYSTEM
SOLVENT=3 REACTION TEMP DEG C=425

9:03 MONDAY, JANUARY 5, 1981 39

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C\$CON*ETIME SYMBOL USED IS E

STATISTICAL ANALYSIS SYSTEM
SOLVENT=3 REACTION TEMP DEG C=440

9:03 MONDAY, JANUARY 5, 1981 40

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C\$CON*ETIME SYMBOL USED IS E

STATISTICAL ANALYSIS SYSTEM
SOLVENT=3 REACTION TEMP DEG C=450

9:03 MONDAY, JANUARY 5, 1981 41

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF CSCON*ETIME SYMBOL USED IS E

NOTE: 56 OBS HAD MISSING VALUES 2 OBS HIDDEN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=3 REACTION TEMP DEG C=460

9:03 MONDAY, JANUARY 5, 1981 42

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF C*CON*ETIME SYMBOL USED IS E

NOTE: 32 OBS HAD MISSING VALUES

STATISTICAL ANALYSIS SYSTEM
SOLVENT=3 REACTION TEMP DEG C=480

9:03 MONDAY, JANUARY 5, 1981 43

PLOT OF PRAD*ETIME SYMBOL USED IS P
PLOT OF CSCON*ETIME SYMBOL USED IS E

NOTE: 54 OBS HAD MISSING VALUES 1 OBS HIDDEN

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EXPERIMENTAL AND PREDICTED SPIN CONCENTRATION VS REACTION TEMPERATURE

SOLVENTS:

- 1 = NAPHTHALENE
- 2 = SHD
- 3 = TETRALIN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=1

9:03 MONDAY, JANUARY 5, 1981 68

PLOT OF C\$CON*DTMP SYMBOL USED IS E
PLOT OF PRAD*DTMP SYMBOL USED IS P

OTE: 8 OBS HAD MISSING VALUES 7 OBS HIDDEN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=2

9:03 MONDAY, JANUARY 5, 1981 69

PLOT OF CSDON*DTMP
PLOT OF PRAD*DTMP

SYMBOL USED IS E
SYMBOL USED IS P

NOTE: 12 OBS HAD MISSING VALUES 15 OBS HIDDEN

STATISTICAL ANALYSIS SYSTEM
SOLVENT=3

9:03 MONDAY, JANUARY 5, 1981 70

PLOT OF C\$CON*OTEMP SYMBOL USED IS E
PLOT OF PRAD*OTEMP SYMBOL USED IS P

NOTE: 11 OBS HAD MISSING VALUES 20 OBS HIDDEN