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FUNDAMENTALS OF COAL DEPOLYMERIZATION: METHODOLOGY FOR
THE IN-SITU INVESTIGATION OF FREE RADICALS IN COAL
DEPOLYMERIZATION UNDER SRC-II PREHEATER/REACTOR CONDITIONS

Quarterly Report for October 1—December 31, 1979

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January 1980

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Gulf Research & Development Company
Pittsburgh, Pennsylvania

MASTER

U. S. DEPARTMENT OF ENERGY

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A Quarterly Report for the Period
October 1 - December 31, 1979

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I. SUMMARY

The overall scope of this project is to monitor the free radicals during coal depolymerization under SRC-II preheater/reactor conditions. Understanding the nature and behavior of the free radicals may not only provide significant mechanistic information for the depolymerization of coal, but it could also impact the design of coal liquefaction processes. Our uniquely designed apparatus will allow us to monitor free radicals and how they are affected by, among others, short residence times, temperature and pressure changes.

This first quarterly report summarizes the work that was done under Task I of the title contract for the period covering October 1 to December 31, 1979. All components of Task I have been completed successfully. Specifically, an experimental design for Task II (screening of main process variables) has been developed; a detailed experimental procedure for obtaining data at high pressures and high temperatures has been developed; and the scheme to separate reacted coal has been outlined and tested. As part of the special cavity testing and development of experimental procedure it was determined that data can be obtained 3-4 minutes after the initiation of the heating process to achieve a high temperature (450°C). Thus, we expect that we will be able to gain significant information on free radical formation and behavior within the first several minutes of subjecting coal to high temperatures and pressures. The free radical concentration can be measured to $\pm 20\%$, while preliminary results indicate that some of the process variables may cause several-fold changes in the free radicals. A new Varian Associates instrument has been purchased by Gulf S&T Co to carry out this work. The next phase of the work will involve the investigation of temperature and pressure effects, heating rate changes, short residence times and the use of process derived solvent.

II. INTRODUCTION

Much effort is being expended in the development of several processes for the conversion of coal to environmentally clean products. Many of these processes have several common elements in that they involve depolymerization of coal, stabilization of the lower molecular weight chemical moieties through hydrogen abstraction, and the presence of mineral matter and/or added catalyst in the coal/solvent slurry that is being reacted.

The work being performed under this contract is geared to the understanding of fundamentals of coal depolymerization during the dissolution stage of direct coal hydroliquefaction processes and especially the Solvent Refined Coal (SRC-II) process. The study is centered on the in situ investigation of free radical formation and quenching through the utilization of a uniquely designed and built high-temperature and high-pressure Electron Spin Resonance (ESR) cavity-reactor. In addition, the work utilizes the extensive analytical capability available at our Laboratory for detailed characterization of the feeds and products. This approach seeks to develop novel and unique information for the fundamental understanding of the chemical and physical phenomena associated with dissolution of coal in the SRC-II preheater/reactor. The clearer understanding of the dissolution of coal will lead, hopefully, to even more efficient hydroliquefaction process.

In this first report, we discuss the methodology that will be used in the study, including the testing of the ESR cavity, the detailed experimental procedure for ESR measurements, the proposed analyses of the products and the experimental design for investigating the effects of the main process variables.

III. COMPLETION OF TASK I

A. Experimental Procedures for ESR Investigations

1. Testing of High Pressure/High Temperature Cavity

The testing of the high temperature, high pressure cavity proceeded step wise from initial microwave testing at room temperature and pressure to operation at near-maximum temperature and pressure conditions. Operation of the cavity at ambient conditions was continued until we had gained sufficient experience with the new cavity and its tuning characteristics. Room temperature ESR runs at 11.71 MPa (1700 psi)* N₂ proceeded without incident; however, a 2% shift to lower microwave frequency was noted on pressurizing the cavity. This is due to an increase in the dielectric constant of the filling medium. High temperature experiments at atmospheric pressure were attempted next. Spectra were obtained at 450°C, however, the noise level in the signal, due to the AC heater source, was unacceptably high. The use of auto batteries corrected the noise problem and good spectra were obtained using an Illinois #6 fusinite sample at 370°C using 50 watts of heater power. In initial experiments with combined elevated temperature and pressure, a very strong effect of cavity pressure on sample temperature was found. Using 50 watts of heater power, sample temperatures obtainable were 370°C at atm. pressure, 285°C at 3.44 MPa (500 psi) H₂ and 211°C at 6.89 MPa (1000 psi). When two 12-volt batteries were connected in series, 180 watts were available for sample heating. 511°C was obtained at 7.44 MPa (1080 psi) and 440°C at 9.71 MPa (1410 psi). At these higher temperatures and pressures, the uncooled pressure vessel lid began to warm noticeably. A quartz heat shield and quartz wool insulation were added, minimizing heat transfer to uncooled areas of the vessel. Using a commercial, regulated, DC power supply, 495°C was reached at 11.23 MPa (1630 psi)* N₂ using 230 watts of heater power. We point out at this stage that this cavity does not allow for shaking or mechanically mixing

* 6.89 MPa = 1000 psi

the coal in the ESR cavity. Some mixing must take place as gases are evolved during heating. We plan to investigate this question in a later time when we compare ESR and shaken autoclave experiments.

2. Sample Preparation

Samples are prepared for ESR measurements by placing 0.3 g of coal in a quartz 4 mm OD, 2.5 mm ID ESR tube (Fig. 1). This quantity of material fills the tube to a length of 7.5 cm, extending through both ends of the cylindrical cavity but not outside the heater. The coal used in Tasks I and that which will be used in Task II is Powhatan #5. This coal was chosen because it has been used extensively in the Gulf P-99 SRC-II reactor and the Pittsburg and Midway SRC-II pilot plant. This coal is also being considered as the feed coal for the proposed 6000 ton/day SRC-II demonstration plant. The sample of Powhatan #5 used in this work has a size distribution of 13% >75 μ m; 33% >45 μ m, <75 μ m, 29% >20 μ m, <45 μ m and 25% <20 μ m. The pertinent analytical data on this coal sample are shown in Table I. The thermocouple used for temperature measurement is imbedded in the sample in the heated zone, about 2-3 mm outside the microwave cavity. When the coal is to be run with a solvent, a very thin capillary tube is placed in the bottom of the ESR tube and the coal is poured in around the capillary. The desired amount of the solvent is then forced through the capillary, which is later removed. After the coal and solvent have been placed in the tube, it is placed into the heater assembly in the cavity. Figure I is a schematic drawing showing the components of the reactor vessel, ESR cavity and the sample location. The thermocouple is inserted into the sample and all closures are tightened. The sample and cavity are then ready for operation.

3. Room Temperature/Baseline Measurement

Baseline measurements on unheated samples are done before each heated run. Samples are prepared as described in the section on sample preparation. Absolute spin concentration determinations are made for each

sample. An internal standard of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powder sealed in a quartz capillary is taped to the inside wall of the cylindrical cavity. This wall is water cooled, preventing the destruction of the standard. The standard is calibrated by use of a stable char that has had its spin concentration measured relative to a solution of DPPH in benzene. Calibration of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ reference is necessary due to its location, the effective microwave field and modulation field at the wall being different from that at the axis of the cavity. The ESR spectrum of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and the char or coal sample are obtained on a single 1000 gauss scan. The spin concentration of the sample is calculated from the following equation:

$$\text{spin conc. sample} = \frac{A_{\text{sample}} \times \text{No. spins std} \times A_{\text{Cu std}}}{A_{\text{std}} \times A_{\text{Cu sample}} \times \text{wt. sample}}$$

where A_{sample} = Area under the sample peak

A_{std} = Area under the standard char peak

$A_{\text{Cu std}}$ = Area under the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ peak in the standard spectrum

$A_{\text{Cu sample}}$ = Area under the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ peak in the sample spectrum

A single char standard/ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ spectrum can be used to calculate many experimental spectra. However, after several experiments, the integrity of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ internal standard is checked by running it against the char standard and comparing peak areas. An alternative method is to check for systematic variations in the spin concentration of the unheated coal which is obtained in each experiment. Significant changes in the coal spin concentration, particularly an increase, would suggest deterioration of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ standard.

When narrower scans (100 gauss) are used to obtain larger, detailed spectra, the spin concentration of the coal sample must be calculated by indirect methods since the scan width is not sufficient to include the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ standard signal. This is done by comparing the area under the coal signal in the 100 gauss scan to that obtained in a 1000 gauss scan in which the concentration of spins has been calculated from the internal standard.

The scaling factor, 10 in this case, must be applied to the area of the 100 gauss scan, and the 1000 gauss scan and the 100 gauss scan must have been run sequentially under the same spectrometer settings.

The spin concentration of the unheated Powhatan #5 coal was obtained in each of the seven experiments. Both pure coal and coal/solvent mixtures were run. The sample descriptions are tabulated in Table II. Table III is a listing of the results obtained for 10 min, 1000 gauss scans and 1 and 2.5 min, 100 gauss scans. Earlier measurements on this coal using a commercial dual cavity and the same char standard gave an average spin concentration of 10.2×10^{18} spins/g. As a result of these findings, we conclude that we will be able to monitor free radicals during the first 10-15 minutes of the reaction.

4. Heating Rates

Sample heating rates are changed by varying the amount of time from initial power input to final equilibrium power. The most rapid heating is done by applying the predetermined equilibrium power for any particular temperature and pressure from the beginning. To reach 450°C, at 10.34 MPa, 240 watts are required. When this power is initially applied, ~370°C is reached in ~1 min. Within 2 min, the sample is within 10°C of the final temperature. Equilibration to the final temperature and pressure is usually complete after a total heating time of 3 min and the spectrometer can then be tuned and the automatic frequency control for the Klystron can be locked on. The shortest time from the beginning of heating until data can be taken is about 3.5 to 4 min or about 1 min after equilibrium temperature is achieved. Using heater power in excess of that needed for maintaining the final temperature was considered to obtain faster heating rates but temperature control to avoid over shooting the desired temperature is extremely difficult and such excessive currents would probably cause the 26 gauge heater wires to fail.

Slower heating rates of any degree can be achieved. We have arbitrarily used a procedure of increasing voltage at 2 V/min, reaching 450°C

in 15 min. Both this heating and the more rapid heating are nonlinear. Heating uniformity is believed to be reasonably good since the sample is heated over its entire length, which is more than the length of the cavity, by four quartz enclosed heater wires placed at 90° intervals around the tube axis. Thus, on the basis of these experiments, we expect that we will be able to obtain data within approximately 4 minutes after initiating the heating process. Table IV summarizes some typical data for rapid and slow heating.

5. In Situ Heating Experiments and Determination of Free Radical Concentration

In the in situ heating experiments, both pure coal and coal/solvent mixtures were used. The sample descriptions and the number of scans recorded before, during, and after heating are listed in Table II. The sample preparation is described in a separate section. Absolute spin concentration measurements were made relative to a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ standard described in the section on baseline measurements. However, there are some differences in the methods used to calculate the spin concentrations. During heating and after heating to 450°C, the signal intensity grew so much that the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ signal and the coal signal had to be run at different gain and modulation settings. These changes were made mid-scan. A different equation must be used in the spin concentration calculation when the spectrometer settings are different for the unknown sample and the standard. The equation in the baseline measurements section is a specific case of the more general equation given below.

$$\text{Spin conc of sample} = \frac{(\text{No spins std})(A_{\text{sample}})(A_{\text{Cu std}})(G_{\text{std}})(M_{\text{sta}})(G_{\text{Cu sample}})(M_{\text{Cu sample}})}{(A_{\text{std}})(A_{\text{Cu sample}})(\text{wt sample})(G_{\text{sample}})(M_{\text{sample}})(G_{\text{Cu std}})(M_{\text{Cu std}})}$$

where:

A_{sample} = Area under the sample peak

A_{std} = Area under the char standard peak

$A_{\text{Cu std}}$ = Area under the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ peak in the standard spectrum

$A_{\text{Cu sample}}$ = Area under the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ peak in the sample spectrum

G_{std}	=	Gain in the char standard spectrum
M_{std}	=	Modulation in the char standard spectrum
$G_{Cu \text{ sample}}$	=	Gain in the $CuSO_4 \cdot 5H_2O$ spectrum in the sample run
$M_{Cu \text{ sample}}$	=	Modulation in the $CuSO_4 \cdot 5H_2O$ spectrum in the sample run
G_{sample}	=	Gain in the sample spectrum
$G_{Cu \text{ std}}$	=	Gain of the $CuSO_4 \cdot 5H_2O$ spectrum in the char standard run
$M_{Cu \text{ std}}$	=	Modulation of $CuSO_4 \cdot 5H_2O$ spectrum in the char standard run
No. spin std	=	Number of spins in the char standard
wt sample	=	Weight of coal in the sample

At high temperatures, a correction in the spin concentration must be made for the different Boltzmann distribution in the electron spin states. Signal intensity is proportional to the difference in spin populations in the upper (α) and lower (β) Zeeman levels. At any temperature, the ratio of spin populations is given by:

$$\frac{N_{\alpha}}{N_{\beta}} = e^{\frac{-\Delta E}{KT}}$$

For $\Delta E = h\nu$, where ν is 9 GHz and T is 298°K, N_{α}/N_{β} is 0.99855 or a population difference of 1450 ppm. At 450°C or 723°K, $N_{\alpha}/N_{\beta} = 0.99940$, giving a population difference of 600 ppm. To compare spin concentration measurements at 450°C with those made at room temperature, we multiply the high temperature spin concentration by the ratio of the spin population differences at the two temperatures, which is 2.4.

The results of seven in situ heating experiments are shown in Table V. The spin concentrations at 450°C are corrected to 25°C. In all cases, heating to 450°C caused a 7-10 fold spin concentration increase. On cooling to room temperature, spin concentrations are, in general, the same as at the high temperature. They are higher and lower in some duplicate runs, reflecting the scatter in the data. Figures 2-5 are spin concentration vs time from initiation of heating for Powhatan #5 coal at 10.34 MPa H_2 and rapid (<3 min to 450°) heating, with and without solvents. In all cases, most of

the free radical formation has taken place before the initial measurement. This would indicate, at least at 450°C that free radical formation occurs rapidly. As can be seen from these figures, some additional radical formation takes place over a 20-30 minute period after the final temperature is reached. Experiments at somewhat lower temperatures (375 to 425°) may yield more detail on the rate of radical formation.

Figure 6 is a composite of three experiments in which Powhatan #5 coal was run without solvent, with tetralin, and with naphthalene, all heated to the same temperature, at the same rate, with 10.34 MPa H₂. Coal heated with naphthalene has the highest spin concentration, followed by that run in tetralin and the coal only run.

Table VI lists the results of experiments in which the coal sample was heated from room temperature to 450°C for a second time. The values obtained at 450°C are not different from those found on the first heating. Room temperature spin concentrations after the second heating are similar to those measured after the first heating.

6. Standard Experimental Procedure to be Used in Subsequent Runs of Tasks II and III

As a result of experimentation described above, the following experimental procedure has been decided upon for Tasks II and III of the project.

Coal and coal/solvent mixture samples are to be prepared as described in the sample preparation section. A 10-minute, 1000 gauss scan will be recorded at room temperature and the pressure to be used at high temperature. This spectrum gives baseline data on the unheated coal and is a check on the integrity of the CuSO₄·5H₂O standard which will be used to determine the absolute concentrations of the coal free radicals. Calculation of spin concentration will be as in the baseline measurement section.

Sample heating will normally be at the rapid (<3 min) or slow (15 min) rate as described in the sample heating rate section. As soon as the cavity pressure and temperature are stable enough to tune the spectrometer,

short time (1 or 2.5 min) scans using a 100 gauss sweepwidth will be recorded until the peak height is relatively constant. A 10-min, 1000 gauss scan recording both the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and coal signal should be recorded. The previous 100 gauss scan is assigned the spin concentration calculated from the 1000 gauss scan and the other 100 gauss scans calculated relative to that by simple proportionality. A 1000 gauss, 10-min scan spectrum of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ standard and the sample at room temperature is then taken. Additional 100 gauss or narrower scans may be recorded to measure g values or line-widths. A check of the spin concentration of the next unheated coal sample may be used to confirm the assumption that the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ sample has not been affected by the heating experiment. All calculations and corrections are outlined in the sections on baseline measurements and in situ heating experiments.

B. Analysis of Reactor Products

1. Background Information for the Separations Scheme

In order to gain maximum information from the depolymerization studies of this project, a detailed scheme for the analysis of the products is contemplated. Many analytical schemes are described in the literature on coal liquefaction. All of the schemes attempt to quantify a number of dependent variables (i) that can be useful in describing the coal liquefaction reactions, and (ii) that can be easily measured.

The most common dependent variables are the following coal liquid fractions:

- Oils
- Asphaltenes
- Preasphaltenes
- Unreacted Coal

These fractions are usually defined on the basis of their solubility in certain solvents. However, the solvents and the procedures used by the

various investigators vary. In our laboratory and for DOE-related work, the following standard definitions have been used (1):

Oils = n-pentane solubles

Asphaltenes = n-pentane insolubles, benzene solubles

Preasphaltenes = benzene insolubles, pyridine solubles

Unconverted Coal = pyridine insolubles

Neavel (2) used a similar definition, but others define these fractions on the basis of their solubility in different solvents. Thus, the unconverted coal is defined as benzene insolubles by Weller et al. (3) and Hill et al. (4); as xylene insolubles by Curran et al. (5) and tetrahydrofuran (THF) insolubles by Shalabi et al. (6). Whitehurst et al. (7,8) use pyridine solubility to determine the unconverted coal, but redefine the remaining reaction product as specific chromatographic fractions. Brunson (9), on the other hand, uses distillation classes of the feed coal, while Shah et al. (10) classify the products into various boiling fractions, and Burke and Winschel (11) quantify the unconverted coal by a combination of filtration and THF solubility.

Different methods are also used for the characterization of these four base fractions of coal liquefaction products. Schweighardt et al. (12,13) use a silica gel column to obtain saturates, aromatics, heterocompounds, and asphaltenes from centrifuged liquid products (CLP). Each fraction is subjected to further fractionation by TLC and thin layer electrophoresis and is analyzed by ^1H , ^{13}C , and ^{14}N NMR and deuterium exchange reactions. Schweighardt et al. (14) use also a combination of solvent extractions, HCl treatment, ion-exchange chromatography, silylation, NMR, and GC-MS.

Schiller et al. (15) separate the coal liquid products by various chromatographic techniques and analyze the fractions by GC-MS, low and high resolution MS.

Another separation technique using a single silica gel column and

various solvents, ranging from hexane to pyridine, is the Sequential Elution with specific Solvents Chromatography (SESC) developed by Farcasiu (7,8,16). Nine fractions are obtained which can be analyzed by various physical, chemical, and spectroscopic techniques. Investigators at the Bartlesville Energy Research Center (16-20) have used a combination of distillation, aqueous extractions, and adsorption and gel permeation chromatography and have analyzed the fractions by MS and NMR. Ruberto et al. (22-24) and Ruberto (25) have used ion-exchange and adsorption chromatography (SARA analysis) and have analyzed the fractions by GC, MS, and NMR. Seshadri et al. (26) have used these separation techniques to measure the transferable hydrogen in coal liquefaction solvents.

Techniques which make a minimum use of separations are those developed by Aczel (27) using low and high resolution mass spectrometers, operated at low and high voltages, together with sophisticated data acquisition and processing accessories. The use of NMR and IR as process tools has been illustrated by Anderson (28) in connection with the SRC process.

This brief introduction only touches on the number of analytical schemes that can be found in the literature. In addition, variations and modifications of each scheme are numerous.

The scheme that will be used in this project will take cognizance of the diversity of the analytical approaches that have been used and, above all, of the constraints imposed by the sample limitations in our ESR experiments. The schemes that are described below are based to a large extent on the experience that our laboratory has had with DOE (29), EPRI (21,30), and internally sponsored research on coal conversion (22-26), including SRC-II process investigation.

In the following sections, two items will be discussed.

- a. Separation scheme for analyzing the ESR experiments
(small samples)

b. Separation scheme for analyzing the shaken autoclave experiments.

These schemes will provide the information listed in Table VII. The fractions listed as recoverable in this table can be subjected to various analyses such as

^1H and ^{13}C NMR

FTIR

Group-type MS

GC-MS

Elemental (C, H, N...)

Physical (e.g., density, viscosity, etc.)

More detailed separations (HPLC, TLC, etc.)

The extent of these analyses will be determined by the availability of the samples. It is stressed that, while the amount of sample needed to perform all of the above listed analyses may be very small, each analysis will require enough material for sampling. In addition, the amount of each fraction will depend on the degree of conversion obtained in the liquefaction reaction.

It may be advisable, therefore, to decide case by case which analyses will be required and which will be performed on each sample or fraction.

2. Separation Procedure from Products from ESR Tubes Experiments

A schematic of this procedure is shown in Figure 7.

The ESR tubes, tared and containing a weighed amount of total products, are broken into pieces about 3 cm long. These are placed into a tared 20-ml vial which, in turn, is placed into a tared thimble.

A Soxhlet apparatus is prepared with n-pentane solvent. The thimble plus vial is crushed with a pair of pliers to break the vial; it is then placed into the extractor of the Soxhlet, covered with n-pentane and allowed to soak for a few hours. The extraction is then started and continued until the solvent around the thimble is clear.

The thimble containing the n-pentane insolubles and the broken glasses is dried in an oven at ~110°C, under N₂, for 1-3 hours; it is then allowed to cool down to room temperature, weighed and subjected to toluene extraction in another Soxhlet apparatus.

The same procedure is used to extract the toluene insolubles with tetrahydrofuran (THF) to obtain the THF insolubles. The THF insolubles, corrected for the ash that was in the coal, are used to calculate the conversion level of the reaction:

$$\text{wt \% conversion (maf basis)} = \frac{A-B}{A} \times 100$$

where A = wt coal charged to ESR tube (maf)

B = wt THF insolubles, maf

The n-pentane solubles are determined by subtracting the n-pentane insolubles from the total charge to the ESR tubes. They are recovered by evaporating the n-pentane. During this evaporation, the material boiling below ~240°C will be lost. It can be quantified by weighing the residue and subtracting it from the total n-pentane solubles. The toluene and THF solubles are recovered by evaporating the solvents. They can be combined and maintained in THF or analyzed separately.

Two observations need to be made.

- a. This procedure requires the products from at least two ESR tubes, i.e., total material of about 0.6 g of coal.

- b. This procedure is a modification of the Forward Sequential Extraction Technique, described in Reference 3. The Direct Extraction Technique described in Reference 3 is preferred, but it cannot be used due to the small sample size that is available from the experiments.

In order to show that this technique could be used to analyze the materials from the ESR tubes a set of "Blank" runs were made. ESR tubes were charged with coal and tetralin solvent. These were then subjected in pairs to the procedure described above. The data are shown in Table VIII, and indicate that the technique will indeed be applicable. The "Oils and Resins by GLC" were obtained by concentrating the n-pentane solution of oils plus resins to about 10 ml and by measuring the content of n-pentane by GLC. These results indicate that some of the original solvent is lost. They are in agreement with past experience and justify the determination of the low boiling materials from the n-pentane solubles by difference, as described above.

3. Separation Procedure for Products from Shaken Reactor Experiments

The experiments made with this reactor contain 5-6 grams of products, which can be separated by two possible methods.

Method 1. This method is especially effective where the reaction solvent is a single compound such as tetralin. The liquid phase of the reaction products is subjected to GLC to quantify the tetralin, naphthalene, and the other low boiling hydrocarbons. It is then removed by evaporation on an oil bath at $\sim 70^{\circ}\text{C}$, under N_2 , and the residue is subjected to the extraction procedure shown in Figure 7. This method assumes that the material eluting from the GLC is equivalent to the material that evaporates on the oil bath.

The technique has been used extensively on another DOE-sponsored project (29) and Table IX shows some typical data that are described.

Method 2. This method is more applicable when the reaction solvent is a complex mixture such as SRC-II derived material, but requires a larger sample.

The products are filtered obtaining a filtrate and a wet cake. The wet cake is subjected to the extraction procedure described in Figure 7. The filtrate can be analyzed by SARA and/or other separation and spectroscopic techniques (HPLC, GPC, GLC, NMR, MS, etc.). Some typical separation results obtained in our laboratory using this method are shown in Table X (25).

The evaporation step in Method 1, or the filtration in Method 2, are necessary to minimize the co-solvent effect of the coal liquids and of the reaction solvent during the extraction process. This co-solvent effect depends on the composition of the liquefaction products and it is therefore unpredictable, but may be significant.

C. Experimental Design for Task II (Process Variable Screening)

Given the complexity of the project, the total number of experiments that one might have to perform is quite large. Therefore, it has been proposed by us that formal experimental design would be utilized in performing the various tasks of this project.

Table XI of this report identifies the most important variables as well as the ranges of these variables that would be appropriate to investigate. Table XII provides a code identification for these variables as well as a low and high level for each variable. For Task II, we propose to carry out experiments on a 2^5 factorial design. (As is standard practice, in order to perform factorial design, we select a fixed number of levels; two in this case, for each of a number of variables - five in this case. Experiments then are made for all possible combinations of these variables. A two-level experimental design has the advantage that with a few runs it allows one to explore fully a wide region in the variable space and thus determine major

trends which can be explored further at a later stage.) Table XIII provides 32 experiments utilizing the five variables at the two levels as indicated in Table XII.

Task II calls actually for at least 40 experiments. Thus, the additional eight experiments would be utilized to determine reproducibility of the runs as well as perform preliminary experiments or scouting runs for mineral matter and particle size effects. The order for the ESR experiments will be random rather than sequential as indicated in Table XI. The necessary shaken autoclave experiments will be selected from Table XIII.

IV. MISCELLANEOUS ITEMS

All other necessary aspects for proceeding with this project are on hand. Specifically, a new Varian Associates E-LINE Century EPR Spectrometer has been purchased and installed in our Laboratory. This instrument will allow obtaining ESR data much more readily than the previous older model instrument. In addition, all the materials that we expect to be using for this project have been obtained. A sufficient quantity of Powhatan #5 coal (the same material that has been used in pilot plant studies for SRC-II at the Tacoma facility) and heavy distillate product from the same coal have been obtained and will be used in the study. Prof. Gary Maciel of Colorado State University will do carbon-13 high resolution NMR studies to evaluate structural changes that may be taking place in the coal molecular skeletons. Prof. George Gavalas of California Institute of Technology will be cooperating with us in carrying out mechanistic and kinetic studies in conjunction with our ESR measurements.

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Table I
ANALYTICAL DATA ON POWHATAN #5 COAL

<u>Analysis</u>	(As received)	<u>Percent by wt.</u>
Moisture		1.19
C		71.66
H		5.02
N		1.10
Cl		0.06
S		3.32
O (diff)		7.46
Ash		10.19
Vol. matter		40.03
Fixed carbon		48.59

Table II

SUMMARY OF EXPERIMENTS PERFORMED FOR DEVELOPMENT
OF ESR EXPERIMENTAL PROCEDURES AND CAVITY TESTING

<u>Run #</u>	<u>Description</u>	<u>Comments</u>
01-16-1E*	Powhatan #5, no solvent H ₂ /10.34 MPa, 450°C, 65 min to final temp. <u>Step Rate</u>	R.T.** (4)† before heating; 100°C (1); 200°C (1); 300°C (1); 350°C (1); 400°C (1); 452°C (1); R.T. (2 after above heating); 400°C (3); 450°C (1); R.T. (1) after second heating
01-22-1E	Powhatan #5 no solvent H ₂ /10.34 MPa, 450°C, slow heat (15 min to final temp.)	R.T. (1) exp before heating; 450°C (1) R.T. (2) after heating
01-25-1E	Powhatan #5 no solvent H ₂ /10.34 MPa, 450°C, 15 min to final temp. (slow heating rate	R.T. (2) before heating; 450°C (4), R.T. (4) after; (2nd heating) 450°C (2); R.T. (1) after second heating
02-12-1E	Powhatan #5 no solvent H ₂ /10.34 MPa, 450°C, 2 min 45 sec to final temp. (fast heating)	R.T. (2); 450°C (5); R.T. (5); Second heating 450°C (6); R.T. (2) after rapid heat exp)
02-26-1E	Powhatan #5, Tetralin H ₂ /10.34 MPa, 450°C 2 min 30 sec to final temp. (fast heating)	R.T. (7), 450°C (12); R.T. (2); after rapid heat exp.
02-27-1E	Powhatan #5, Tetralin, H ₂ /10.34 MPa, 450°C, 2 min 30 sec to final temp. (fast heating)	R.T. (8); 450°C (12); R.T. (1); after rapid heat exp.
03-03-1E	Powhatan #5, Naphthalene H ₂ /10.34 MPa, 450°C, 2 min 30 sec to 450°C, final temp. (fast heating)	R.T. (2); 450°C (9); R.T. (2); after rapid heat exp.

* (Project month) - (Day) - (Number of experiment) (ESR or Autoclave)

**RT=25°C

† (4) = number of scans

Table III

BASELINE MEASUREMENTS (10^{18} spins/gram)*
 Scan Time (Min)/Scan Width (Gauss)

<u>Exp. #</u>	<u>10 min / 1000 G</u>	<u>1.0 min / 100 G</u>	<u>2.5 min / 100 G</u>
01-16-1E	6.5 (<u>+</u> .3)	-	-
01-22-1E	7.1	-	-
01-25-1E	6.9 (<u>+</u> 0.5)	-	-
02-12-1E	8.4		7.0
02-26-1E	9.6	9.9 (<u>+</u> 1.4)	9.4 (<u>+</u> 0.3)
02-27-1E	9.7 (<u>+</u> 0.5)	9.3 (<u>+</u> 0.2)	9.0 (<u>+</u> .1)
03-03-1E	12.0 (<u>+</u> 0.3)	-	-

*10.34 MPa.

Table IV

HEATING RATE DATA

Time (min)	Run #	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
0		7	13	18	9
0.5		312	346	---	---
1.0		394	427	47	14
1.5		400	448	---	---
2.0		399	452	76	24
3.0			450	103	40
4.0				136	59
5.0				155	84
6.0				212	115
7.0				259	141
8.0				299	174
9.0				343	215
10.0				367	250
11.0				396	296
12.0				428	342
13.0				442	376
14.0				452	426
15.0				459	445
16.0					461
17.0					459

- Run 1. 400°C final temp.; 11.02 MPa (1600 psig H₂)
 2. 450°C final temp.; 10.33 MPa (1500 psig H₂)
 3. 460°C final temp.; 8.27 MPa (1200 psig H₂)
 4. 460°C final temp.; 11.02 MPa (1600 psig H₂)

Table V

RESULTS OF 450°C HEATING EXPERIMENTS AT 10.34 MPa H₂
(10¹⁸ Spins/Gram)

Sample	<u>RT† Before Heating</u>	<u>450°C</u>	<u>R.T.† After Heating</u>
01-16-1E	6.5	84	52
01-22-1E	7.1	49	41
01-25-1E	6.9	27	45
02-12-1E	7.7	53	44
02-26-1E	9.6	64	74
02-27-1E	9.1	85	75
03-03-1E	12.3	129	156

† 25°C

Table VI

FREE RADICAL CONCENTRATION OF COALS OVER TWO HEATING CYCLES*
(10^{18} Spins/Gram)

Run	R.T.† (Before Heating)	<u>First Heating</u>		<u>Second Heating</u>	
		400°C	R.T.† (After Heating)	450°C	(After 2nd Heat.)
01-16-1E	6.5	84	52	77	48
01-25-1E	6.9	27	45	26	23
02-12-1E	7.7	53	44	63	45

* 10.34 MPa

† 25°C

Table VII

INFORMATION OBTAINABLE BY THE ANALYTICAL PROCEDURES

	<u>Products From Reaction in</u>	
	<u>ESR Tubes</u>	<u>Sand Bath Reactor</u>
1. Degree of conversion	yes	yes
2. Content of:		
Unconverted coal	yes	yes
Preasphaltenes	yes	yes
Asphaltenes	yes	yes
Oils and resins	yes	yes
Resins	yes (a)	yes (a)
Aromatics	yes (a)	yes (a)
Saturates	yes (a)	yes (a)
3. Recoverable Sample of:		
Unconverted coal and ash	no	no
Preasphaltenes	yes	yes
Asphaltenes	yes	yes
Oils and resins	yes (b)	yes (b)
Resins	yes (a,b)	yes (a,b)
Aromatics	yes (a,b)	yes (a,b)
Saturates	yes (a,b)	yes (a,b)

(a) This is possible in principle; in practice it will depend on the size of the sample and on the content of each fraction in that sample.

(b) Excluding material with B.P. 240°C which will be lost in removing the solvents used to carry out the separations.

Table VIII

ANALYSIS OF "BLANK" RUNS (COAL AND TETRALIN)

	<u>SAMPLE NO.</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
<u>Charge to ESR Tubes</u>			
Total, grams	1.6498	1.6529	1.6207
Total, wt %	100.0	100.0	100.0
Coal, wt %	50.5	48.6	49.5
Tetralin, wt %	49.5	51.4	50.5
<u>Analysis, Wt % of Charge</u>			
Oil and resins	53.7	56.1	55.4
Asphaltenes	0.5	0.7	0.0
Preasphaltenes	1.4	*	2.7
Unconverted coal	44.4	34.5*	43.3
Oils and resins by GLC	32.0	30.1	37.5
(see text)	32.0	30.1	37.5

*Some coal was lost during the THF extraction.

Table IX

EXAMPLES OF ANALYSES OF PRODUCTS FROM SHAKEN REACTOR†
(Not Sample Limited)

Coal Used	<u>Kentucky</u>		<u>Illinois</u>	
	A	A	B	B
Run Conditions				
Recovery, wt %	95.8	97.6	97.6	94.4
Conversion, Wt %	63.2	64.1	18.2	17.3
<u>Product Analysis, Wt of Products</u>				
Tetalin	33.0	33.6	54.8	62.3
Naphthalene	35.3	31.8	8.5	10.0
Other Hydrocarbons	14.8	11.7	10.6	3.8
n-Pentane Insolubles, maf	15.6	15.5	22.3	20.1
Toluene Insolubles, maf	9.4	9.2	19.2	19.3
Asphaltenes, maf	6.2	6.3	3.2	0.9
Oil Make	13.1	7.1	3.9	6.1
Naphthalene Make	34.0	31.7	7.2	9.9

† Ref. 29

Table X

EXAMPLES OF ANALYSIS USING METHOD 2†

<u>Run No.</u>	<u>A</u>	<u>B</u>
<u>Filtrate, Wt % of Products</u>	80.6	80.8
Neutral Oils	31.5	43.7
Saturates	1.5	0.7
Aromatics	30.0	43.0
Resins	35.8	24.6
Asphaltenes	13.3	12.5
<u>Wet Cake, Wt % of Products</u>	19.4	19.2
ϕ H Soluble	11.6	12.2
ϕ H Insoluble	7.8	7.0
% Conversion, maf basis	88.0	89.5

Note: In these cases, benzene was used instead of toluene and no THF extractions were carried out.

† Ref. 25

Table XI

RANGE OF VARIABLES FOR
INVESTIGATION OF MAIN EFFECTS (TASK II)

Temperature	350 - 475°C
Pressure	6.89 - 13.78 MPa
Residence Time	up to 1 hour
Heating Rate (Room-Highest Temp)	~3 - 30 minutes
Solvent/Coal Ratio	1:1 - 2:1
Gases	H ₂ ; N ₂
Solvents	Tetralin; SRC-II Process Derived Components
Coal	Powhatan #5

$$1\text{b}/1\text{n}^2 = 6.89 \times 10^3 \text{ Pa}$$

Table XII

INDEPENDENT VARIABLES
AND SELECTED LEVELS FOR EACH

Variables Code	Variable	Level	
		Low	High
1	Pressure	- (8.27 MPa)	+ (11.02 MPa)
2	Temperature	- (400°C)	+ (460°C)
3	Heating Rate	- (<3 min)	+ (15 min)
4	Solvent	- (Tetralin)	+ (Process Derived)
5	Gas	- (N ₂)	+ (H ₂)

Table XIII

EXPERIMENTAL DESIGN FOR INVESTIGATION
OF MAIN EFFECTS (TABLE XII)

(A 2^5 Factorial Design)

Experiment Number	Experimental Variable ⁺				
	1	2	3	4	5
1	-	-	-	-	-
2	+	-	-	-	-
3	-	+	-	-	-
4	+	+	-	-	-
5	-	-	+	-	-
6	+	-	+	-	-
7	-	+	+	-	-
8	+	+	+	-	-
9	-	-	-	+	-
10	+	-	-	+	-
11	-	+	-	+	-
12	+	+	-	+	-
13	-	-	+	+	-
14	+	-	+	+	-
15	-	+	+	+	-
16	+	+	+	+	-
17	-	-	-	-	+
18	+	-	-	-	+
19	-	+	-	-	+
20	+	+	-	-	+
21	-	-	+	-	+
22	+	-	+	-	+
23	-	+	+	-	+
24	+	+	+	-	+
25	-	-	-	+	+
26	+	-	-	+	+
27	-	+	-	+	+
28	+	+	-	+	+
29	-	-	+	+	+
30	+	-	+	+	+
31	-	+	+	+	+
32	+	+	+	+	+

⁺ For Code (see Table XII)

FIGURES

FIGURE 1

HIGH TEMPERATURE, HIGH PRESSURE CAVITY COMPONENTS

SPIN CONCENTRATION vs TIME

RUN 03-03-1E

Fig. 2 Powhatan #5, naphthalene and H₂. Spin concentration vs. time. Temperature at T=0 is ~20°C. At T>0, temperature is 450°C.

SPIN CONCENTRATION vs TIME

RUN 02-26-1E

Fig. 3 Powhatan #5, tetralin and H₂. Spin concentration vs. time. Temperature at T=0 is ~20°C. At T>0, temperature is 450°C.

SPIN CONCENTRATION vs TIME

RUN 02 - 27 - 1E

Fig. 4 Powhatan #5, tetralin and H₂. Spin concentration vs. time.
Temperature at T=0 is ~20°C. At T>0, temperature is 450°C.

SPIN CONCENTRATION vs TIME

RUN 02-12-1E

Fig. 5. Powhatan #5 and H₂. Spin concentration vs. time. Temperature at T=0 is ~20°C. At T>0, temperature is 450°C.

SPIN CONCENTRATION vs TIME

Fig. 6 Composite of Powhatan #5 and H₂ with Naphthalene, tetralin and no solvent. Spin concentration vs. time. Temperature at T=0 is ~20°C. At T>0, temperature is 450°C.

COAL LIQUIDS + UNCONVERTED COAL + ASH

Figure 7

GENERAL SEPARATION SCHEME

RT before heating 10.34 MPa H₂
10 min scan 1 KG

[illegible]

450°C
1500 psi

02 12 1E

At 450°C, 10.34 MPa H_2

10 min Scan 1KG

LR25844 Powder, Coal $CuSO_4 \cdot 5H_2O$ FS 1017
100-1600-2-200150 10 min 1KG
450°C 1500 psi
Expt 100-1600-2-200150 10 min 1KG
450°C 1500 psi

Amplitude = $(2.6 \times 10^{-4}) \times (3.2 \times 10^4) \times (1.6 \times 10^4) = 1.37 \times 10^{-4} = 1.37 \times 10^{-4}$ units

Amplitude = $(2.6 \times 10^{-4}) \times (3.2 \times 10^4) \times (1.6 \times 10^4) = 1.37 \times 10^{-4} = 1.37 \times 10^{-4}$ units

(1302-1305)

Fig #6 (450°C) 1. Kistler Paramagnetic $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Ref. FS 3580 Kistler 8990294
1500 gauss/hr 100 = 1900 - 2 = 2000 20 2.5 mm
(3.0 mm p.f. for log) 1000 1000
last figure 6

02121E

At 450°C, 10.3Y MPa H_2
2.5 min scan 100 G

44

8500 Hz
4460 G

$$\frac{22.11}{185} = \frac{1}{165} = \frac{165 \times 22.11}{185} = 2000 \text{ G}$$

$$\frac{22.11}{144625} = \frac{1}{83075} = \frac{83075 \times 22.11}{144625} = 2000 \text{ G}$$

02-12-1E

AT RT, 10.3% H_2 after 1st heating
10 min 5 sec 1 KG

(Exp. #6) LR25844 Powdered coal $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 11/18/79
RT 100-1000-2-3200 150 10 min ES 3300 Hz
1500 Hz 100-1000-2-3200 150 10 min ES 3300 Hz

450°C
1500 psi H

02121E

At 450°C second cycle, 10.34 MPa H₂
10 min scan 1KG

LR2544 furnace, Coe CuSO₄·5H₂O FS 1017
100-1600-2-3200150 10 min
Exp 46
450°C
1500 psi H

Approx 10 min scan
1500 psi H
10.34 MPa H₂
10 min scan 1KG
450°C
1500 psi H

03-03 IE
 AT 448°C 10.47 MPa
 1 min Scan 100 G

#3 448°C 1000 psi 12/05/79 0936 4 min / 15 sec
 (50%) 1.0 min / 1500 psi 100-800-2-1000 1.0 min / 1500 psi
 FS 3605 8997223

47

1924
 1401702

50.11 50.112 50.720 50.720 50.720
 39952 39952 39952 39952 39952
 50.72 50.72 (50.72) 50.72 50.72
 39952 39952 39952 39952 39952

10 min scan 1KG

0951

[illegible]

49

$R_T / \text{spool} = \frac{12.15 \text{ kg}}{(10 \text{ mm})^2}$

$$\begin{aligned}
 & \text{Solving for } \theta: \\
 & \left(\begin{array}{ccc} \text{Sine} & \text{Cosine} & \text{Hypotenuse} \\ 12.7 & 100 & 127 \\ 3000 & 1000 & 3000 \end{array} \right) \left(\begin{array}{ccc} \text{Angle} & \text{Angle} & \text{Angle} \\ 12.7^\circ & 100^\circ & 127^\circ \\ 3000^\circ & 1000^\circ & 3000^\circ \end{array} \right) = 3.6 \times 10^4 \text{ g} \cdot \text{cm}^2 \cdot \text{s}^{-2}
 \end{aligned}$$

02 27 IE

At 450°C, 10.34 MPa H₂
1 min scan 100 G

PL 11/27/79
(450°C) (50/50) (AR 24844)

34.0 min

1431

ES 3605.5
FWS 8909220

02-26-1E

At 450°C 10.34 MPa H₂

10 min Scan 1 KG

11/26/79
 10.34 MPa H₂ 10 min Scan 1 KG
 450°C 10.34 MPa H₂ 10 min Scan 1 KG
 11/26/79 10.34 MPa H₂ 10 min Scan 1 KG
 450°C 10.34 MPa H₂ 10 min Scan 1 KG
 11/26/79 10.34 MPa H₂ 10 min Scan 1 KG
 450°C 10.34 MPa H₂ 10 min Scan 1 KG

53

10.34 MPa H₂ 10 min Scan 1 KG
 450°C 10.34 MPa H₂ 10 min Scan 1 KG
 11/26/79 10.34 MPa H₂ 10 min Scan 1 KG
 450°C 10.34 MPa H₂ 10 min Scan 1 KG
 11/26/79 10.34 MPa H₂ 10 min Scan 1 KG
 450°C 10.34 MPa H₂ 10 min Scan 1 KG

*77d 11/26/79

DATE	TIME	LOCATION	COUNT	ACTING	REMARKS
10/18/79	NH	00-8000-2	100	100g	36/10/79

+2

$$\frac{31.78}{2.0155} = \frac{x}{2.151} = (31.78) \times \frac{2.1150}{2.151} = 31.91 \times 10^3$$

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Appendix A

CAVITY PHOTOGRAPHS

58-59