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

Quarterly Report for Period July 1–September 30, 1980

By
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I. EXECUTIVE SUMMARY

This Quarterly Report presents and summarizes work for the period ending October 1, 1980. The overall objective of the project is to study the fundamentals of coal depolymerization under direct liquefaction preheater/reactor conditions. A uniquely designed and fabricated high pressure/high temperature Electron Spin Resonance (ESR) apparatus is used to monitor the formation and behavior of free radicals, which are generally assumed to be the key factor in coal liquefaction.

Previous reports summarized the experimental design for the project, the testing of the ESR apparatus and development of a method for the observation of free radicals in the depolymerization of coal. The current report is based on work completed under Task 2 of the work statement. The objective of this task was to determine the effects of process variables and prioritize their relative importance. Task 2 required the performance of 40 experiments, most of them based on a 2^5 factorial design that was to test five variables each at two levels. In effect, some 60 experiments have been carried out using the ESR cavity. In addition, a certain number of shaken autoclave experiments were carried out that paralleled those in the high temperature/high pressure ESR cavity. The purpose of the shaken autoclave experiments was to prepare larger quantities of materials for some detailed analyses, and also to attempt to correlate the in situ measurements with the batch experiments which have been the only experiments possible up to now.

The main conclusions that have been reached through the completion of the second task are as follows: (1) The methodology that has been developed indeed allows the observation of the free radical formation and behavior at conditions relating to direct liquefaction preheater/reactor conditions. Measurements can be made continually three minutes after the heating of the coal slurry is started. Temperatures up to 500°C and pressures up to 1800 psi are accessible. (2) The observed changes in the concentration of free radicals due to variations of process variables are a real effect. Concentrations can be determined to $\pm 40\%$, but process variable manipulation

has produced a 12-fold increase. (3) Temperature is the single most significant process variable that affects free radical formation. For the Powhatan No. 5 coal there is a 9-fold increase in going from 400°C to 460°C. (4) At 460°C the other process variables tested can affect significantly the free radicals but at 400°C solvent, residence time and other conditions have essentially no effect on free radicals formed. (5) The next most significant effect is due to the combination of solvent and resident time. Tetralin and the SRC-II heavy distillate quench the free radicals from Powhatan No. 5 to the same extent with one significant difference. Whereas in tetralin maximum concentration is observed shortly after the slurry achieves its highest temperature, in the SRC-II heavy distillate experiments the highest concentration is not observed even after 1 hour of reaction. This would indicate some considerable different chemistry taking place especially in the first half-hour of the reaction when the SRC-II distillate is used as the solvent. This effect is particularly pronounced at 460°C. (6) Within the context of the variables tested, the heating time (3 and 15 minutes to reach highest temperature) and pressures and types of gas used (1250 and 600 psi, N₂ and H₂) affect the free radical concentration to a much smaller extent. However, in our experiments there is a large excess (200-fold) of replaceable hydrogens. (7) The conversions obtained in the in situ ESR experiments using SRC-II heavy distillate as the solvent are comparable to the shaken autoclave conversion. However, the corresponding tetralin values are lower in the ESR component to the shaken autoclave, although the patterns (oils, asphaltenes) of conversions are similar for the two experimental modes. In general, we also find that overall conversion and oil yield increase with residence time except with SRC-II heavy distillate at 460°C when both, overall conversion and oil yield, decrease. In fact, at these conditions there are negative oil yields, as there were also at lower temperatures and short (3 min) residence times. The data again indicate some complex chemistry with some SRC-II heavy distillate components, especially at the higher temperature. The data also indirectly support the contention of the importance of the recycling of the mineral matter.

Task 3 will investigate more closely the most significant variables, temperature and the combination solvent and residence times. In addition, mineral matter effects will be investigated, especially in combination with residence times and SRC-II heavy distillate components.

II. INTRODUCTION

The basic mechanism of coal pyrolysis and direct hydroliquefaction is generally agreed to be complex and governed by interrelated physical and chemical phenomena. It is believed, however, to be basically free radical in nature.^(1,2) The types of products formed may be governed by the reactions of these free radicals which are formed upon bond breaking as coal is heated in processing. In non-donor processes, or when the free radical has no access to an external hydrogen donor, the free radicals may either abstract hydrogen from the already hydrogen-poor coal "molecules" and form a product typical of coal tar, or combine with other large free radical fragments and form a high molecular weight char. This is typical of coking. When a hydrogen donor is present, the free radical may abstract hydrogen from the donor and from a relatively low molecular weight product. The donor solvent then can be rehydrogenated. Although this postulated mechanism of coal liquefaction appears reasonable, direct evidence is lacking.

To establish unequivocally this generally accepted concept of coal liquefaction, it would be desirable to investigate the dependence of free radical formation and behavior on process variables as well as determine the degree of conversion and quality of product obtained. Figure 1 is a schematic representation of this concept. Studies to date have attempted to make the direct correlation by carrying out autoclave experiments at the end of which the quality of the product is assessed (broken arrow top of Figure 1). Our approach is shown by the lower solid line that proceeds through the in situ investigation of free radicals with the possibility of making time dependent measurements and then assessing the quality of the product obtained. The emphasis so far of our work has been on part one (dependence of free radicals on process conditions) while now we are in the process of obtaining data relating to degree of conversion and product quality.

Electron spin resonance (ESR) spectroscopy is a convenient method for studying and measuring the properties of free radicals. Naturally occurring free radicals have been measured in coal by ESR methods since

1954^(3,4,5) and thermally formed free radicals have been measured in coals subjected to many different chemical and physical treatments.^(6,7,8,9,10) However, most of these measurements on thermally treated coal have been carried out at room temperature after the treatment was completed. We report ESR measurements made on free radicals in coal under high temperature and pressure, typical of coal liquefaction conditions.

Making ESR measurements on coal in situ under the conditions of coal hydroliquefaction has several advantages. The most important feature is that it allows measurement of the properties of the free radicals under realistic conditions similar to those found in larger liquefaction processing units such as the SRC-II preheater/reactor. There is no need to assume what is being measured is what exists at high temperature and pressure as is the case in the study of coal liquefaction products and residues. Free radicals can be studied as they are forming, i.e., within 3 minutes after heating is begun, and as they react over any period of time, all on the same sample. There is no need to prepare many samples to be run at different residence times. Disadvantages of in situ ESR liquefaction runs are the inability to stir the sample, possible inhomogeneity in the sample caused by bubble formation, and the small amount of material involved which makes product analysis difficult. Repeating experiments, to some extent, gives a check on the inhomogeneity problem and provides additional material for product analysis.

Task 2 was designed to study the effect of various process and feed variables on the free radicals in Powhatan No. 5 coal. The process variables (temperature, heating time and pressure) and the feed variables (gas and solvent) and the levels of each used are summarized in Table I. These are also discussed in a previous report outlining the 2^5 factorial design used.⁽¹¹⁾ An additional process variable, residence time (τ), was a continuous variable rather than one used at two levels, since free radical concentrations were measured at many intervals ranging from 3 minutes after the start of heating, in some cases, up to one hour. In addition to the two solvents, tetralin and SRC-II heavy distillate, used in the factorial design experiments, a few experiments with naphthalene were also done.

The scope of the work, to this point, is to examine the effects of the process and feed variables upon the free radicals in Powhatan No. 5 coal and assess which are of sufficient importance to merit more detailed study. We do not attempt to explain the mechanism of coal liquefaction at this point nor do we imply that the variables discovered as being important in these experiments are necessarily important to the free radical chemistry of all other coals. Such a study would require much further effort. We have attempted to study the variables over ranges of values that might practically be used or may be considered in typical liquefaction processes. Much more extreme conditions may produce effects not encountered here.

In addition to the ESR experiments described above, we have carried out 40 shaken autoclave experiments using much larger amounts of material but under very similar conditions. These parallel experiments were done to prepare additional material for IR, NMR and other analyses as well as glass free tetrahydrofuran (THF) insoluble residues for ^{13}C NMR and petrographic studies. We compare the results of both the ESR and autoclave experiments from a free radical and product quality viewpoint.

III. EXPERIMENTAL

The in situ ESR experiments, summarized in Tables II and III, in which all of the Powhatan No. 5 coal and tetralin or SRC-II heavy distillate were run in hydrogen or nitrogen, are experiments in the factorial design outlined in Table XIII of the first quarterly report,⁽¹¹⁾ reproduced here as Tables IV and V. Table V explains the notation used in Table IV. The procedure used in these experiments and the methods of calculating spin concentration are outlined in detail in an earlier report.⁽¹¹⁾ Briefly, the experiments involved mixing 0.5 g of Powhatan No. 5 coal and 0.5 g of tetralin in a quartz ESR tube, inserting it in the high pressure, high temperature cavity and, after placing the thermocouple in contact with the coal, tightening all closures. Spectra are recorded of the unheated coal at atmospheric as well as the higher pressures used in the experiment. The coal solvent slurry is then heated to the desired temperature at a predetermined rate and the spectra are recorded within a minute or two after the sample attains the desired temperature. After spectra have been recorded during the liquefaction run for 40 minutes to an hour, the sample is allowed to cool to room temperature and several additional spectra are recorded to determine the residual spin concentration at high pressure. The system is then depressurized and the sample removed from the cavity and saved. In experiments where temperature excursions exceed the normal 3 to 4°C fluctuations, the experiment was repeated. Duplicate runs were made for some sets of conditions to prepare enough samples for soxhlet extraction and to check reproducibility.

More than 40 autoclave runs have been done using tetralin or SRC-II heavy distillate and Powhatan No. 5 coal with N₂ or H₂ gas (Table VI). In these experiments, about 5 g each of tetralin and Powhatan No. 5 coal are mixed in a 22 ml stainless steel autoclave. In all but four experiments, the mixture was shaken vigorously for several minutes under pressure for premixing and then immersed in a preheated fluidized sand bath with shaking to begin the reaction. Three experiments were done without any shaking. After the desired reaction time, from 2 to 40 minutes, the reactor is removed from the sand bath, cooled initially with air and then with dry ice before depressurizing.

Heating and cooling data for this system have been included in a previous report.⁽¹²⁾ The material for the autoclave is then transferred, in most cases, to a short glass test tube with the aid of a methylene chloride wash. The methylene chloride and excess liquefaction solvent is evaporated off by a stream of nitrogen while the test tube is heated to less than 60°C in an oil bath. The test tube and liquefaction residue is placed in a cellulose soxhlet thimble, crushed and placed in a soxhlet extractor for sequential extraction with pentane, toluene and tetrahydrofuran (THF). After each solvent extraction, the thimble and contents are dried in a vacuum oven and weighed to determine the extent of conversion. In some cases, when a glass free residue was desired, the contents of the autoclave were transferred directly into a cellulose soxhlet thimble and extraction was begun. Glass free residues are necessary for ¹³C NMR spectroscopy and petrographic analysis.

All of the ESR and autoclave experimental data have been entered into an IBM computer data bank. This system has the Statistical Analysis System (SAS) software package for data handling, performing calculations, and preparing graphs, charts and tables. The figures contained in this report were produced via the SAS data package.

IV. RESULTS AND DISCUSSION

A. Powhatan No. 5 Coal and Tetralin Experiments

More than 25 ESR experiments were performed with Powhatan No. 5 coal and tetralin. Spin concentration vs. time plots are shown for the 400°C, hydrogen gas experiments in Figures 2 through 6 and for the 400°C, nitrogen gas experiments in Figures 7 through 12. Note that these plots show spin concentration to be relatively constant with time and that the spin concentration is approximately equal to that of the unheated coal/tetralin slurry, shown at the left margin at time zero. Those experiments with the 3 minute heating time have data points (after $t=0$) starting around 0.1 hour. The longer, 15 minute heating time experiments have data which began after 0.25 hours. Time in these plots is measured from the initiation of heating. Although these figures show no significant change in spin concentration due to heating or time, liquefaction reactions are occurring. This is known from preliminary conversion determination data on a few of these runs obtained by soxhlet extractions. These will be discussed in more detail later.

The spin concentration vs. time plots for the 460°C tetralin Powhatan No. 5 coal experiments are shown in Figures 13 through 27, Figures 13 through 20 are those with H_2 gas and 21-25 are the N_2 gas experiments. In the H_2 gas experiments there is a significant rise (factor of 3 to 5) on going from $t=0$, the unheated state, to $t>0$, when the temperature is $\sim 460^\circ C$. After the initial data point at $t=0$, there is little change with time, i.e., the spin concentration vs. time curve is relatively flat. There doesn't appear to be any significant influence by pressure or heating time, as the differences in spin concentrations between experiments carried out at different pressures or heating times are within the experimental scatter found among duplicate experiments. In Figures 21 through 25, the N_2 gas experiments with tetralin and Powhatan No. 5 coal, there is a consistent difference in spin concentrations as a function of time due to gas pressure. In the two experiments at 1200 psig (8.27 MPa) H_2 pressure, Nos. 06-06-1E and 06-11-1E, shown in Figures 21 and 22, the response of the spin concentration to the initial

heating, and its values over time are consistent with what are observed for the tetralin, H_2 gas experiments discussed above. However, in Figures 23 through 25, the 1600 psig (11.0 MPa) H_2 experiments, the spin concentrations are abnormally low compared to all other 460°C runs using tetralin. The reason for this pressure dependence of spin concentration in the N_2 runs is unknown at this stage, and some limited effort is under way to gain some insight into the problem.

B. Powhatan No. 5 Coal and SRC-II Heavy Distillate

More than 20 successful ESR experiments at high temperature and pressure were completed with Powhatan No. 5 coal and SRC-II heavy distillate using either H_2 or N_2 gas. The SRC-II heavy distillate was produced at the Ft. Lewis pilot plant operating on Powhatan No. 5 coal. Figures 26 through 34 are the spin concentration vs. time plots for the 400°C Powhatan No. 5, SRC-II heavy distillate experiments. The results of the H_2 gas experiments are shown in Figures 26 through 29 and those of the N_2 gas experiments are shown in Figures 30 through 34. The 400°C experiments, overall show a slight increase in spin concentration (20-30%) due to the initial heating with several experiments showing a modest rise in spin concentration over time. This is shown in Figures 28 and 29, the 400°C experiments with H_2 gas at 1600 psig, where the spin concentration almost doubles over a one hour period. In general, the results of these experiments are similar to those of the tetralin experiments except that the spin concentrations are slightly higher and show slight increases in spin concentration with time.

The 460°C experiments with Powhatan No. 5 coal and SRC-II heavy distillate are shown in Figures 35 through 46. There is an increase in spin concentration by a factor of 2 to 4 upon the initial heating of the slurry as can be seen by comparing the spin concentration of $t=0$, the unheated state and the first data point, which is at 460°C. The SRC-II heavy distillate experiments shown here are distinctly different from the tetralin experiments, in that in nearly every case, there is significant rise in spin concentration over time. This is particularly evident in Figures 37 through 39, 41, 42, 44

and 46 where the increase in spin concentration is nearly threefold in some cases over time. Solvent blank experiments gave no ESR signal at 460°, thus, the increase in free radical concentration with time must be due to free radicals being formed in the coal, unless some constituent of coal catalyzes a solvent cracking reaction.

Figure 47 is a plot of all the experimental data gathered. The alphabetical symbols correspond to the number of observations at each point e.g., "C" is three, "D" is four, etc. Note that at 400° none of the variables has much of an effect. At higher temperatures, particularly at 460°C where a lot of data exist, there is a large spread in values. This spread reflects significant real effects such as residence time, solvent and the gas pressure cross-effect discussed in the tetralin results section, as well as experimental scatter.

Spin concentration vs. measured temperature plots for the SRC-II heavy distillate experiments are shown in Figures 48 and 49. The printed symbol H stands for hydrogen, N for nitrogen. Figure 48 is a plot of 15 minute heating time experiments and Figure 49 is the corresponding plot for the 3 minute heating time data. There is little difference between the two plots, reflecting the negligible effects of heating time on spin concentration found in this work. In each figure, the points around 460° represent higher spin concentration and are spread out much more. This spread of values shows the effect of residence time on the spin concentration at this temperature, as was seen in the spin concentration vs. time plots for these experiments. The "N"s and "H"s are overprinted and no distinct clustering due to gas effects occurs.

Similarly, the tetralin experimental spin concentration vs. temperature plots are shown in Figures 50 and 51, corresponding to the 15 minute and 3 minutes heating times, respectively. As was the case in the previous pair of plots of the SRC-II heavy distillate data, there is no appreciable difference between the two plots corresponding to the 15 minute and 3 minute heating time experiments when tetralin was used as a solvent. The effect of

temperature is apparent in both figures, with those data points at 460° representing higher spin concentrations. The pressure, nitrogen gas cross-effect is very visible in Figure 50 at 460°C where the "N" symbols at high spin concentration correspond to the 1200 psig N₂ gas experiments and those at lower spin concentration are the 1600 psig N₂ experimental data. The same effect occurs at the shorter (3 minute) heating time, however, the data are somewhat obscured by overprinting in Figure 51.

To ascertain the difference in carrying out an experiment in the high temperature, high pressure cavity and the shaken autoclave, two shortened quartz ESR tubes were filled with the usual amount (0.5 g each) of tetralin and Powhatan No. 5 coal and placed in the shaken autoclave (22 ml) reactor. The autoclave experimental was then done in the usual manner, using a 40 minute residence time, 460°, and 1600 psig H₂ gas. The spin concentrations of these samples, measured in the high temperature cavity operated at ambient temperature were approximately 9 and 13 x 10¹⁸ spins/g, respectively. Typical values of 20°C measurements made after a normal high temperature, high pressure cavity run under the same conditions range from 25-40 x 10¹⁸ spins/g. Conversion experiments to compare % conversion of the autoclave ESR tube product and the usual ESR tube experiment product are under way to see how these values compare.

C. Conversion Determination Experiments

Autoclave Results

More than 40 autoclave runs have been completed for the determination of maltenes (referred to as oils in the following figures), asphaltenes and overall conversion, as well as the preparation of THF insolubles. Maltenes are the pentane soluble liquefaction product, asphaltenes represent the toluene soluble, pentane insoluble, portion and overall conversion refers to the sum of the pentane, toluene and tetrahydrofuran soluble materials. In the figures that follow, maltenes are represented by the symbol "O". The actual toluene soluble, pentane insoluble portion would be the difference

between "A" and "O" and the THF soluble, toluene insoluble portion, the so-called preasphaltenes would be the differences between "C" and "A" symbols. Figures 52 and 53 are plots of % conversion vs. residence time for the tetralin and Powhatan No. 5 coal experiments at 400 and 460°C respectively. N₂ and H₂ gas experiments at 1200 and 1600 psi have been combined in these figures. Upon close examination and by comparing the two figures, several points are evident. The higher temperature produces a higher overall extent of conversion as well as higher maltene yields. Increased residence time beyond 10 minutes does not increase overall THF conversion at 460° but does increase oil and asphaltene yields. This is similar to the results that have been obtained by others (1). At 400°C, the overall conversion is higher at longer residence time.

The results of the SRC-II heavy distillate and Powhatan No. 5 runs are shown in Figures 54 and 55. The 400°C experiments, shown in Figure 54 have a definite trend to higher conversion of longer residence time. Oil yields, which are very low or negative at three minutes residence time, increase somewhat in the 40 minute residence time experiments. Overall conversion approximately doubles at the longest residence time. The 460°C experiments, shown in Figure 55, show the opposite trend in conversion with residence time. Overall conversion, asphaltene and oil yield all decrease markedly on going to the longest residence time, 40 minutes. Oil yields are all negative at 40 minutes at 460°C. Apparently, from the negative yields of pentane soluble materials (oils), the SRC-II heavy distillate is reacting with the coal to form higher molecular weight, pentane insoluble material, at least under certain conditions.

The results of a few naphthalene experiments are shown in Figure 56. There is a moderate increase in the overall yield as well as pentane soluble material with time at 460°C. Comparing the three solvents at 460°C, the oil yield is approximately the same for naphthalene and tetralin, however, the tetralin runs have a much higher overall conversion as well as a higher yield of asphaltenes. The SRC-II heavy distillate runs gave lower oil yields than either naphthalene or tetralin. The overall conversion in the SRC-II

runs was comparable to those of naphthalene at three and 10 minutes but much worse at 40 minutes.

Figure 57 shown the results of a single pair comparison of shaken autoclave vs. non-shaken runs for Powhatan #5 coal and tetralin at 460°C and 11.0 MPa (1600 psig) H₂. At short residence times, the levels of conversion to the various fractions were about the same, however, at 40 minutes, the shaken runs show a much higher oil (pentane soluble material) yield.

Table VII summarizes the conversion determinations done on the ESR experiments. The most notable feature of the data here is the low pentane soluble yields of the SRC-II heavy distillate runs. This result is the same as that found in the shaken autoclave runs. The low pentane soluble yields found for nearly all these experiments are consistent with the finding that non-shaken runs at 40 minutes or longer residence should have lower pentane soluble yields than those that are agitated. However, the overall conversion in these experiments and the low pentane soluble yields in the short (four minute) residence time experiments cannot be reconciled with the results of the autoclave experiments.

V. DISCUSSION AND CONCLUSIONS

1. Free radicals can be observed in coal at temperatures and pressures approximating realistic liquefaction conditions. Measurements can be made continually from as little as three minutes after the initiation of heating for as long as is desired. Although we have emphasized free radical concentration measurements, g-values linewidths and lineshapes can be measured.
2. The effects observed in free radical concentration measurements are real effects caused by the manipulation of the variables. While experimental scatter between duplicate runs may be $\pm 40\%$ and within a given run may be $\pm 20\%$, the observed effects caused by variable manipulation are much greater. A maximum 12-fold increase in free radical concentration has been observed for the experiments performed.
3. Residual free radical concentration, i.e., the free radical concentration in a sample measured at room temperature after a given treatment, is similar to the free radical concentration during the treatment. Variations between the two types of measurement were not systematic. Data in the literature collected by measuring residual free radicals are valid, however, in situ measurements offer great advantages in that the sample need not be handled between treatment and ESR measurements, and time series data can be collected easily and on the same sample.
4. Temperature is the single most important process variable that affects free radical concentration. Regardless of other conditions, in experimental runs with Powhatan No. 5 coal and tetralin, there is essentially no change in free radical concentration at 400°C from the value obtained on the unheated slurry. There are slight changes ($\sim 50\%$ or so) at 400° when SRC-II heavy distillate is used, compared

to the free radical concentration in unheated samples. On the other hand, up to 9-fold increases in free radical concentration, compared to the unheated or 400°C concentrations, are found at 460°C. The extent of the increase is determined by the levels of the other process and feed variables. Other conditions, such as higher temperatures, poorer hydrogen donor solvents, etc., could conceivably result in an even larger temperature effect.

5. Next to temperature, the most significant effects are due to the combination of solvent and residence time. In general, the baseline radical concentrations in tetralin and SRC-II heavy distillate runs are about the same; however, when SRC-II heavy distillate is used as the liquefaction solvent, the increase to a maximum level is more gradual. The maximum level in free radical concentration observed is often not reached up to an hour after heating has begun. Higher spin concentration may be reached, however, most experiments are terminated at one hour. This finding indicates the possibility of significantly different chemistry in the SRC-II heavy distillate experiments compared to the tetralin liquefaction runs, especially in the first half-hour of reaction. At a given temperature, the free radical concentration is essentially "flat" with respect to residence time in the tetralin experiments but with SRC-II heavy distillate, up to a 3-fold increase in free radical concentration is observed from the time the first measurement of the experimental is taken until the last measurement at one hour. This increase in free radical concentration with residence time is more pronounced at the higher level of temperature (460°C) but is also observed at 400°C.
6. In general, under the conditions employed in those experiments, heating time, pressure, and type of gas affect the free radical concentration to a much lesser extent than does temperature, solvent or residence time. It may be surprising that hydrogen gas, or its absence, does not cause a significant effect, but it must be

remembered that, in the case of tetralin at least, there is a ratio of ~200 to 1 of donatable hydrogen molecules to radicals. This is based on an assumed value of 100×10^{18} radicals/g in absence of a solvent, four hydrogen molecules per tetralin molecule, and 0.5 grams each of coal and tetralin.

7. a. From experiments to date using SRC-II heavy distillate as the liquefaction solvent, the conversions (total THF conversion, asphaltenes and oils) obtained in the in situ ESR experiment are comparable to the shaken autoclave conversions. The need for duplicate ESR runs to provide enough sample for extractions necessarily limit the amount of data available.
- b. The overall conversion in the ESR tube experiments is somewhat lower when SRC-II heavy distillate is the solvent (27-36%) compared to the corresponding tetralin experiments (32-58%). For the same ESR experiments, the oil yields with SRC-II heavy distillate solvent are considerable lower (2-6%) compared to the corresponding tetralin runs (12-40%).
- c. The patterns of conversion due to the different levels of the variables in the ESR experiments are similar to the patterns observed with the autoclave experiments, even though the levels are different. For example, the overall THF conversion of Powhatan No. 5 coal in the ESR experiments using SRC-II heavy distillate in the ESR tubes is 27-33% and in the autoclave experiments, they are 20-30%, while the same coal with tetralin as the liquefaction solvent yields conversions in the ESR tubes of 32-58% and 75-85% in the autoclave. That is, tetralin gives higher overall conversions in both reactor systems, but the increase in conversion, due to using tetralin as the solvent, is larger in the autoclave. Similarly, the oil yield with SRC-II heavy distillate as the solvent is 2-6% in the tubes and -11 to

5% in the autoclave, while with tetralin as the solvent, the oil yield in the ESR tube is 12-40% compared to 30-60% in the autoclave. Again, the tetralin runs have higher oil yields in both reactor systems, but the oil yield increases due to using tetralin as the solvent is greater in the autoclave reactor.

- d. There is disagreement between the ESR tube and autoclave absolute conversion and oil yields when tetralin is used as the liquefaction solvent. The values obtained with the ESR runs are lower, although the two reactor systems gave similar absolute numbers with SRC-II heavy distillate as the solvent. It is not clear, at this stage, as to the reason for this discrepancy.
8. In general, overall conversion and oil yield were found to increase with residence time in the autoclave runs except in the case of the SRC-II heavy distillate runs at 460°C where the conversion and oil yield decrease as residence time increases. Total conversion decreased from 50 to 25% in these runs on going from three minute to 40 minute residence times. Overall, tetralin is a "better" solvent than the total cut SRC-II heavy distillate without added mineral matter, i.e., higher total conversion and higher oil yields with tetralin. However, at lower temperatures (400°C) and long residence times (40 minutes) the overall conversions with SRC-II heavy distillate are similar to those obtained with tetralin. Thus, under certain conditions, SRC-II heavy distillate is as good a liquefaction solvent as tetralin as far as total conversion is concerned.
9. Under certain conditions and with total SRC-II heavy distillate solvent, negative oil yields are observed. By negative oil yields, we mean that the pentane insoluble material from the liquefaction run weighed more than the coal charged to the reactor. The combination of 460°C and long (40 minute) residence times consistently gave negative oil yields. These negative yields were also obtained at

other sets of conditions, such as 400°C at three minutes residence time. This would indicate some complex chemistry taking place with the possibility of components of the total SRC-II heavy distillate, without added mineral matter, causing the negative oil yields. Another possibility is that the expected pentane solubles are irretrievably complexed or absorbed by the coal. These results indicate the need to investigate more closely the chemistry of various SRC-II heavy distillate components, especially in the presence of added mineral matter, at various residence times and temperatures.

REFERENCES

1. R. C. Neavel, Fuel 55, 237 (1976).
2. W. H. Wiser, "Scientific Problems of Coal Utilization", DOE Symposium Series 46, 1978, pp. 219-236.
3. J. Uebersfeld, A. Etienne, and J. Combrisson, Nature (London) 174, 615 (1954).
4. D. J. E. Ingram, J. G. Tapley, R. Jackson, R. L. Bond, and A. R. Murnaghan, Nature (London), 174, 797 (1954).
5. H. Tschamler and E. DeRuiter "Chemistry of Coal Utilization," Supplementary Vol., (H. H. Lowry, Ed.) John Wiley and Sons, Inc., New York, NY, 1963, pp. 78-85.
6. H. L. Retcofsky, J. M. Stark, and R. A. Friedel, Anal. Chem. 40, 1699 (1968).
7. D. E. G. Austen, D. J. E. Ingram, P. H. Given, C. R. Binder, and L. W. Hill, "Coal Science" Advances in Chem. Series 55, 344 (1966).
8. L. Petrakis and D. W. Grandy, Anal. Chem. 50, 303 (1978).
9. D. W. Grandy and L. Petrakis, Fuel 58, 239 (1979).
10. L. Petrakis and D. W. Grandy, Fuel 59, 227 (1980).
11. L. Petrakis, D. W. Grandy, R. G. Ruberto, and N. L. Carr, "Fundamentals of Coal Depolymerization," Quarterly Report for 10/1/79 to 12/31/79, DOE/ET/14940-1 NTIS, Springfield, VA, 1980.
12. L. Petrakis, D. W. Grandy, and G. L. Jones, "Fundamentals of Coal Depolymerization," Quarterly Report for 1/1/80 to 3/31/80, U.S. DOE Contract DE-ACO-179ET 14940, April 1980.

Table I

VARIABLES IN TASK II

Coal	Powhatan No. 5
Solvent	Tetrahydronaphthalene (tetralin) or SRC-II heavy distillate derived from Powhatan No. 5 coal
Gas	Hydrogen or Nitrogen
Temperature	400 or 460°C
Pressure	8.27 MPa (1200 psig) or 11.0 MPa (1600 psig)
Heating time	~3 min or 15 min
Residence time (~)	Continuously from ~1 min after the desired temperature has been reached to one hour.

Table II

POWHATAN NO. 5 AND TETRALIN ESR EXPERIMENTS

<u>EXP. NO.</u>	<u>SEQ. NO.</u>	<u>GAS</u>	<u>HEATING TIME (min)</u>	<u>PRESSURE*</u> <u>(psig)</u>	<u>TEMPERATURE °C</u>
02-26-1E	7	HYD	3	1500	450
02-27-1E	8	HYD	3	1500	450
04-16-1E	10	HYD	15	1200	460
04-17-1E	11	HYD	3	1200	460
04-24-1E	12	HYD	3	1200	400
04-29-1E	13	HYD	3	1200	400
04-31-1E	14	HYD	3	1600	400
05-04-1E	15	HYD	15	1600	460
05-13-1E	16	HYD	15	1600	460
05-15-1E	17	HYD	3	1600	460
05-19-1E	18	HYD	3	1600	460
05-21-1E	19	HYD	3	1600	460
05-25-1E	20	HYD	15	1200	400
05-27-1E	21	HYD	15	1600	400
05-28-1E	22	HYD	3	1600	460
06-04-1E	23	NIT	3	1200	400
06-06-1E	24	NIT	3	1200	460
06-10-1E	25	NIT	15	1200	400
06-11-1E	26	NIT	15	1200	460
06-12-1E	27	NIT	3	1600	400
06-21-1E	29	NIT	3	1200	400
06-23-1E	30	NIT	15	1600	460
06-23-2E	31	NIT	15	1600	400
06-26-1E	32	NIT	15	1600	460
06-27-1E	33	NIT	3	1600	460
07-03-1E	34	NIT	3	1200	400
07-17-1E	39	HYD	3	1600	460
07-17-2E	40	HYD	3	1600	460

* 1200 psig = 8.27 MPa
 1500 psig = 10.3 MPa
 1600 psig = 11.0 MPa

Table III.

POWHATAN NO. 5 AND SRC-II HEAVY DISTILLATE EXPERIMENTS

<u>EXP. NO.</u>	<u>SEQ. NO.</u>	<u>GAS</u>	<u>HEATING TIME (min)</u>	<u>PRESSURE*</u> <u>(psig)</u>	<u>TEMPERATURE °C</u>
07-28-1E	43	HYD	3	1600	460
07-30-1E	44	HYD	3	1600	460
08-07-1E	46	HYD	3	1200	400
08-09-1E	47	HYD	15	1200	400
08-12-1E	48	HYD	3	1600	460
08-13-1E	49	HYD	15	1600	460
08-14-1E	50	HYD	3	1600	400
08-15-1E	51	HYD	15	1600	400
08-16-1E	52	HYD	3	1200	460
08-19-1E	53	HYD	15	1200	460
08-22-1E	54	HYD	15	1200	460
08-23-1E	55	HYD	3	1200	460
08-27-1E	56	NIT	15	1200	400
08-28-1E	57	NIT	3	1600	400
08-29-1E	58	NIT	3	1600	460
09-02-1E	59	NIT	3	1600	400
09-03-1E	60	NIT	3	1600	400
09-06-1E	61	NIT	15	1600	460
09-09-1E	62	NIT	3	1200	460
09-11-1E	63	NIT	15	1200	460
11-06-1E	80	NIT	15	1600	400

* 1200 psig = 8.27 MPa
 1600 psig = 11.0 MPa

Table IV

**EXPERIMENTAL DESIGN FOR INVESTIGATION
OF MAIN EFFECTS**

(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	+	+	+	+	+

Table V

**INDEPENDENT VARIABLES
AND SELECTED LEVELS FOR EACH**

<u>Variables Code</u>	<u>Variable</u>	<u>Level</u>	
		<u>Low</u>	<u>High</u>
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 VI

POWHATAN NO. 5 AUTOCLAVE EXPERIMENTS

<u>EXP. NO.</u>	<u>TEMP °C</u>	<u>PRESSURE (Psig)**</u>	<u>GAS</u>	<u>RESIDENCE (Min)</u>	<u>SOLVENT</u>
06-14-1A	400	1200	H ₂	40	Tetralin
06-17-1A*	400	1200	H ₂	40	Tetralin
06-18-1A	460	1600	H ₂	40	Tetralin
06-19-1A	460	1600	H ₂	10	Tetralin
06-20-1A*	460	1600	H ₂	40	Tetralin
06-21-1A*	460	1600	H ₂	10	Tetralin
06-25-1A	460	1600	H ₂	2	Tetralin
06-26-1A*	460	1600	H ₂	2	Tetralin
06-27-1A	460	1600	H ₂	40	Tetralin
06-27-2A	460	1600	N ₂	40	Tetralin
06-28-1A	460	1600	N ₂	3	Tetralin
07-10-1A	400	1200	H ₂	40	Tetralin
07-10-2A	460	1600	H ₂	10	Tetralin
07-11-1A	460	1600	H ₂	40	Tetralin
07-15-1A	400	1200	N ₂	40	Tetralin
07-15-2A	400	1200	N ₂	10	Tetralin
07-18-1A	460	1600	N ₂	40	Tetralin
07-18-2A	460	1600	N ₂	10	Tetralin
07-22-1A	460	1200	N ₂	40	Tetralin
07-22-2A	460	1200	N ₂	10	Tetralin
07-23-1A	400	1600	H ₂	40	Tetralin
07-24-1A	400	1600	H ₂	10	Tetralin
07-24-2A	400	1200	H ₂	10	Tetralin
07-25-1A	460	1200	H ₂	10	Tetralin
07-30-1A	460	1600	H ₂	10	SRC-II HD
07-30-2A	460	1600	H ₂	10	SRC-II HD

* non shaken run

** 1200 psig = 8.27 MPa

1600 psig = 11.0 MPa

Table VI (Continued)

POWHATAN NO. 5 AUTOCLAVE EXPERIMENTS

<u>EXP. NO.</u>	<u>TEMP °C</u>	<u>PRESSURE (Psia)**</u>	<u>GAS</u>	<u>RESIDENCE (Min)</u>	<u>SOLVENT</u>
08-06-1A	400	1200	H ₂	3	SRC-II HD
08-06-2A	400	1200	H ₂	10	SRC-II HD
08-07-1A	400	1200	H ₂	40	SRC-II HD
08-08-1A	460	1200	H ₂	40	SRC-II HD
08-09-1A	460	1600	H ₂	3	SRC-II HD
08-09-2A	400	1600	H ₂	40	SRC-II HD
08-14-1A	400	1200	H ₂	40	SRC-II HD
08-15-1A	400	1200	H ₂	10	SRC-II HD
08-15-2A	400	1200	H ₂	3	SRC-II HD
08-16-1A	400	1600	H ₂	40	SRC-II HD
08-21-1A	460	1200	H ₂	40	SRC-II HD
08-21-2A	460	1600	H ₂	10	SRC-II HD
08-22-1A	460	1600	H ₂	3	SRC-II HD
08-22-2A	460	1600	H ₂	40	SRC-II HD
08-24-1A	400	1200	N ₂	40	SRC-II HD
08-24-2A	400	1200	N ₂	10	SRC-II HD
08-30-1A	400	1600	N ₂	40	SRC-II HD
08-3--2A	400	1200	N ₂	3	SRC-II HD
09-10-1A	460	1600	N ₂	10	SRC-II HD
09-10-2A	460	1600	N ₂	40	SRC-II HD

* non shaken run

** 1200 psia = 8.27 MPa

1600 psia = 11.0 MPa

Table VII
LIQUID IN ESR TUBES

<u>SOLVENT</u>	<u>EXP. NO.</u>	<u>HT</u>	<u>TEMP.</u>	<u>PRESS.</u>	<u>GAS</u>	<u>RES. TIME</u>	<u>PENT.</u>	<u>TOL.</u>	<u>THF</u>
T	04-24-1E 04-29-1E	3	400	1200	H ₂	~40	15.7	30.3	41.6
T	05-04-1E 05-13-1E	15	460	1600	H ₂	~40	15.7	31.2	31.8
T	07-07-1E 07-08-1E	3	460	1600	H ₂	4	5.0	19.9	34.1
T	07-08-2E 07-09-1E	3	460	1600	H ₂	4	12.4	28.0	32.2
T	05-15-1E 05-18-1E	3	460	1600	H ₂	~40	40.5	51.	58.8
T	05-21-1E 05-28-1E	3	460	1600	H ₂	22 68	36	39.5	43.8
SHD	08-16-1E 08-23-1E	3	460	1200	H ₂	68 68	2.1	25.3	27.0
SHD	08-12-1E 07-28-1E	3	400	1600	H ₂	30 50	5.9	31.9	36.3
SHD	08-19-1E 08-22-1E	15	460	1200	H ₂	55 68	6.4	30.7	33.6

Table VIII

COMPARISON OF YIELDS IN CONVERSION OF POWHATAN NO. 5

<u>Solvent</u>	<u>Overall Conversion (%)</u>		<u>Oil Yields (%)</u>	
	<u>ESR</u>	<u>Autoclave</u>	<u>ESR</u>	<u>Auto-clave</u>
SRC-II ⁺	27-36	20-30	2-6	(-11)-5
Tetralin ⁺	32-58	75-85	12-40	30-60

⁺460°C, low residence time

FREE RADICALS: KEY TO COAL LIQUEFACTION?

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Fig. 1
Schematic Representation
of Coal Liquefaction Concepts

Fig. 2
 Powhatan #5 & Tetralin
 400°C, 1200 psig H_2
 HT = 3, 04-24-1E²

NOTE: 1 DRS HIDDEN

Fig. 3
Powhatan #5 & Tetralin
400°C, 1200 psig H₂
HT = 3, 04-29-1B

NOTE: 2 ORS HIDDEN

Fig. 4
 Powhatan #5 & Tetralin
 400°C, 1600 psig H₂
 HT = 3, 04-31-18

NOTE: 1 OHS HIDDEN

Fig. 5
Bowhatan #5 & Tetralin
400°C, 1200 psig H₂
HT=15, 05-25-1E

NOTE: 2 OPS. HIDDEN

Fig. 6
Powhatan #5 & Tetralin
400°C, 1600 psig H₂
HT=15, 05-27-1E

NOTE: 3.0RS HIGHEN

Fig. 7
Powhatan #5 & Tetralin
400°C, 1200 psig N₂
HT=3, 06-04-1E

NOTE: 2 H-S HIDDEN

Fig. 8
Powhatan #5 & Tetralin
400°C, 1200 psig N₂
HT=15, 06-10-1E

NOTE: 1 OBS. HIDDEN

Fig. 9
Powhatan #5 & Tetralin
400°C, 1600 psig N₂
HT=3, 06-12-1E

NOTE: 1 OBS. HIDDEN

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Fig. 11
Powhatan #5 & Tetralin
400°C, 1600 psig N₂
HT=15, 06-23-1E

NOTE: 2 PPS HIDDEN

Fig. 12
 Powhatan #5 & Tetralin
 400°C, 1200 psig N₂
 HT=3; 07-03-1E

NOTE: 2 DMS HIDDEN

FIG. 13
 Powhatan #5 & Tetralin
 460°C; 1200 psig H₂
 HT-15, 04-16-1F

Fig. 14
Powhatan #5 & Tetralin
460°C, 1200 psig H₂
HT=3, 04-17-1E

NOTE : 2 PGS. W/IN EN

Fig. 15
Powhatan #5 & Tetralin
460°C, 1600 psig H₂
HT=15, 05-04-1E

NOTE: 2 OPS HIDDEN

Fig. 16
 Powhatan #5 & Tetralin
 460°C, 1600 psig H₂
 HT=15, 05-13-1E

NOTE: 4 OPS HIDDEN

Fig. 17
 Powhatan #5 & Tetralin
 460°C, 1600 psig H₂
 HT=3, 05-15-1E

NOTE: 2 OPS MIDDEN

Fig. 18
 Powhatan #5 & Tetralin
 460°C, 1600 psig H₂
 HT=3, 05-19-1E

NOTE: 2 OBS HIDDEN

NOTE: 3 OBS HIDDEN

Fig. 20
 Powhatan #5 & Tetralin
 460°C, 1600 psig H₂
 HT=3, 05-28-1E

NOTE: 5 ORS WIDEN

Fig. 21
Powhatan #5 & Tetralin
460°C, 1200 psig
HT=3, 06-06-1E

NOTE: 3 OPS HIDDEN

NOTE: 1 OPS HAD MISSING VALUES OR WERE OUT OF RANGE 2 OPS HIDDEN

Fig. 23
 Powhatan #5 & Tetralin
 460°C, 1600 psig N₂
 HT=3, 06-27-1E

NOTE: 2 HRS HIDDEN

Fig. 24
 Powhatan #5 & Tetralin
 460°C, 1600 psig N₂
 HT=15, 06-23-1E

NOTE: * ORS HIDDEN

Fig. 25
 Powhatan #5 & Tetralin
 460°C, 1600 psig N₂
 HT=15, 06-23-1E

NOTE: 1 ORS MIDDEN

Fig. 26
 Powhatan #5 & SRC-II HD
 400°C, 1200 psig H₂
 HT=3, 08-07-1E

Fig. 27
 Powhatan #5-6 SRC-11 HD
 400°C, 1200 psig H₂
 HT=15, 08-09-1E

NOTE: 3 OBS HIDDEN

Fig. 28
 Powhatan #5 & SRC-11 HD
 400°C, 1600 psig H₂
 HT=3, 08-14-1E

NOTE: 1 OBS HAD MISSING VALUES (W WERE OUT OF RANGE)

Fig. 29
 Powhatan #5 & SRC-11 HD
 400°C, 1600 psig H₂
 HT=15, 08-15-1962

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

Fig. 30:
Powhatan #5 & SRC-11 HD
400°C, 1200 psig N₂
HT=15, 08-27-1E

NOTE: 2 OBS HAD MISSING VALUES OR WERE OUT OF RANGE 3 OBS HIDDEN

Fig. 31
 Powhatan #5 & SRC-II HD
 400°C, 1200 psig N₂
 HT-3, 08-28-1E

NOTE: 1.0 HRS. HIDDEN

Fig. 32.
 Powhatan #5 & SRC-11 HD
 400°C, 1600 psig N₂
 HT=3, 09-02-1E 2

NOTE: 3 DRS HIDDEN

Fig. 33
 Powhatan #5-6 SRC-II HD
 400°C, 1600 psig N₂
 HT=3, 09-03-1E

Fig. 34
 Powhatan #5 & SRC-II HD
 400°C, 1600 psig N₂
 HT-15, 11-06-1E

NOTE: 3 THIS HIDDEN

Fig. 35
 Powhatan #5 & 6 SRC-II HD
 460°C, 1600 psig H₂
 HT=3, 07-28-1E

NOTE: 3 DMS HIDDEN

Fig. 36
 Powhatan #5 & SRC-11 HD
 460°C, 1600 psig H₂
 HT=3, 07-30-1E

NOTE: 2 OBS HIDDEN

Fig. 37
 Powhatan #5 & SRC-11 HD
 460°C, 1600 psig H₂
 HT=3, 08-12-1E

NOTE: 3 DIS HIDDEN

Fig. 38
 Powhatan #5 & SRC-11 HD
 460°C, 1600 psig H₂
 HT=15, 08-13-1E

NOTE: 3. HRS. WIDEN

Fig. 39
 Powhatan #5 & SRC-11 HD
 460°C, 1200 psig H₂
 HT=3, 08-16-1E

NOTE: 3 DSS WIDEN

Fig. 40
 Powhatan #5 & SRC-11 HD
 460°C, 1200 psig H₂
 HT=15, 08-19-1E

NOTE: 2 OBS HIDDEN

Fig. 41.
Powhatan #5 & SRC-II HD
460°C, 1200 psig H₂
HT=15, 08-22-1E

NOTE: 1 OBS MINIMUM

Fig. 42
 Powhatan #5 & SRC-11 HD
 460°C, 1200 psig H₂
 HT=3, 08-23-1E

NOTE: 2 OBS HIDDEN

● ● ● ● ●

NOTE :

Fig. 44.
 Powhatan #5 & SRC-11 HD
 460°C, 1200 psig N₂
 HT-3, 09-09-1E

NOTE: 2 OBS HIDDEN

Fig. 45
Powhatan #5 & SRC-11 HD
460°C, 1600 psig N₂
HT=15, 09-06-1E

Elapsed Time (Hours)	Value (Y-axis)
0.0	0
0.0	10
0.0	20
0.0	30
0.0	40
0.0	50
0.0	60
0.0	70
0.0	80
0.25	18
0.3	18
0.35	20
0.35	22
0.35	24
0.4	22
0.4	24
0.45	22
0.5	24
0.55	22
0.6	24
0.7	22
0.8	24
0.9	22
1.0	24
1.1	25

NOTE: 2 OBS HIDDEN

Fig. 46
 Powhatan #5 & SRC-11 HD
 460°C, 1200 psig N₂
 HT=15, 09-11-1E

LEGEND: A = 1 OH%, H = 2 OH%, FVC.

A11 Powhatan #5 ESR Experiments

2 DRS HAD MISSING VALUES (R= 0.01, R1= 0.01) IN RANGE

7 HAS HIDDEN

PLOT OF CSCNONTEMP SYMBOL IS VALUE OF GAS

Fig. 48
Powhatan #5 and SRC-II HD
1200 and 1600 psig

NOTE: 2 OBS HAD MISSING VALUES OR WERE OUT OF RANGE 48 OBS HIDDEN

PLOT OF C5CON%TEMP SYMBOL IS VALUE OF GAS

Fig. 49
Powhatan #5 and SRC-II HD
1200 and 1600 psig

NOTE: 62 GRS H111FN

PLOT OF CSCON*TEMP SYMBOL IS VALUE OF GAS

Fig. 50
Powhatan #5 and Tetralin
1200 and 1600 psig

NOTE: 42 UNS HIDDEN

PLOT OF CSCON*MTMP SYMBOL IS VALUE OF GAS

Fig. 51
Powhatan #5 and Tetralin
1200 and 1600 psig

NOTE: 95 OBS HIDDEN

MATERIAL BALANCE DATA BANK
SOLVENT=TF7 TEMP=400

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PLOT OF DELORTIME SYMBOL USED IS O
PLOT OF ASPHORTIME SYMBOL USED IS A
PLOT OF CONVORTIME SYMBOL USED IS C

Fig. 52
Conversion Data for Powhatan #5
and Tetralin Autoclave Exp.
400°C

NOTE: O OBS HIDDEN

PLOT OF DELORTIME SYMBOL USED IS O
 PLOT OF ASPHORTIME SYMBOL USED IS A
 PLOT OF CONVORTIME SYMBOL USED IS C

Fig. 53
 Conversion Data for Powhatan #5
 and Tetralin Autoclave Exp.
 460°C

NOTE: 16 OILS HIDDEN

PLOT OF DILORTIME SYMBOL USED IS O
 PLOT OF ASPHORTIME SYMBOL USED IS A
 PLOT OF CINVRTIME SYMBOL USED IS C

Fig. 54
 Conversion Data for Powhatan #5
 and SRC-II HD Autoclave Exp.
 400°C

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

PLOT OF OIL*RTIME SYMBOL USED IS O
 PLOT OF ASPH*RTIME SYMBOL USED IS A
 PLOT OF CONV*RTIME SYMBOL USED IS C

Fig. 55
 Conversion Data for Powhatan #5
 and SRC-II HD Autoclave Exp.
 460°C

NOTE: 4 OBS HAD MISSING VALUES OR WERE OUT OF RANGE 4 OBS HIDDEN

PLOT OF OIL*RTIME	SYMBOL USED IS O
PLOT OF ASPH*RTIME	SYMBOL USED IS A
PLOT OF CONV*RTIME	SYMBOL USED IS C

Fig. 56
Conversion Data for Powhatan #5
and Naphthalene Autoclave Exp.
460°C

**% CONVERSION VS RESIDENCE TIME
FOR SHAKEN AND NON-SHAKEN RUNS
460°C/H₂ GAS 11.0 MPa (1600 psig)
POWHATAN#5 AND TETRALIN**

Fig. 57
Shaken and Nonshaken
Autoclave Experiments. Per-
cent Conversion vs. Time.