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(DE84013283)

# HETEROFUNCTIONALITY INTERACTION WITH DONOR SOLVENT COAL LIQUEFACTION

Final Progress Report for the Period August 1982—April 1984

By
D. C. Cronauer

May 1984
Date Published

Work Performed Under Contract No. FG22-82PC50782

Gulf Research & Development Company
Pittsburgh, Pennsylvania

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Distribution Category UC-90d

# HETEROFUNCTIONALITY INTERACTION WITH DONOR SOLVENT COAL LIQUEFACTION

FINAL PROGRESS REPORT
August 1982-April 1984

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GR&DC Contract No. 625CL106
File No. FT07
Date Published--May 1984

Prepared for the United States Department of Energy
Under Contract No. DE-FG22-82PC50782

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# ABSTRACT

This project was undertaken to understand the role of the coal liquefaction solvent through a study of the interaction between the hydrogen donor solvent characteristics and the heterofunctionality of the solvent. Specifically, hydroxyl- and nitrogen-containing solvents were studied and characterized.

The polar components of coal liquefaction solvents have been isolated using activated ion exchange resins. The OH-concentrate of SRC-II contains primarily one- and two-ring phenolic compounds consisting of phenol (~4%), methyl phenols (~9%), $C_2$ to $C_5$ phenols (~9%), and indanols (~8%). Only 0.4% are naphthols. The total aromaticity of this fraction is about 77%. The aliphatic groups consist of methyl groups (26% of the H), long-chain alkyls (average of five carbons at 17% of the H), and a fairly substantial level of hydroaromatics (6% of the H). There is also present a nominal level (1%) of methylene bridges between rings. The SRC-II N-concentrate has about an equivalent aromaticity at 72%, and its nominal ring size is between 1 and 2. It contains both nitrogen and hydroxyl functionality (but apparently not on the same ring). The alkyl groups are divided among methyl groups (20%), long-chain alkyls (average of three carbons at 23% of the H), and a high level of hydroaromatics (12%). Anthracene oil, which is derived as a coke oven by-product, has a N-concentrate with a high level of aromaticity (95%) and an apparent ring size of 1 to 2. The N-concentrate again contains both nitrogen and hydroxyl functionality. The aliphatic carbon is divided among methyl groups (16% of the H), short-chain aliphatics (1.4%), and a low level of hydroaromatics (2.1%).

Coal liquefaction experiments were carried out using both micro-autoclave and CSTR units. In the micro-autoclave experiments conducted at 450°C, 1-naphthol has been found to be a surprisingly good solvent to convert coal to THF solubles. It is considerably poorer than tetralin but significantly better than the efficient hydrogen shuttling agent phenanthrene. Loss of solvent 1- and 2-naphthol by adduction to the coal liquids is a major

problem, as indicated by a loss of oil yield in that less oil is recovered than originally fed as solvent. This occurs even in solutions containing substantial amounts of tetralin. Series of experiments were carried out at 450°C in a continuous feed stirred-tank reactor (CSTR) to observe the effect of adding phenolics to anthracene oil (AO) and SRC-II recycle solvents. At nominal space times of 4 and 15 minutes, the levels of conversion (THF solubles) were significantly higher with SRC-II recycle solvent than with anthracene oil. The addition of phenol to AO at a ratio of 5/65 resulted in a nominal increase in coal conversion to THF solubles, but the amount of asphaltenes more than doubled resulting in a sizable net loss of solvent. The addition of m-cresol to both AO and SRC-II solvents had a positive effect on coal conversion.

Hydroaromatics having nitrogen functionality should be good solvents for coal liquefaction considering their effective solvent power, ability to penetrate and swell coal, and their ability to readily transfer hydrogen, particularly in the presence of oxygen functionality. However, these benefits are overshadowed by the strong tendency of the nitrogen-containing species to adduct with themselves and coal-derived materials. As demonstrated in microautoclave experiments in which nitrogen compounds including tetrahydroquinoline (THQ), phenanthroline, acridine, etc., are used as solvents, high levels of asphaltenes are recovered. These asphaltenes have high nitrogen contents. The level of adduction is further demonstrated by observing the attachment of labeled species into both preasphaltene- and tetrahydrofuran-insoluble fractions. The use of THQ in CSTR units appears to be of some advantage in improving a poor donor solvent. Moreover, it appears that this light solvent is readily stripped into the vapor space, thereby limiting the extent of adduction reactions.

In the supercritical extraction of Pittsburgh Seam coal, a hydrogen donor-water mixture with hydrogen donor in dilute concentration (10 wt%) is an effective solvent for high levels of conversion. Higher concentrations of donor may not be beneficial. The addition of a hydrogen atmosphere increases the conversion for solvents which are not good hydrogen donors, although it is not as effective as that of using a good hydrogen donor. The use of nitrogen-containing solvents (quinoline and tetrahydroquinoline) results in high levels of solvent adduction as indicated by high nitrogen levels in the heavy product fractions.

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## OBJECTIVE AND SCOPE OF WORK

The objective of this program is to understand the role of the coal liquefaction solvent through a study of the interaction between the hydrogen donor solvent characteristics and the heterofunctionality of the solvent. In particular, phenolic- and nitrogen-containing solvents are being studied with respect to their effect on coal liquefaction in hydrogen donor systems and the kinetics thereof. A considerable effort is being directed toward solvent adduction, both the extent and the point(s) of attachment of specific solvent molecules to the coal liquids.

### Subtasks 1 and 2: Isolation and Analysis of Acidic and Basic Components

The phenolic- and nitrogen-containing components of a representative coal liquefaction will be recovered using appropriate ion exchange resins. The bulk solvent and distillate cuts will be treated with Amberlyst-15 resin (Rohm and Haas) to remove a major portion of the basic nitrogen-containing compounds. The nitrogen-containing fractions will be recovered using appropriate solvents. In a similar manner, the isolation of phenolics and stripped solvents will be obtained using Amberlyst IRA-904 resin. Samples of the various fractions will be analyzed using techniques reported in the literature or developed at GR&DC.

### Subtask 3: Liquefaction Experiments Using Batch Units

Coal liquefaction experiments will be done using a combination of micro-unit and 1-liter autoclaves, all of which are currently in operation and available for this program. The batch reactors (2) are of 1-liter stirred type with the capability of rapidly injecting coal and/or reactants after the bulk reactor system is at temperature.

Experiments will be done to observe the effects of the phenolic- and nitrogen-containing fractions on coal liquefaction conversion at about three levels of hydrogen donor solvent capacity. The stripped solvent will also be run as a standard. Experiments will also be undertaken using model compounds having functional groups typical of those expected in recycle coal liquefaction solvents, including quinoline, tetrahydroquinoline, carbazole, phenol, and 1-naphthol, all having $^{13}C$ labels to facilitate determination of the amounts of adduction and the points of attachment to the coal liquids. Gel permeation chromatography will be used to provide estimates of molecular weights and the amounts of adduction by hydrogen bonding.

Experimentation will also be done with a supercritical aqueous system with various nitrogen-containing solvents to observe coal conversion and solvent adduction. This work will be undertaken at the University of Pittsburgh with a major portion of the product characterization at GR&DC.

Subtask 4: <u>Liquefaction Experiments Using Bench Units</u>

About 15 additional bench-scale runs will be made using (1) solvents treated to remove phenolics or nitrogen compounds, (2) stripped solvents with various levels of the previously removed polar compounds, and (3) solvents with added labeled compounds. Emphasis will be placed on the interaction of hydrogen donor capacity and the effectiveness of the polar component.

Subtask 5: <u>New Research Concepts</u>

Effort will be directed to using the information gained in the above studies to formulate leads for new coal conversion concepts.

## DETAILED DESCRIPTION OF TECHNICAL PROGRESS

## I. SUBTASKS 1 AND 2: Isolation and Analysis of Acidic and Basic Components

The isolation of bulk quantities of basic components from both raw anthracene oil (AO) and SRC-II recycle (product) solvent has been done using Rohm and Haas Amberlyst-15 ion exchange resin. The recovery of acidic components from a sample of SRC-II recycle solvent was accomplished by the use of Rohm and Haas IRA-904 resin. These basic and acidic fractions underwent elemental analysis with subsequent spectroscopic characterization and GC/MS analysis. In addition, selected samples were used as additives in coal liquefaction experiments.

Prior to presenting a detailed discussion, it is noted that the A-15 resin is not exclusive in retaining only species containing basic functional groups. In addition, the resin is somewhat size exclusive in that large molecules are only held at the surface and do not penetrate into the resin. Therefore, in the preparation of a bulk nitrogen concentrate (N-CONC), a high ratio of resin to oil was used to retain as much as possible. (Reference is made to the various Quarterly Reports of DOE Contract DE-AC17-80BC10313 concerning the removal of nitrogen-containing species from shale oils.)

### Experimental

### 1. Solvents and Preparation

Acidic and basic concentrates were recovered by contacting samples of anthracene oil and SRC-II derived recycle solvent with appropriate anionic and cationic resins with subsequent stripping with methanol solutions of high acid or base functionality. The resins were obtained from Rohm and Haas Co., and they were activated prior to use to ensure high functionality. The resins were IRA-904 and Amberlyst-15, respectively. The anthracene oil was used as received from Reilly Tar and Chemical Co., and the SRC-II solvent was recovered product from the liquefaction of Pittsburgh Seam coal at The Pittsburg & Midway Coal Mining Co. facility at Tacoma, Washington. The analyses of these oils are given in Table 1.

Similar procedures were used in contacting the solvents with both ion exchange resins. The procedure used with IRA-904 is described below.

1. As-received IRA-904 was contacted with about a 10x excess of 2.2% aqueous NaOH overnight.
2. It was flushed ten times with distilled water to a neutral pH and subsequently flushed three times with acetone.
3. It was then dryed over the weekend with a nitrogen flow.
4. The resin was contacted with SRC-II solvent at a ratio of 0.43/1.0, overnight with limited agitation.
5. After filtration, the resin bed was flushed with pentane. The flush liquid was stripped and combined with the filtrate.
6. The resin was contacted over the weekend with a methanol solution saturated (cold) with $CO_2$.
7. The solution was removed by filtration, and it was stripped to remove methanol.
8. The resin from step 7 was then contacted with a 2.5% solution of formic acid in methanol.
9. The mixture was filtered and the filtrate was stripped to remove formic acid and methanol.

The recovery of OH-concentrate was 4.1% based on the feed solvent (about 91% from the $MeOH \cdot CO_2$ step), and the resin loading was about 0.094 g OH-concentrate per g resin.

The analyses of the OH-concentrate and treated solvent are given in Table 1. Obviously only a portion of the total acids was isolated.

## Table 1

## Analyses of Solvents

| Solvent | Anthracene Oil | | SRC-II | | | |
|---|---|---|---|---|---|---|
| Treatment | Raw AO | Nitrogen Concentrate | Raw SRC-II | Nitrogen Concentrate | OH Concentrate | OH Reduced |
| Chemical Analysis (wt%) | | | | | | |
| Carbon | 91.17 | 86.73 | 87.25 | 83.95 | 81.98 | 88.44 |
| Hydrogen | 5.84 | 5.99 | 8.69 | 7.55 | 7.85 | 8.45 |
| Nitrogen | 1.03 | 3.80 | 0.88 | 4.32 | 1.10 | 0.90 |
| Oxygen | 1.33 | 2.91 | 2.82 | 3.24 | 8.86 | 1.88 |
| Sulfur | 0.63 | 0.57 | 0.36 | 0.94 | 0.21 | 0.33 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Specific Gravity (60/60) | 1.132 | - | 1.020 | - | - | - |

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The treatment of the samples of AO and SRC-II solvent with Amberlyst-15 was similar. The resin was activated with a dilute (3 wt%) HCl aqueous solution, flushed with water and acetone, and then dryed. The bulk samples were prepared at a resin-to-solvent ratio of about 0.6/1.0 to ensure resin saturation. The resin was stripped using a concentrated $NH_3$•methanol solution. The recovery of N-concentrate from the SRC-II was about 17.5 wt% with a resin loading of 0.35 g/g resin. The recovery was about 18 wt% in the case of AO, and the loading was about 0.37 g/g resin.

## 2. NMR Analyses

Samples of the N- and OH-concentrates were dissolved in $CDCl_3$, and TMS was added as an internal reference. Spectra were run on a Varian Associates XL-200 spectrometer. $^1H$ spectra were run using a 27° flip angle and an acquisition time of 1.3 seconds. $^{13}C$ spectra were run after adding $Cr(acac)_3$ at a concentration of 0.05 M to the sample. The operating conditions were a 90° flip angle, a 0.4-second acquisition time, a pulse delay of 2 seconds, and gated decoupling. This ensured quantitative results for the $^{13}C$ spectra.

## 3. GC/MS Analyses

The typical chromatographic conditions and the mass spectrometer parameters are given below:

### GC/MS Parameters

Chromatograph: Finnigan 9600

Column: 60 m x .24 mm ID fused silica capillary coated with DB-5

Temperature Program: Isothermal at 50°C for 2 min then 4°/min to 250°C, then hold 38 min

Injector Temperature: 260°C

Detector Temperature: 250°C
Interface Temperature: 250°C
Carrier Gas: Helium, ca. 1.5 cc/min
Split: ca. 100:1
Injection Size: 0.2-0.5 μl
Mass Spectrometer: Finnigan 4510
Data System: Incos 2000
Electron Energy: 70 eV
Mass Range: 33-500 amu

## Results and Discussion

The basic concentrates (N-CONC) of anthracene oil and SRC-II desired coal liquefaction product were recovered by treatment of these oils with a strongly acidic ($-SO_3H$) cation exchange resin of Rohm and Haas, Amberlyst-15. Similarly, the acidic concentrate (OH-CONC) of SRC-II solvent was recovered using a strongly basic ($-N(CH_3)_3\cdot Cl$) anion exchange resin, IRA-904. The N-CONC and OH-CONC fractions were released by subsequent treatment of the resins with strong basic ($NH_3\cdot$methanol) or acidic ($CO_2\cdot$methanol and $H_3COOH\cdot$methanol) solutions. The goal of this set of experiments was to produce a maximum of concentrate; therefore, a relatively high loading of solvent to resin was used.

The elemental analyses of the concentrates are given in Table 1. It is noted that the nitrogen contents of the N-CONC's are about four times those of the raw solvent feeds, and there is also an increase in the oxygen contents over those of the raw solvent. Likewise, the oxygen content of the OH-CONC of SRC-II solvent is about three times that of the raw solvent, and there is also a nominal increase in nitrogen content. In summary, the N-CONC and OH-CONC fractions of coal-derived solvents are obviously polyfunctional, and they make up a sizable portion of the liquid.

The concentrates were characterized by both spectroscopic and GC/MS analyses. These results will be reported separately below and subsequently combined in the Summary Section.

## 1. Spectroscopic Analysis of the SRC-II Hydroxyl Concentrate

The $^1H$ spectrum of this fraction is shown in Figure 1, and the results are summarized in Table 2. This fraction has aromatic, hydroxyl, hydroaromatic, and alkyl substituent functionality. The aromatic region spans from 6 ppm to 8.6 ppm and cannot be easily divided into mono, di, and triaromatics due to the presence of large amounts of oxygen and some nitrogen. These aromatic hydrogens represent 39.7% of the total hydrogen. Even though the nitrogen content is relatively low (1.1%), the small amount of intensity between 8.4 ppm and 8.6 ppm in the aromatic region can be assigned to protons ortho to the nitrogen in pyridine-type structures. These protons represent less than 0.3% of the hydrogen.

There is a broad resonance at 5.4 ppm which can be assigned to hydroxyl hydrogen. This accounts for 11.3% of the hydrogen in the spectrum. There is a sharp signal at 3.4 ppm which is due to residual methanol left in the fraction.

In the region around 3.4 ppm are several smaller signals which can be assigned to methylene bridges between aromatic rings. These methylene bridge hydrogens represent 0.9% of the hydrogen present.

The main type of aliphatic substituent is methyl groups on aromatic rings as evidenced by the sharp signals at 2.2, 2.5, and 2.8 ppm. These signals account for 25.7% of the hydrogen present. There are also some (16.7% of hydrogen) long-chain aliphatic substituents with an average chain length of five carbons. There is also a broad signal at 1.7 ppm which is indicative of hydroaromatic protons. Together with an equivalent amount of intensity from the signal at 2.8 ppm, about 5.6% of the hydrogen is hydroaromatic.

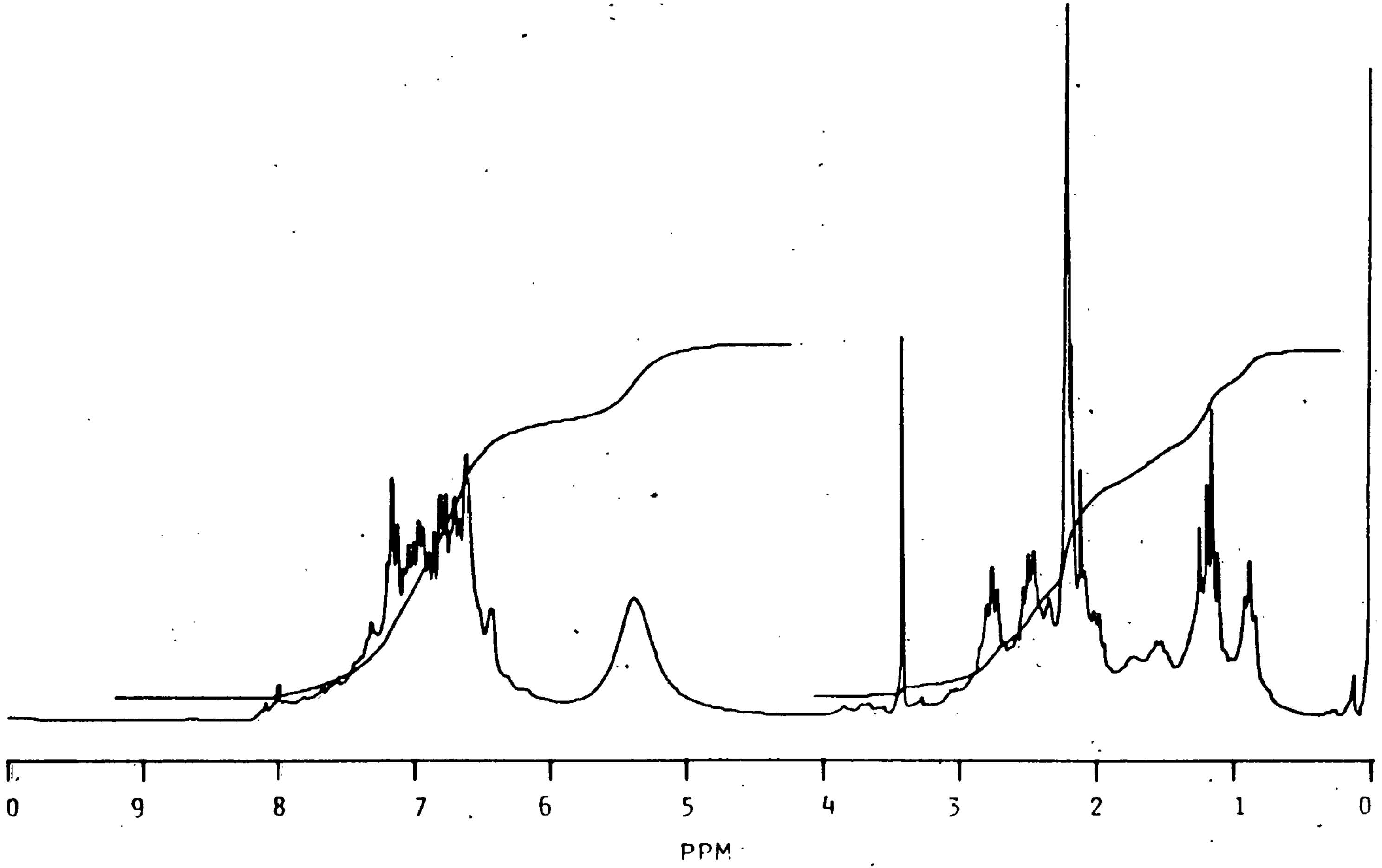

FIGURE 1 $^1$H NMR SPECTRUM OF SRC-II DERIVED HYDROXYL-CONCENTRATE

## Table 2

## $^1H$ NMR Analysis of SRC-II Hydroxyl Concentrate

| | | |
|---|---|---|
| Aliphatic Hydrogens | | |
| Methylene bridge | 0.9% | |
| Methyl | 25.6 | |
| Hydroaromatic | 5.6 | |
| Long alkyl chain (i.e., $C_5$) | 16.7 | |
| Total aliphatic | | 48.7 |
| Hydroxyl Hydrogens | | 11.3 |
| Aromatic Hydrogens | | |
| Aromatic hydrogen ortho to N | 0.3 | |
| Others | 39.7 | |
| Total aromatic | | 40.0 |
| Total | | 100.0% |

The $^{13}C$ NMR spectrum, given in Figure 2, shows this fraction to have an aromaticity of 77.4%. The ratio of aromatic carbons to hydroxyl-bearing carbons is 8.5:1. This is calculated from the ratio of the area of the aromatic region to that of the area of the region from 152 ppm to 156 ppm, which is due to hydroxyl-bearing carbon. The ratio of total carbon to oxygen is 10.9:1, which is reasonably consistent with that of the elemental carbon-to-oxygen analysis of 12.3:1. As a check, the amount of aromatic hydroxyl-bearing carbon was calculated using the aromatic region from 110 ppm to 117 ppm which is due to unsubstituted carbons ortho to a hydroxyl group. This area is divided by 2 to get the amount of hydroxyl-bearing carbon. From this calculation the ratio of aromatic carbon to hydroxyl carbon is 10.9:1, and the ratio of total carbon to oxygen is 14.1:1. The calculated ratio is expected to be higher using the observed ortho carbons because not all of the ortho carbons are being counted; namely, those that are substituted are shifted out of the range being used.

If it is assumed that hydroxyl-bearing carbons are not discriminated against during data acquisition, then the difference between the two values for the ratio of aromatic carbon to hydroxyl-bearing carbon gives a measure of the amount of ortho substitution. The difference between the two on an area basis indicates that 22.2% of the hydroxyl-bearing carbons have ortho substituents. Of that 22.2%, 13.3% can be accounted for by ortho methyl groups which have their signals at 15-16 ppm. The remaining 8.9% may be due to naphthols. The distinguishing ortho signals for 1- and 2-naphthol are at 108.8 ppm and 109.6 ppm, respectively. To verify that 1- and 2-naphthols would be seen, a sample of the hydroxyl concentrate was doped with 19.5% 2-naphthol by weight and the $^{13}C$ NMR spectrum obtained. The ortho signal was seen at 110.5 ppm with an estimated 2-naphthol content of 18.1%, thereby verifying the experimental technique. If the area from 111 ppm to 107 ppm is considered to be due to 1- and 2-naphthols, a total of 4.5% of the hydroxyl carbon is present as 1- and 2-naphthols which are not ortho substituted. The remaining 4.5% are either ortho-substituted naphthols or other ortho-substituted phenols.

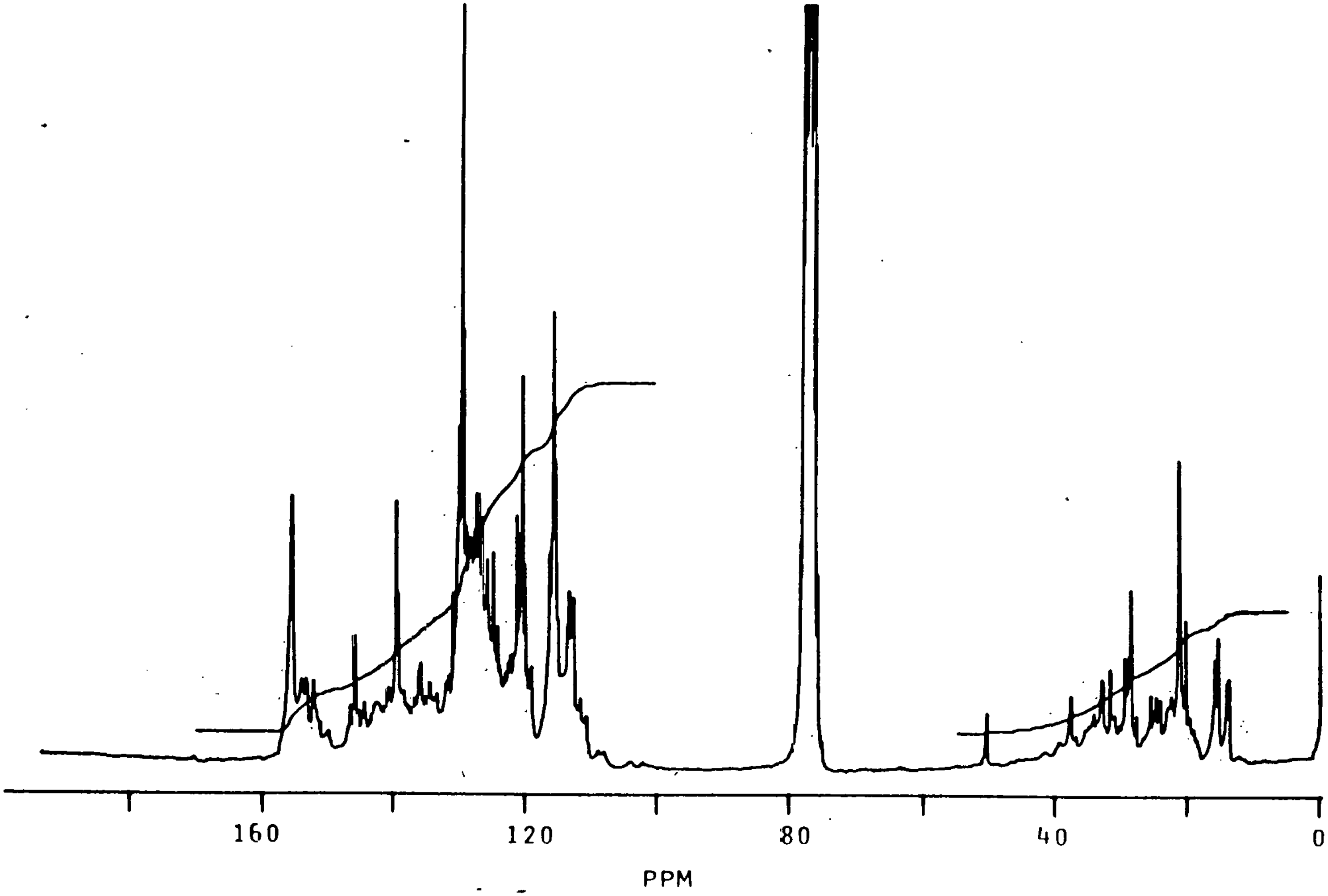

FIGURE 2 $^{13}$C NMR SPECTRUM OF SRC-II DERIVED HYDROXYL-CONCENTRATE

Meta-substituted hydroxyl groups in single-ring phenols have hydroxyl-bearing carbon signals at 154-155 ppm. The largest signal in the region from 152 ppm to 155 ppm is at 155.6 ppm, and it represents 44.4% of the hydroxyl groups. Methyl groups which are meta and para to hydroxyl groups cannot be distinguished from each other on the basis of the chemical shift of the methyl groups but must be calculated from the position of the hydroxyl carbon. Therefore, the remaining 33.4% of the hydroxyl groups is believed to be para substituted. This value can be checked from the positions of the unsubstituted ortho carbons. Meta-substituted hydroxyl groups have one ortho carbon signal at 113 ppm because one ortho carbon is also para to an alkyl group. From the signals at 113 ppm it appears that 42% of the hydroxyl carbons are meta substituted. The signals at 113.5-117 ppm include ortho carbons from all other hydroxyl-substitution patterns, and therefore, they cannot be used as a diagnostic tool for any single isomer.

Since the observed ratio of aromatic carbons to hydroxyl-bearing carbons is 8.5:1 and every molecule theoretically has an acidic hydroxyl group, the OH-CONC consists of a mixture of one- and two-ring systems. Because only a small amount of the concentrate has been identified as naphthols, the remainder of two-ring systems should be comprised of single rings joined by short alkyl bridges. The $^{1}H$ spectrum shows evidence for such methylene bridges. There is also a small amount of intensity in the carbon spectrum between 40 ppm and 45 ppm which is the region for methylene bridges. This intensity accounts for 1.4% of the total carbon, which would amount to about 20% of the carbons present as substituted diphenylmethane-type species.

If ethyl bridges between rings were found, they would have signals in the region of 38 ppm. There is a sharp signal in the spectrum at 37.8 ppm which can be assigned to either ethyl bridges or to methylene carbons on long chains attached to aromatic rings. This area represents 2.0% of the total carbon intensity. Some of the remaining alkyl groups are found as methyl groups attached to aromatic rings (5.7%) and as hydroaromatic structure (7.3%). The amount of long-chain alkyl carbon cannot be readily determined from the $^{13}C$ spectrum but can be estimated from the $^{1}H$ spectrum at 5-6%.

The total alkyl-substituted aromatic carbon is 12.8%. This was determined by summing the methylene bridge area times 2, the ethyl bridge area, one half the hydroaromatic area, and the methyl groups on aromatic rings area. The total nonprotonated aromatic carbon is difficult to determine from the normal spectral regions due to the presence of hydroxyl groups which induce an upfield shift to the carbons ortho and para to it. To estimate how many signals in the aromatic region fall outside of the normal region for nonprotonated carbons, a NORD-CDRE (noise off-resonance decoupled convolution difference resolution enhancement) experiment was run. We observed a small number of signals at 125-126 ppm in addition to those which appeared below 129.5 ppm. These upfield signals are due to bridge carbons which are ortho or para to hydroxyl groups in 1- and 2-naphthols. The total bridge carbon is 15.5% as determined from the difference between the total nonprotonated carbon and the alkyl-substituted carbon plus hydroxyl-bearing carbon (11.8%). Therefore, the level of protonated aromatic carbon is 58.5% of the aromatic carbon. A summary of the above $^{13}C$ NMR results is given in Table 3.

## 2. GC/MS Analysis of the SRC-II Hydroxyl Concentrate

The hydroxyl concentrate of SRC-II was added to a small amount of methylene chloride and mesitylene and analyzed by capillary GC/MS. The reconstructed ion chromatogram (RIC) of the OH-CONC fraction is given in Figure 3. The majority of the components are concentrated in the low molecular weight region (<170 MW) following a broad, poorly resolved envelope. In the following discussion, the baseline was normalized in calculating the peak areas and mesitylene was used as an internal standard.

The greatest portion (22%) of the chromatographic peaks other than solvent was phenol (4%) or alkyl-substituted phenols (18%). Methyl phenols (9%) account for approximately half of the alkyl-substituted phenols with the remainder (9%) being $C_2$ to $C_5$ phenols. Other peaks included $C_9H_{10}O$ isomers (4%) and $C_{10}H_{12}O$ isomers (4%) which are probably indanols and methyl indanols. A hydroxybiphenyl (.4%) and carbazole (1.2%) were identified. Polynuclear aromatic hydrocarbons accounted for 7% of the peaks. The largest of these was methyl phenanthrene (2%). About 60% of the sample was included in the small peaks and in the broad envelope.

## Table 3

## $^{13}$C NMR Analysis of SRC-II Hydroxyl Concentrate

| | | | |
|---|---|---|---|
| Aliphatic Carbons | | | |
| Methylene bridges between rings | | 1.4% | |
| Other carbons to aromatic rings | | 2.0 | |
| Methyl groups attached to rings | | 5.7 | |
| Hydroaromatic carbons | | 7.3 | |
| Long-chain alkyls (from $^1$H) (est.) | | 6.2 | |
| Total aliphatic carbons | | | 22.6% |
| Aromatic Carbons (Ar-C) | | | |
| Ortho methyl groups (to OH) | 3.0 | | |
| Naphthols | 1.0 | | |
| Unknown ortho substituents | 0.9 | | |
| Total substituted Ar-C's ortho to OH groups | | 4.9 | |
| Substituted Ar-C's meta to OH groups | | 9.9 | |
| Substituted Ar-C's para to OH groups | | 7.4 | |
| | | | 22.2* |
| Hydroxyl substituted Ar-C | | | 9.3 |
| Protonated Ar-C | | | 45.9 |
| Total | | | 100.0 |

---

*This is also subdivided as follows:

| | |
|---|---|
| Alkyl-substituted Ar-C | 10.0 |
| Aromatic bridge carbons | 12.2 |
| Total | 22.2 |

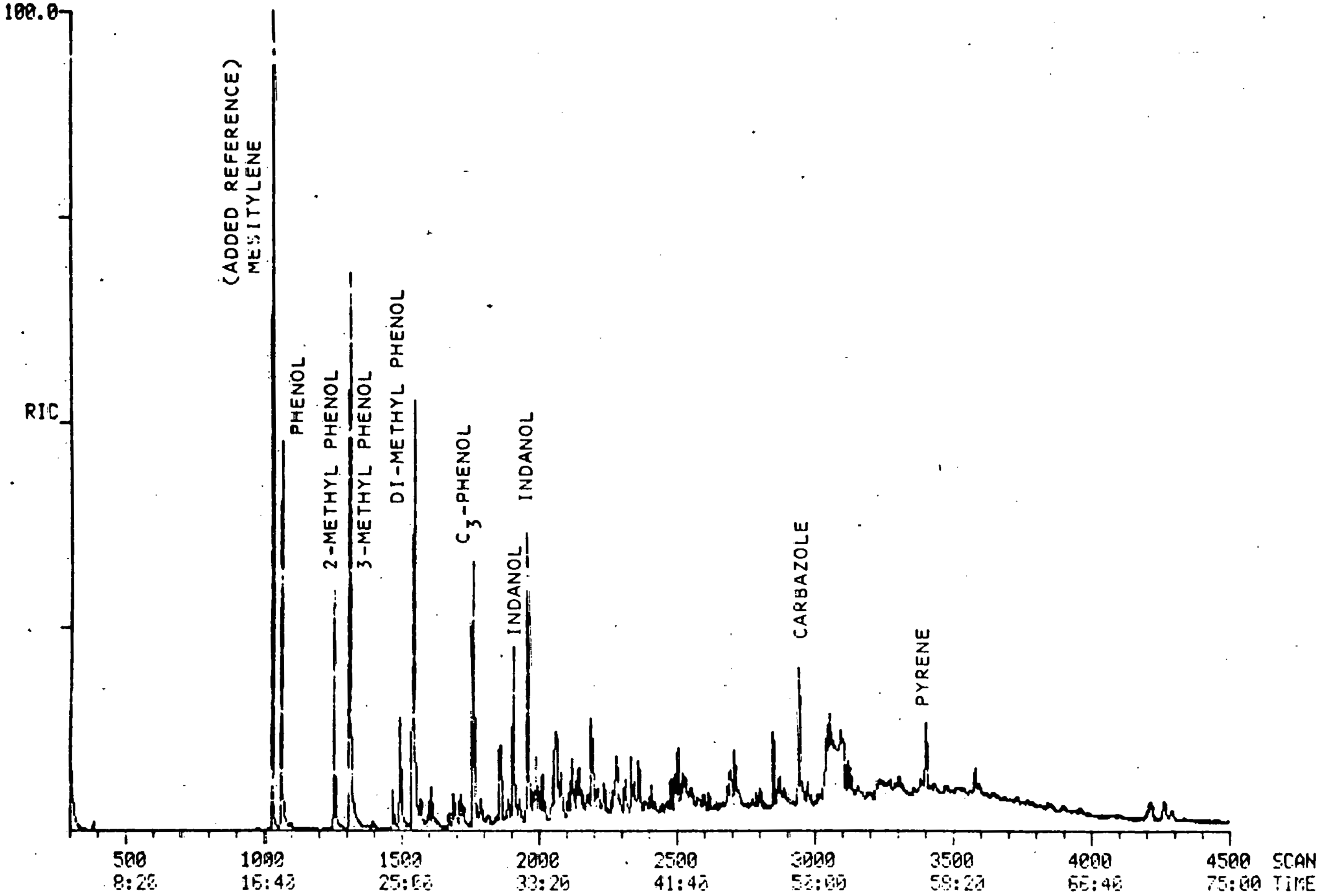

FIGURE 3 GC/MS SCAN OF SRC-II DERIVED HYDROXYL-CONCENTRATE

### 3. Spectroscopic Analysis of the SRC-II Nitrogen Concentrate

The $^1H$ and $^{13}C$ NMR spectra for this fraction are shown in Figures 4 and 5, respectively. Examination of the $^1H$ spectrum shows that there are significant differences between it and that of anthracene oil. There is a larger amount, 65.6%, of aliphatic protons. There are signals at 0.91 ppm and 1.20 ppm indicating alkyl chains with an average carbon number of three. This long-chain hydrogen comprises 23.4% of the hydrogen. The broad signal at 1.72 ppm and part of the signal at 2.75 ppm are assignable to hydroaromatic structures like tetralin. These structures represent 12.3% of the hydrogen, which is about twice that in the OH-CONC. Much of the remaining aliphatic hydrogen is seen in signals at 2.25, 2.41, and 2.75 ppm. These sharp signals are due to methyl groups on aromatic rings and comprise 19.9% of the hydrogen. The remaining broad aliphatic absorption, which stretches from 2.95 ppm to 4.0 ppm, can be assigned to methylene groups $\alpha$ to aromatic rings either in the form of methylene bridges or as part of long alkyl chains. These methylene hydrogens comprise 10% of the hydrogen. These results are summarized in Table 4.

The $^{13}C$ spectrum shows an aromaticity of 71.5%. The carbon-to-oxygen ratio as determined from elemental analysis is 34.5:1, and the carbon-to-nitrogen ratio is 22.7:1. There is evidence for phenols from the signals at 153-155 ppm and 112-115 ppm. By comparison with the INEPT spectrum of this fraction, it is possible to see some possible division between protonated carbons, due to pyridine and quinoline systems, and nonprotonated carbons, due to hydroxyl carbons, at 153 ppm. The hydroxyl-bearing aromatic carbons represent a maximum of 5.7% of the aromatic carbon. This accounts for more than the amount of oxygen determined by elemental analysis indicating that there are also some alkyl-substituted nitrogen compounds in this region. These hydroxyl groups do not appear to be incorporated into hydroxypyridines since there are no signals upfield of 110 ppm or downfield of 160 ppm. If bifunctional molecules are present, they are present as 3-hydroxypyridines or as hydroxyquinolines where the hydroxyl group is on a separate ring from the nitrogen-containing ring.

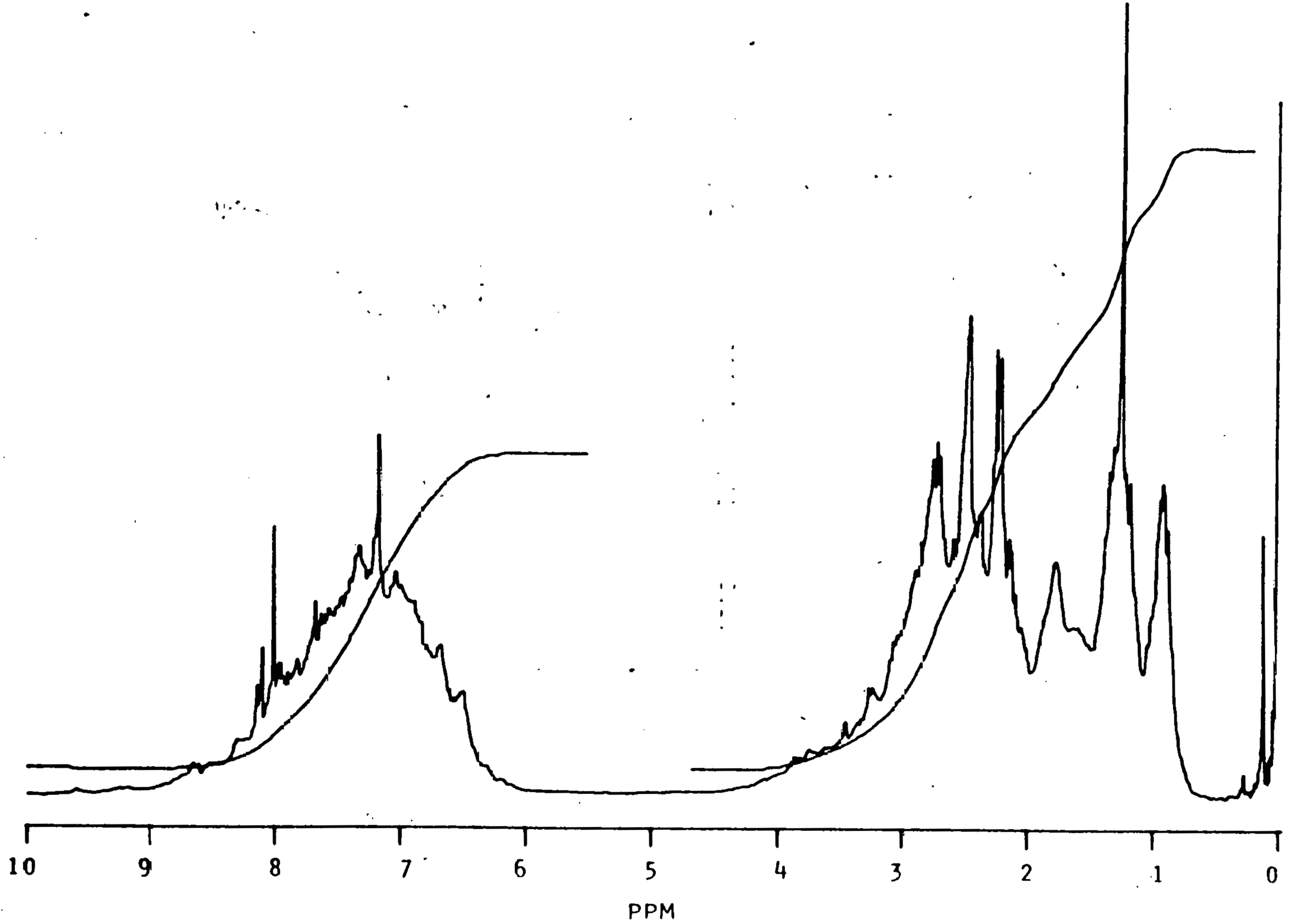

FIGURE 4 $^{1}$H NMR SPECTRUM OF SRC-II DERIVED NITROGEN-CONCENTRATE

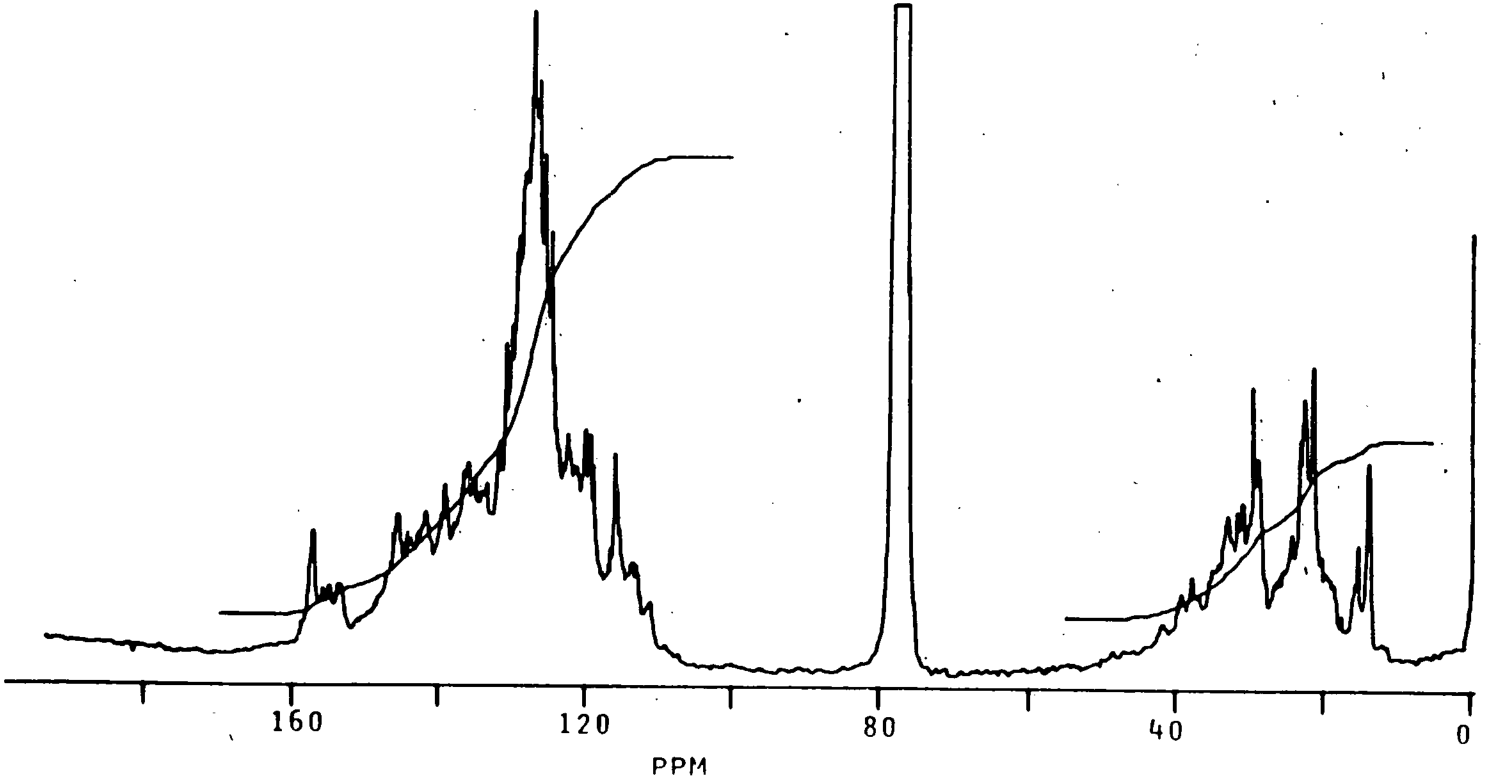

FIGURE 5 $^{13}C$ NMR SPECTRUM OF SRC-II DERIVED NITROGEN-CONCENTRATE

## Table 4

## $^1H$ Analysis of SRC-II Nitrogen Concentrate

| | | |
|---|---|---|
| **Aliphatic Hydrogens** | | |
| Long alkyl chain | 23.4% | |
| Hydroaromatic | 12.3% | |
| Methyl | 19.9% | |
| Methylene | 10.0% | |
| Total aliphatic | | 65.6 |
| **Aromatic Hydrogens** | | |
| Aromatic hydrogens ortho to N | 0.8 | |
| Others | 33.6 | |
| Total aromatic | | 34.4 |
| Total hydrogens | | 100.0% |

There is protonated aromatic carbon between 143.5 ppm and 153 ppm as seen from the INEPT experiment. These protonated carbons must be due to carbons ortho to nitrogen in pyridine ring systems. If all the intensity in this region is due to these structures, then carbons ortho to nitrogen represent 8.6% of the aromatic carbon. However, this accounts for more nitrogen than accounted for by elemental analysis. Therefore, some of the signals of this region are due to alkyl-substituted aromatic carbons. Because the INEPT spectrum is not quantitative, the amount due to alkyl-substituted aromatic carbon can only be determined by an examination of the alkyl substituents.

The predominant type of alkyl substituent is methyl groups on rings. These are seen by the signals at 20 and 16 ppm and represent 32.3% of the alkyl carbon. There are signals in the region of hydroaromatic structure (22-31 ppm) which represents up to 25.8% of the aliphatic structure. This is an artificially high number because there are some long alkyl chains present which will contribute to this region. This long-chain material can represent up to 15.1% of the aliphatic carbon. The remaining aliphatic carbon can be accounted for by carbons next to aromatic rings in alkyl chains and represents 26.9% of the alkyl carbon.

From the alkyl carbon attached to aromatic rings, it is possible to determine the total amount of alkyl-substituted aromatic carbon. A total of 20.5% of the aromatic carbon can be alkyl substituted. This means that the remaining carbon is due to carbons ortho to nitrogen and to bridge carbon. If bridge carbon occurs only in the normal range of 129.5 ppm to 133 ppm, it comprises 8.0% of the aromatic carbon and the carbon ortho to nitrogen represents 7.4%. These results are summarized in Table 5 and are normalized to 100%.

## Table 5

## $^{13}$C NMR Analysis of SRC-II Nitrogen Concentrate

| | | |
|---|---|---|
| **Aliphatic Carbons** | | |
| Methyl groups attached to rings | 9.2% | |
| Hydroaromatic carbon | 7.4 | |
| Long-chain alkyl carbon | 4.3 | |
| Carbons attached to aromatic rings | 7.6 | |
| | | 28.5% |
| **Aromatic Carbons** (Ar-C) | | |
| Ar-C's bearing hydroxyls | 4.1 | |
| Aromatic carbons ortho to nitrogen | 5.5 | |
| Bridge aromatic carbon | 5.7 | |
| Alkyl-substituted aromatic carbon | 14.6 | |
| Protonated aromatic carbon | 41.6 | |
| | | 71.5 |
| | | 100.0% |

## 4. GC/MS Analysis of SRC-II Nitrogen Concentrate

The GC/MS analysis of the SRC-II nitrogen concentrate in methylene chloride resulted in poor separation of components as shown in Figure 6. Numerous peaks were observed. These were distributed on a very broad envelope. It was not possible to effectively isolate and identify all of the individual components, but the following generalizations are noted.

The majority (23%) of the components were polynuclear aromatic hydrocarbons ranging from methyl tetralin ($C_{11}H_{14}$) to pyrene ($C_{16}H_{10}$). These included methyl tetralin, $C_1$-$C_4$ naphthalenes, acenaphthene, fluorene, methyl biphenyl, methyl fluorene, dihydrophenanthrene, phenanthrene, and pyrene. The isolated nitrogen compounds (10%) ranged from substituted pyridines ($C_7H_9N$) to carbazole ($C_{12}H_9N$). These included dimethyl and trimethylpyridine, methyltetrahydroquinoline, dimethylquinoline, and carbazole. The sample also contained methyl phenol (2%). About 65% of the sample was accounted for in the small peaks or the broad envelope.

## 5. Spectroscopic Analysis of the Anthracene Oil Nitrogen Concentrate

To ensure that the spectral analysis of the bulk AO N-CONC sample was representative, two additional samples of N-CONC were prepared using resin to AO ratios of 0.5:1 and 0.25:1. The N-CONC samples were recovered at levels of 18.2 and 8.5% (on feed); this is equivalent to resin loadings of 0.37 and 0.34 g N-CONC/g resin. The nitrogen analyses of the N-CONC samples were 4.1 and 4.9%, respectively. The $^{13}C$ NMR spectra of these samples were essentially direct reproductions of that of the bulk N-CONC sample discussed below.

The $^{1}H$ and $^{13}C$ NMR spectra of the bulk N-CONC (AO) are shown in Figures 7 and 8, respectively. The $^{1}H$ spectrum has 16.2% of its intensity at 2.31 ppm indicative of ortho methyl groups in a pyridine ring system. There is a smaller amount of intensity, 1.4%, in the region due to long-chain material. There is a broad signal at 1.7 ppm indicative of hydroaromatic structure. This signal with an equivalent amount of intensity at 2.8 ppm represents 2.1% of the hydrogen present. The small signals at 3.4 to 3.8 ppm

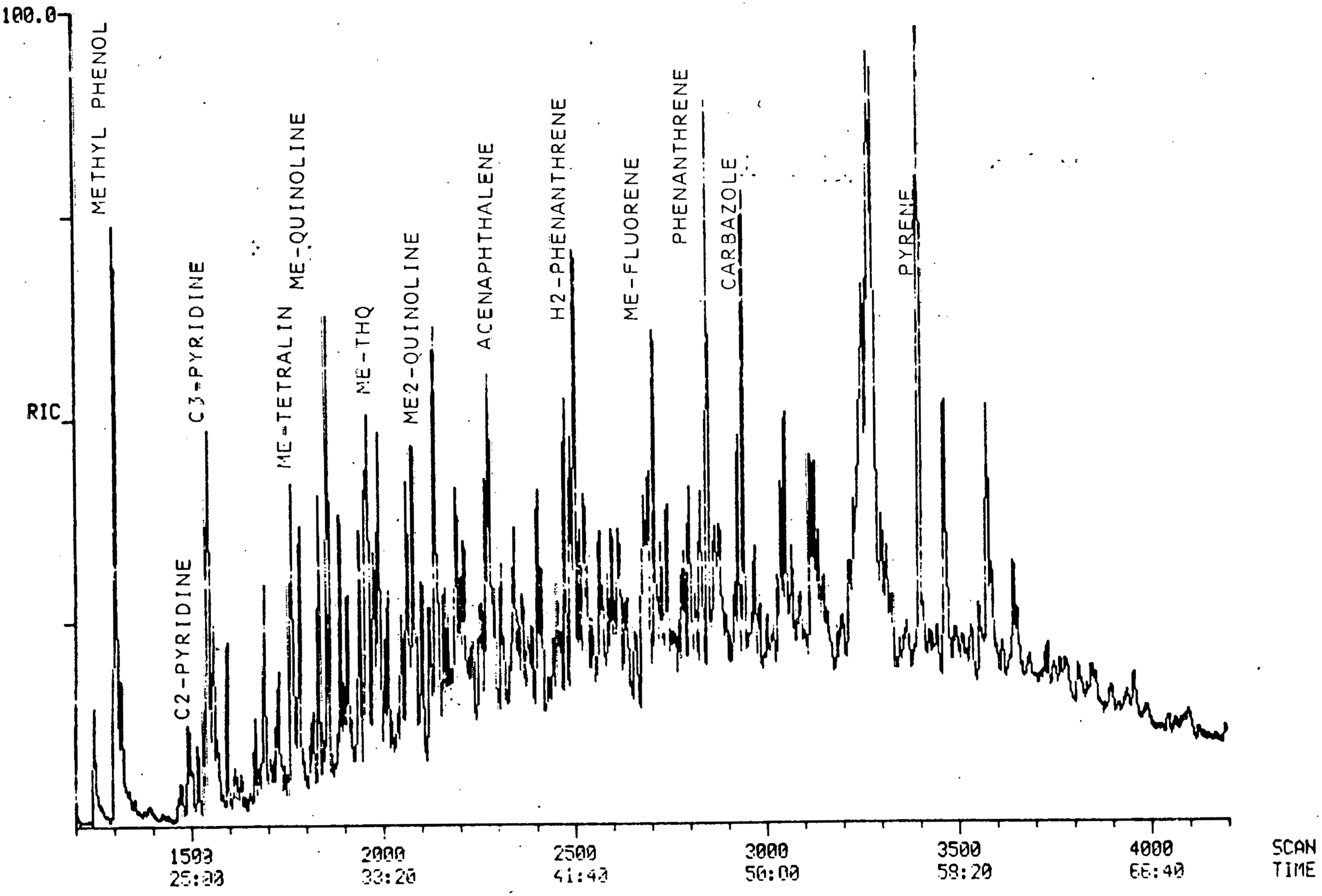

FIGURE 6 GC/MS SCAN OF SRC-II DERIVED NITROGEN-CONCENTRATE.

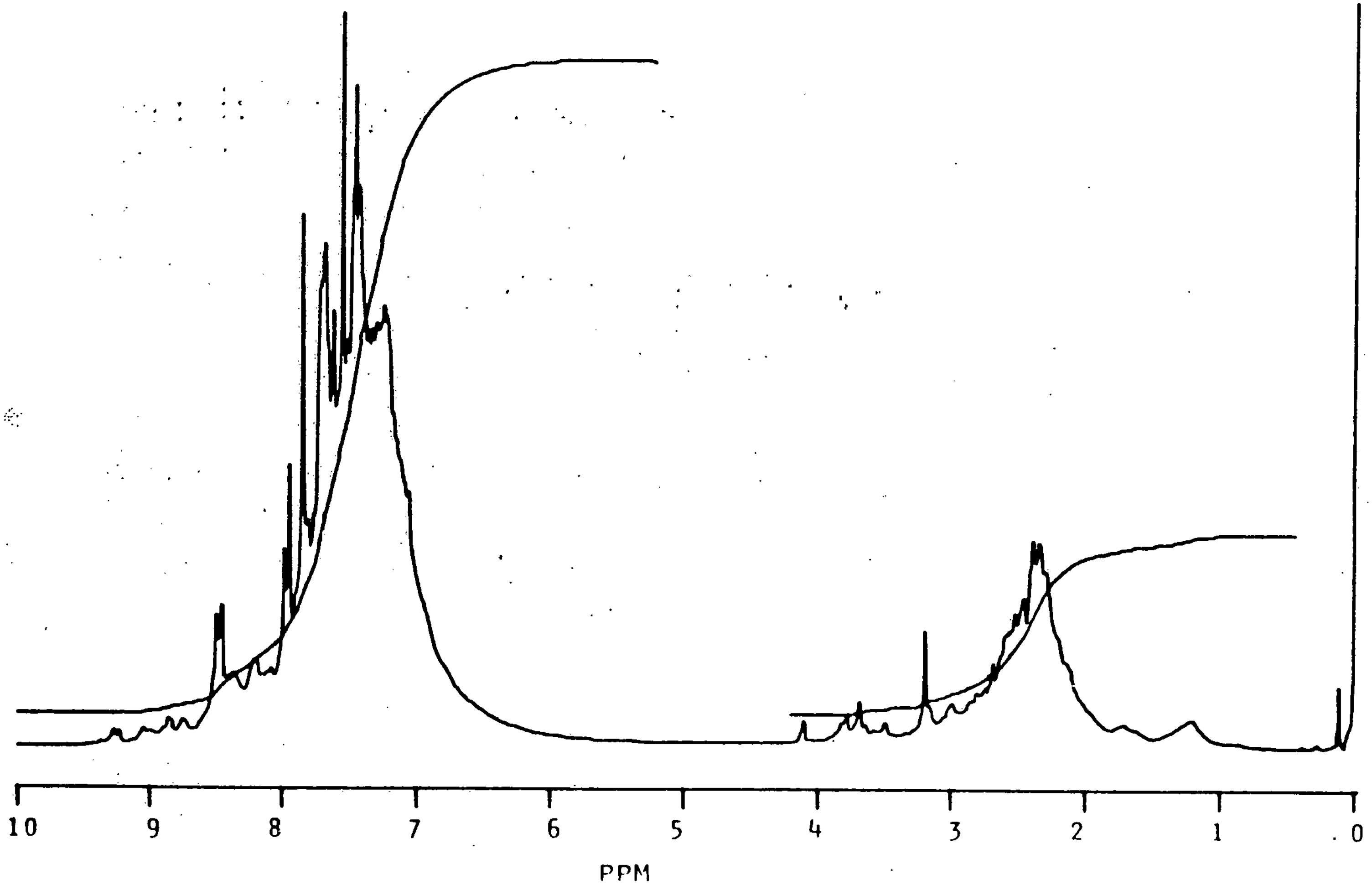

FIGURE 7 $^1$H NMR SPECTRUM OF ANTHRACENE OIL DERIVED NITROGEN-CONCENTRATE

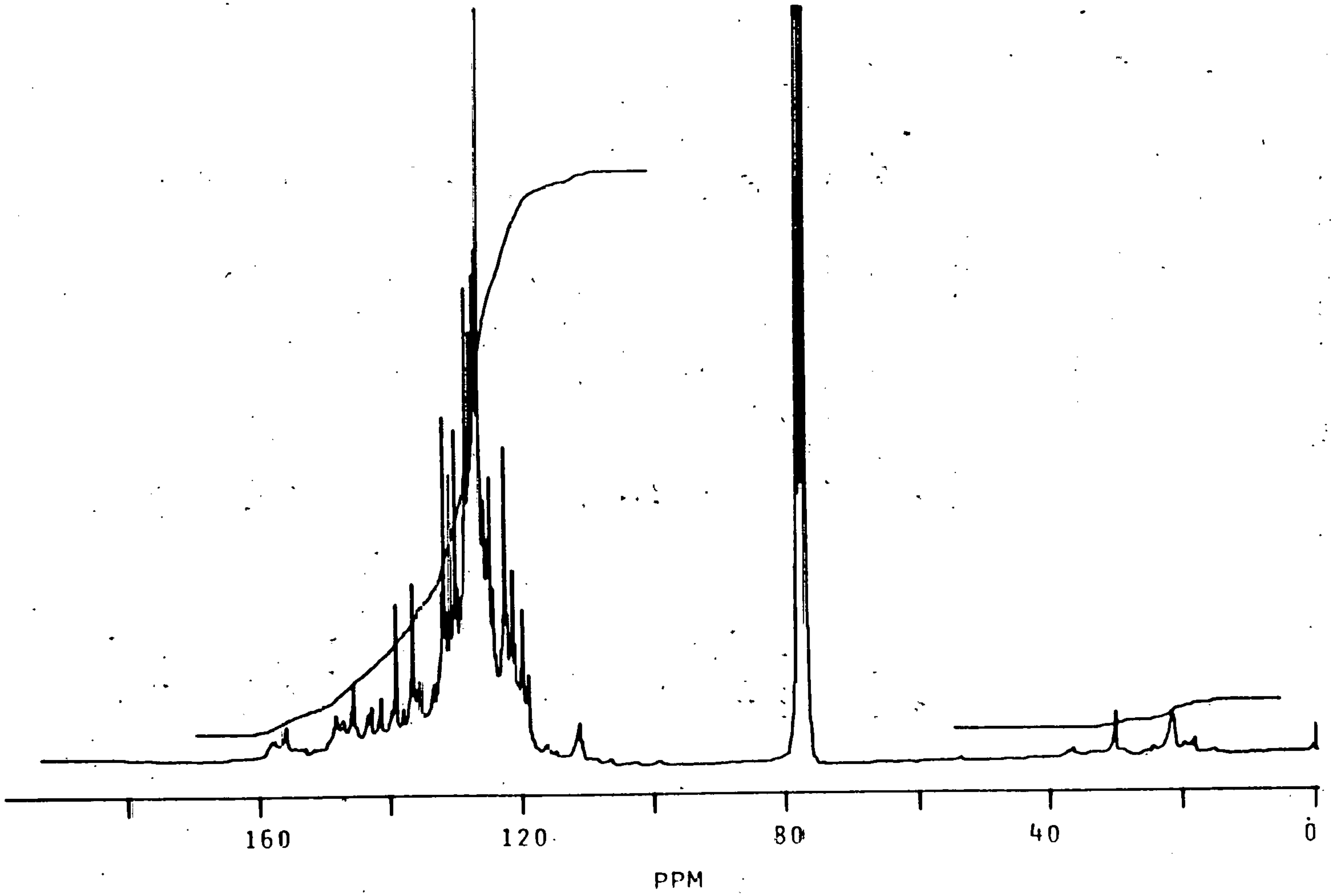

FIGURE 8 $^{13}$C NMR SPECTRUM OF ANTHRACENE OIL DERIVED NITROGEN-CONCENTRATE are indicative of methylene bridges between aromatic rings and represent 1.5% of the available hydrogen. Although division of the aromatic region into mono and diaromatics is difficult due to the presence of 3.4% nitrogen and 2.6% oxygen, one important feature of the aromatic region is the intensity below 8.4 ppm. This region is characteristic of protons on carbons ortho to nitrogen in pyridine ring systems and represents 5.1% of the hydrogen. The remaining 73.7% of the hydrogen is found attached to aromatic rings. A summary of these results is given in Table 6.

From the $^{13}C$ NMR spectrum, this sample contains 94.6% aromatic carbon. The elemental analysis indicates that the carbon-to-nitrogen ratio is 26.6:1, and the carbon-to-oxygen ratio is 39.8:1. There are small signals present in the region of 152 ppm to 158 ppm. Solely on the basis of chemical shift, these signals can be assigned to either pyridine or phenolic structures. However, the signal at 112 ppm indicates that part of the region from 152 ppm to 158 ppm is due to phenols. To verify that phenols were present, a sample of the fraction was dissolved in methylene chloride and evaporated at 50°C to remove traces of residual methanol. The absence of methanol was verified using $^{1}H$ NMR. An infrared spectrum showed absorption in the region of 3440-3200 $cm^{-1}$ indicating the presence of strongly hydrogen-bonded N-H or O-H groups. However, there is no evidence for N-H, since all of the nitrogen appears as basic nitrogen in the $^{13}C$ NMR spectra. In addition, because there are no signals upfield of 110 ppm, indoles are not present, unless they are 3-alkyl substituted.

From a comparison of intensity of the signal at 112 ppm (ortho carbons) with the intensity of the region from 152 ppm to 158 ppm, it appears that 30.8% of the downfield region is due to phenolic structures. The remaining portion, 69.2%, is due to carbons ortho or para to nitrogens in pyridine structures. About 59.5% of the nitrogen is present in these structures. Quinoline-type structures have signals at 150.9 and 149.0 ppm due to the carbons ortho to the nitrogen. If these carbons are ortho or para substituted, they are shifted upfield by 0.5-3.0 ppm. Since there are only a few alkyl substituents, the area in the region from 146 ppm to 152 ppm can be

## Table 6

## $^{1}$H NMR Analysis of Anthracene Oil Nitrogen Concentrate

| | | |
|---|---|---|
| % Aromatic Hydrogen Ortho to N | 5.1% | |
| % Other Aromatic Hydrogen | 73.7% | |
| Aliphatic Hydrogen | | |
| Methyl | 16.2% | |
| Hydroaromatic | 2.1 | |
| Long alkyl chain | 1.4 | |
| Methylene bridge | 1.5 | |
| Total aliphatic | | 21.2% |
| Aromatic Hydrogen | | |
| Aromatic hydrogens ortho to N | 5.1 | |
| Others | 73.7 | |
| Total aromatic | | 78.8 |
| Total hydrogens | | 100.0% |

assigned to nitrogen-containing compounds of the quinoline type. There is sufficient intensity in this region to account for the remaining 40.5% nitrogen.

The 2- and 4-isomers of hydroxypyridines have signals below 160 ppm. Specifically, the 2-isomer has a signal at 106.0 ppm, and the 4-isomer has a signal at 117 ppm. The 3-isomer has a 154-ppm signal but no signal upfield of 120 ppm. From the $^{13}C$ spectrum, there is virtually no intensity upfield of 110 ppm or downfield of 160 ppm. This indicates that if there are any hydroxypyridines present, only the 3-isomer is present. Alternatively, hydroxyquinolines may be present.

About 46% of the alkyl substituents are methyl groups on aromatic rings (broad absorption at 20 ppm). There is a small amount (1.1%) of hydroaromatic structure as seen from the absorption between 22 ppm and 31 ppm. There is some long-chain material which would interfere with this region. The long-chain material (signals at 37-38 ppm) represents up to 33.5% of the alkyl substituents.

The alkyl-substituted aromatic carbon can be obtained from the amount of the alkyl groups directly attached to aromatic carbons. This represents 3.1% of the aromatic carbon. The remaining aromatic carbon is divisible into protonated and bridge aromatic carbon. However, the presence of nitrogen and oxygen in this fraction makes the normal division points between protonated and nonprotonated aromatic carbons incorrect. To determine the positions of nonprotonated carbons, an INEPT experiment was run. This approach enhances only those carbons with attached protons. Nonprotonated carbons are conspicuous by their absence. In the INEPT spectrum of this fraction, the nonprotonated carbons are predominantly downfield of 129.5 ppm. There appear to be no signals upfield of this region. The two predominant downfield signals are at 135 ppm and 148 ppm which are due to protonated aromatic carbons that are para and ortho to the nitrogen in pyridine and quinoline systems. There is also a variety of small signals between 140 ppm and 153 ppm in the INEPT spectrum. The protonated aromatic carbons from the area upfield of 129.5 ppm and from the small signals which are downfield of 129.5 ppm represent a maximum of 64.8% of the aromatic carbon. The remaining 27.8% of the aromatic carbon is due to bridge aromatic carbon. These results are summarized in Table 7.

### 6. GC/MS Analysis of the Anthracene Oil Nitrogen Concentrate

The capillary GC/MS analysis of a methylene chloride solution of the nitrogen concentrate of anthracene oil indicated a wide range of polynuclear aromatic hydrocarbons and heterocyclics (see Figure 9). The polynuclear aromatic hydrocarbons ranged from methylnaphthalene ($C_{11}H_{10}$) to methylbenzanthracene ($C_{19}H_{14}$). The three largest peaks in the chromatogram, phenanthrene (7%), fluoranthene (5%), and pyrene (4.5%), are included in this group. The heterocyclics include sulfur-, oxygen-, and nitrogen-containing compounds. The largest of these are nitrogen containing and range from quinoline ($C_9H_7N$) to naphthoquinoline ($C_{17}H_{11}N$). The three largest nitrogen heterocyclics are benzoquinoline (2.4%), phenanthridine (2.3%), and naphthoquinoline (1.8%). Examples of oxygen and sulfur heterocyclics are dibenzofuran (0.8%) and dibenzothiophene (0.5%). Most of the peaks are chromatographically well resolved, and spectra for the majority of the peaks match well with library spectra, often with purity values of >900.

### Summary of Fraction Characterization

The analyses of the OH-concentrate of SRC-II solvent and of the N-concentrates of SRC-II and anthracene oil show that a wide range of individual components is present. The OH-concentrate of SRC-II contains primarily one- and two-ring phenolic compounds consisting of phenol (~4%), methyl phenols (~9%), $C_2$ to $C_5$ phenols (~9%), and indanols (~8%). Only 0.4% are naphthols. The total aromaticity of this fraction is about 77%. The aliphatic groups consist of methyl groups (26% of the H), long-chain alkyls (average of five carbons at 17% of the H), and a fairly substantial level of hydroaromatics (6% of the H). There is also present a nominal level (1%) of methylene bridges between rings.

## Table 7

## $^{13}C$ NMR Analysis of Anthracene Oil Nitrogen Concentrate

| | | |
|---|---|---|
| **Aliphatic Carbons** | | |
| Methyl groups | 2.5% | |
| Hydroaromatic | 1.1 | |
| Long-chain alkyl | 1.8 | |
| Total aliphatic carbons | | 5.4 |
| **Aromatic Carbons** (Ar-C) | | |
| Ar-C's bearing hydroxyls | 1.0 | |
| Aromatic carbons ortho or para to nitrogen | 3.1 | |
| Alkyl-substituted aromatic carbons | 2.9 | |
| Bridge aromatic carbon | 26.3 | |
| Unsubstituted aromatic carbon | 61.3 | |
| | | 94.6 |
| | | 100.0 |

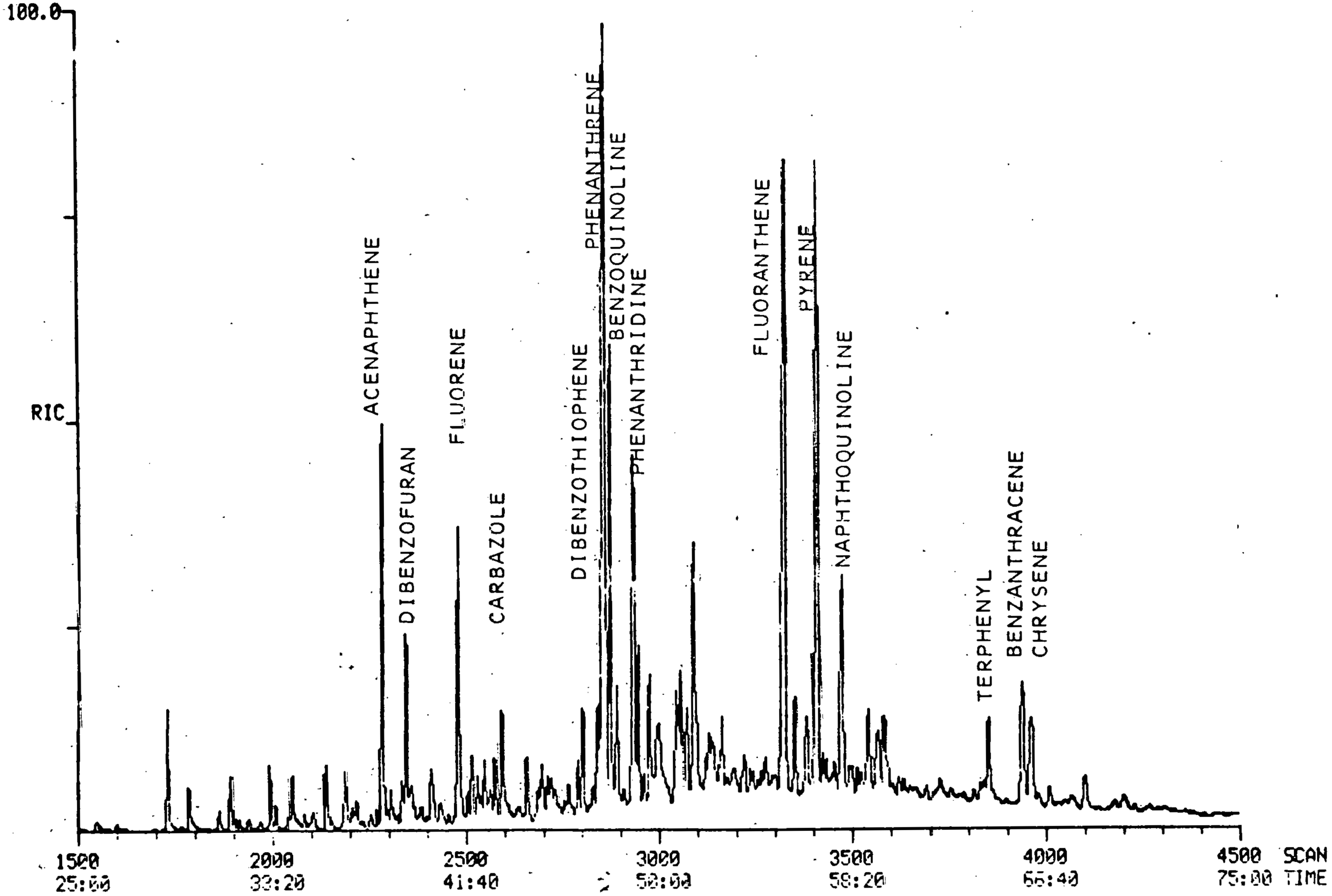

FIGURE 9 GC/MS SCAN OF ANTHRACENE OIL DERIVED NITROGEN-CONCENTRATE

The SRC-II N-concentrate has about an equivalent aromaticity at 72%, and its nominal ring size is between 1 and 2. It contains both nitrogen and hydroxyl functionality (but apparently not on the same ring). The alkyl groups are divided among methyl groups (20%), long-chain alkyls (average of three carbons at 23% of the H), and a high level of hydroaromatics (12%).

The anthracene oil, which is derived as a coke oven by-product, has a N-concentrate with a high level of aromaticity (95%) and an apparent ring size of 1 to 2. The N-concentrate again contains both nitrogen and hydroxyl functionality. The aliphatic carbon is divided among methyl groups (16% of the H), short-chain aliphatics (1.4%), and a low level of hydroaromatics (2.1%).

## II. SUBTASKS 3 AND 4: Liquefaction Using Batch and Bench (Continuous) Units

Rather than directing this report toward a discussion of the types of units and then the runs made therein, we will describe first the experiments with phenolics and then those with various nitrogen-containing species. However, due to a similarity of approaches, the experimental procedures will only be given for the runs made with oxygen-containing materials.

### A. Liquefaction with Phenolic Compounds

Experimentation has been directed toward providing an understanding of the role of phenolic species in the liquefaction of a bituminous coal, Powhatan No. 5 (Pittsburgh No. 8 Seam). To this end, series of micro-unit runs have been made with $^{13}$C-labeled and unlabeled 1-naphthol and tetralin; the objective being to provide information on the extent of irreversible adduction of the naphthol (i.e., attachment by other mechanisms than hydrogen bonding) as a function of residence time in the reactor and the hydrogen donor capacity of the solvent. Subsequently, experiments were made in a continuous feed stirred-tank reactor (CSTR) to specifically observe the overall effects of adding phenolics to anthracene oil (AO) and SRC-II recycle solvents. The following section, presented in manuscript form, describes both aspects of this work.

## Introduction

Phenolic components of coal liquefaction solvents have long been considered to be beneficial for conversion of coal (1,2). Orchin and Storch (2), for example, reported that the addition of small amounts of cresol to tetralin increased the conversion of coal compared with the yield observed with tetralin alone. And Kamiya and co-workers (3) observed a similar effect with phenol or cresol added to a solvent composed of tetralin and 1-methylnaphthalene; the magnitude of the increase was dependent upon the coal used.

The reported effect has been ascribed to a variety of factors, one of which is a hydrogen-bonding interaction between the phenolic species and ethers in the coal (2,3), leading to increased cleavage of diaryl ethers, alkyl, and aralkyl types being labile under coal liquefaction conditions. Kamiya et al. (3) carried out some model compound work which indicated that 2,2'-dinaphthyl ether in tetralin at 450°C decomposes more rapidly in the presence than in the absence of phenolic species; the results, however, are not completely convincing because of the absence of information on mass balance from the ether and the presently known (4) tendency of phenols for adduction. Later work by others on the decomposition of o- and p-alkyl phenols at 400°C (5) provides some doubt that the very large effects noted for some of the model compounds are due to hydrogen bonding.

Yoshii and co-workers (6) found that catechol added to tetralin produced an effect similar to that described above. They observed a catalytic effect of the reactor and stirrer surfaces on the conversion of coal; such an effect is not unexpected in view of the work of others (7,8), but the magnitudes with the different coals are surprising (roughly a factor of 2).

Awadalla and Smith (9) observed an increase in conversion with p-cresol but suggested that the effect was an artifact of the extraction process, a co-solvent effect arising from lack of prior removal of the phenolic material. These authors demonstrate that the extraction technique used by Kamiya and co-workers leads to higher conversions than does their own, which minimizes solvent effects. Yoshii and co-workers determined coal conversions by a procedure similar to that of Kamiya.

Franz et al. (10) discussed a procedure for the quantitative determination of hydrogen donor strengths by a method of comparing the rearrangement of o-alkylbenzyl radical to hydrogen transfer to the radical from a donor solvent. 1-Naphthol was found to have a much higher donor strength than phenol and, in turn, tetralin. However, this work was done at a relatively low temperature (160°C) and at conditions in which side reactions such as adduction would not occur.

Larsen et al. (4), investigating the use of phenol as a solvent for liquefaction of Bruceton Pittsburgh Seam coal, found that a solvent/coal ratio and reaction temperature similar to those expected for a large-scale unit (1.5 and 460°C) led to a weight increase of the coal of 9% after a 15-min reaction. This large amount of adduction and a 10% conversion to pyridine-soluble material are suggestive that phenol is a very poor solvent under these conditions. To be sure, this was only one run, and there is no possibility of knowing whether adduction reaches a maximum near this time as tetrahydroquinoline has been shown to do (11). Runs made at 482°C resulted in an increase in conversion, up to 82% for a 10/1 phenol/coal feed. However, the liquid product contained 14% by weight phenol of which 6% was attached to the coal by other than hydrogen-bonding interactions. An additional 8% was exchangeable with unlabeled material.

The results of all these experiments indicated to us that phenolic species in the solvent may have an adverse effect on coal liquefaction in that they may not increase the conversion above that available in their absence but also that they may be lost from the solvent by adduction, which can take two forms, hydrogen bonding or C-C or C-O bond formation. The micro-autoclave experiments were designed to test this view using a solvent with a critical point higher than that of phenol (421°C) and to investigate the effect of substituents on the ability of phenolic species to assist in converting coal. All of these micro-autoclave experiments were done in aged reactors, and the conversions were determined in such a way as to minimize co-solvent effects which would produce spuriously high yields. To test the conclusions drawn from the micro-autoclave experiments, subsequent experiments were done in a bench-scale flow unit capable of continuous coal slurry feed and withdrawal.

## Experimental

The coal was Powhatan #5, Pittsburgh No. 8 Seam, ground to pass at least 98% through 100 mesh screen. Proximate and ultimate analyses are given in Table 8.

The micro-autoclave runs were carried out in stainless-steel tubular reactors of inside diameter 1 cm and length 15 cm, placed vertically in a fluidized bed sand bath (12). Mixing was ensured by placing a stainless-steel ball inside the reactor, which was shaken at 800 strokes per minute using a 2.5-cm stroke. Reaction conditions and charges are listed in the appropriate tables.

At the conclusion of each micro-autoclave run, as much product as possible was collected by decantation. Then 10 cc of methylene chloride was added to the reactor and mixed well with the residue, the liquid product being added to that obtained above. The reactors were then cleaned with a steel spatula and a wire brush, and these products were also added to the above. The methylene chloride was removed under a gentle stream of nitrogen at room temperature, and then the sample was placed on a steam bath for at least two full days under a stream of nitrogen to ensure removal of as much solvent as possible.

## Table 8

## Analyses of Powhatan No. 5 Coal

| | | |
|---|---|---|
| A. | Proximate Analysis (Dry Basis) | |
| | Ash | 9.7% |
| | Volatile Matter | 40.1% |
| | Fixed Carbon | 50.2% |
| B. | Ultimate Analysis (Dry Basis) | |
| | Carbon | 72.3% |
| | Hydrogen | 5.1% |
| | Nitrogen | 1.5% |
| | Chlorine | 0.03% |
| | Sulfur | 3.6% |
| | Oxygen | 7.9% |
| | Ash | 9.7% |
| C. | Vitrinite Content | 89.2 vol% |
| D. | Initial Tetrahydrofuran (THF) Solubility | 10.25% (Moisture-Ash-Free Basis) |

The bench-scale liquefaction runs were made in a continuous feed stirred-tank reactor (CSTR) system. A flow diagram of the coal liquefaction unit is shown in Figure 10. The unit consisted of a feed tank, Moyno recirculating pump, Milton-Roy high pressure pump, preheater, a stirred autoclave, letdown valves controlled from unit pressure, receivers, and a gas chromatograph. The reactor was 293 $cm^3$ in volume with an inside diameter of about 7.6 cm. The reactor was equipped with a single large (5.1 cm) diameter impeller. There were four baffles in the reactor. Agitation (1000 rpm) was previously shown to be sufficient for effective agitation without mass transfer effects.

The residues were subjected to sequential Soxhlet extraction using pentane, toluene, and tetrahydrofuran (THF), for periods of 4, 1, and 2 days, respectively. Fractions were defined as follows using as a basis MAF coal feed:

wt% oils = {(MAF coal-pentane insolubles)/MAF coal} x 100
wt% asphaltenes = {pentane insoluble, toluene soluble/MAF coal} x 100
wt% preasphaltenes (PA) = {toluene insoluble, THF soluble/MAF coal} x 100
wt% THF insolubles = {THF insoluble material/MAF coal} x 100

From the above definition, "oils" are classified as all of the coal product that is not insoluble in pentane as determined by Soxhlet extraction. While this includes liquid products, it also includes gases and other by-products such as ammonia, hydrogen sulfide, water, etc. In the event that the extent of adduction to the three heavier fractions gives a pentane-insoluble fraction that is greater that the MAF feed coal, a negative value of oil yield is obtained. As shown by gel permeation chromatography of the preasphaltenes, the extraction procedure essentially removes all solvent material by the toluene step, with the result that no co-solvent effect can occur.

Gel permeation chromatography was done with a Waters Associates instrument using THF as the solvent.

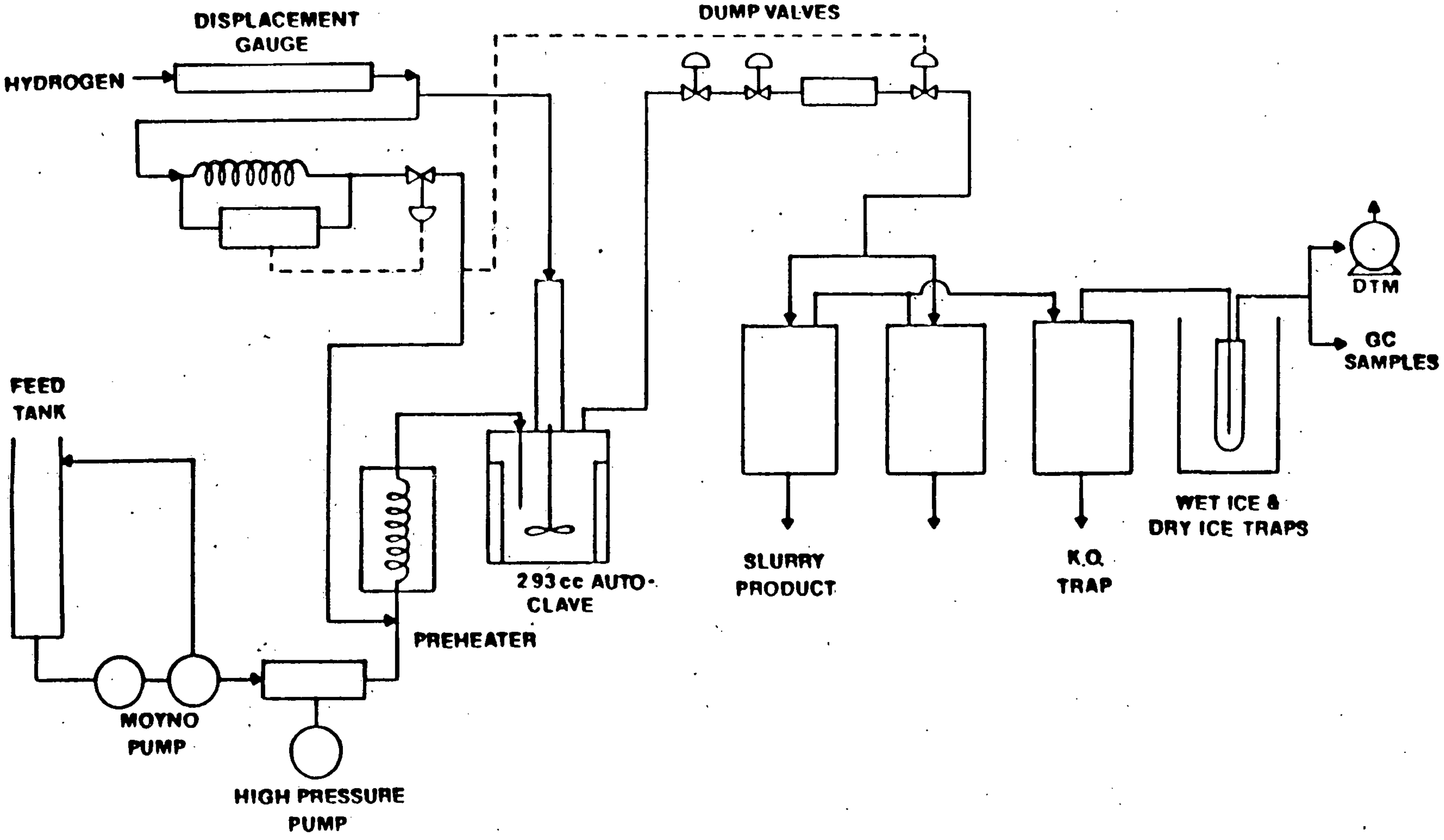

FIGURE 10 SCHEMATIC OF THE CSTR BENCH-SCALE LIQUEFACTION UNIT

## Results and Discussion

### 1. Micro-Autoclave Experiments

1-Naphthol. A series of coal liquefaction runs was made with 1-naphthol as the solvent. Conditions and yields are shown in Table 9. The extent of conversion as a function of time at 450°C follows the same pattern as that observed for tetralin (Table 10), a high percentage of the total conversion taking place at short times, with very little change after 10 min. Unlike the tetralin results, however, there is only a small amount of upgrading with increasing residence time. The yield of preasphaltenes does not decrease significantly, upgrading to asphaltenes being balanced by production from the insoluble material. The yield of asphaltenes decreases initially (0 to 5 min) but then increases again at longer times, behavior suggestive of adduction. Further evidence for adduction is provided by the negative oil yield, which decreases with time after a zero minute residence time. This negative oil yield is a result of less pentane-soluble product (including gases and by-products) being recovered than solvent being fed. This obviously would result in process failure.

To ensure that the increased levels of asphaltenes and preasphaltenes are not a result of physically entrapped naphthol, selected samples of these fractions were passed through a gel-phase chromatographic unit. Considering the high level of solvent, tetrahydrofuran, and the column retention time, the concentration of these fractions is about 2 ppm, so dispersion of naphthol should be complete. This dispersion was also confirmed with calibration samples. Typical GPC plots are shown in Figure 11 with the following points being noted. The preasphaltenes (PA) are of higher molecular weight (shorter retention time) than the asphaltenes. The asphaltenes contain litle (0.3%) naphthol at a retention time of 23.5 min, and the PA's are essentially naphthol-free. The trapped naphthol is presumably held by hydrogen bonding. It would be exchangeable with solvent naphthol and would correspond to the exchangeable phenol observed by Larsen for a 482°C/15 min run (4). The asphaltenes contain a limited amount (5.3%) of toluene

## Table 9

### Coal Liquefaction with 1-Naphthol Solvent[a]

| T (°C) | Time (min) | Yield in wt% MAF Coal[b] | | | |
|---|---|---|---|---|---|
| | | Oils | Asph | Preasph | THF Solubles |
| 400 | 30 | -34.0 | 68.3 | 22.3 | 56.6 |
| 450 | 0 | -49.1 | 65.7 | 29.9 | 46.5 |
| 450 | 5 | -9.0 | 48.8 | 20.7 | 60.5 |
| 450 | 10 | -20.1 | 61.0 | 19.6 | 60.5 |
| 450 | 30 | -31.3 | 81.6 | 17.7 | 68.0 |

---

[a] 70:30 (wt) 1-naphthol:Powhatan No. 5 coal, 3.45 MPa hydrogen.

[b] Oils, asphaltenes (Asph), preasphaltenes (Preasph), and THF solubles are defined and discussed in the text.

# Table 10

## Coal Liquefaction with Tetralin Solvent[a]

| Time (min) | Yield in wt% MAF Coal<br>Oils | Asph | Preasph | THF Solubles |
|---|---|---|---|---|
| 0 | 19.6 | 23.9 | 21.2 | 64.7 |
| 5 | 35.3 | 24.6 | 13.5 | 73.1 |
| 30 | 45.2 | 27.0 | 18.9 | 81.1 |
| 30 | 42.8 | 27.0 | 19.7 | 80.3 |

---

[a] 70:30 (wt) solvent:coal (3.5 g:1.5 g), 3.45 MPa hydrogen.

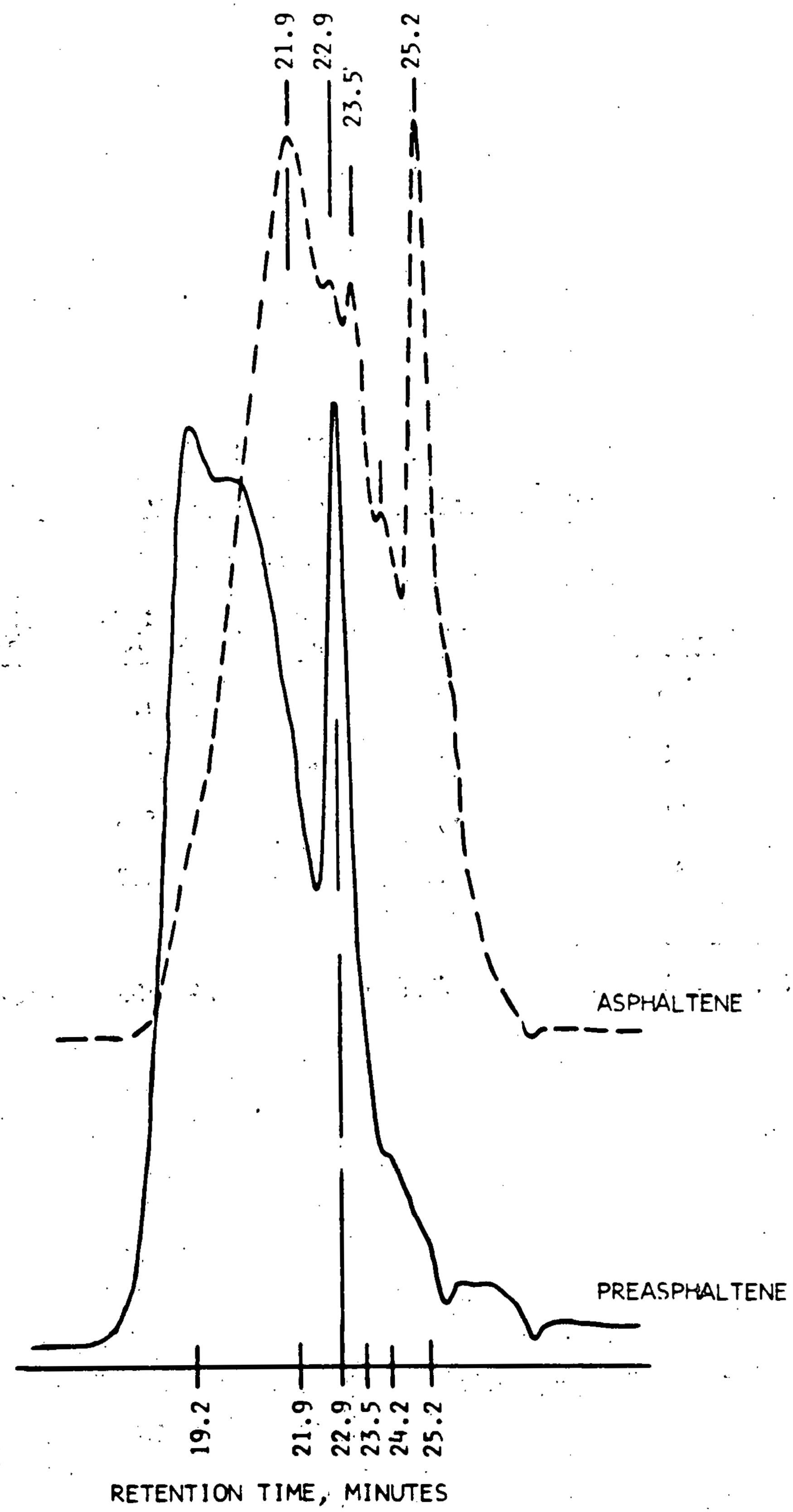

FIGURE 11 GPC PLOTS OF THE ASPHALTENE AND PREASPHALTENE FRACTIONS OF THE RUN WITH 1-NAPHTHOL SOLVENT AT 450 C AND 30 MIN.

(retention time of 25.2 min) as a result of incomplete stripping of the extraction solvent prior to GPC injection. There also appears to be a higher molecular weight material (retention time 22.9 min and a level of 4-9%) present in the PA's with a limited amount (<0.2%) in the asphaltenes. From the apparent molecular weight of the material with the 22.9-min retention time it is likely to be a condensation/dimerization product of 1-naphthol as described in-depth by Poutsma and Dyer (13).

The behavior of 1-naphthol is much like that observed previously for phenanthrene (14), a moderately good hydrogen shuttling agent (15), though the extent of conversion by the phenolic material is about 9 absolute percent higher at each run time. Naphthalene, which is a poorer shuttling agent than phenanthrene, is capable of even less conversion of coal (14). 1-Naphthol, then, is considered quite a good solvent for coal liquefaction, much better than one might expect on the basis of its classical hydrogen shuttling capability and lack of tetrahydroaromatic structure. However, it also engages to a very large extent in adduction with the nascent coal liquids, leading to loss of solvent.

An indication of the beneficial effects of the presence of 1-naphthol in hydrogen donor systems and the seriousness of the adduction problem is provided by liquefaction studies with mixtures of this material and tetralin, an excellent hydrogen donor solvent. As shown in Table 11, conversion provided by 1:1 (wt) mixtures of 1-naphthol and tetralin are roughly equivalent to those obtained from tetralin alone for a mixture of 70:30 solvent:coal. Further, no increase in conversion is noted above that from tetralin when the solvent:coal ratio was raised by addition of 1- or 2-naphthol. We conclude, in agreement with Awadella and Smith (9), that the apparent increase in conversion provided by phenolic species is most probably due to the extraction procedure. Like theirs, our method of extraction minimizes co-solvent effects on total conversion.

## Table 11

### Coal Liquefaction with 1-Naphthol/Tetralin Mixtures(a)

| Naphthol/ Tetralin | Time (min) | Yield in wt% MAF Coal | | | |
|---|---|---|---|---|---|
| | | Oils | Asph | Preasph | THF Solubles |
| 1:1 | 0 | -32.0 | 61.2 | 37.6 | 67.3 |
| 1:1 | 5 | -43.5 | 87.4 | 30.6 | 75.5 |
| 1:1 | 10 | -22.7 | 68.5 | 23.5 | 70.4 |
| 1:1 | 30 | -7.9 | 68.9 | 17.0 | 77.9 |
| 2:7(b) | 30 | 16.9 | 53.1 | 11.3 | 82.0 |
| 4:7(c) | 30 | -32.8 | 94.2 | 19.3 | 80.7 |
| 2:7(b,d) | 30 | -4.9 | 70.7 | 14.3 | 80.1 |

---

(a) 450°C, 70:30 total solvent:coal (3.5 g:1.5 g), 3.45 MPa hydrogen.
(b) 20:70:30 naphthol:tetralin:coal (1.0 g:3.5 g:1.5 g).
(c) 40:70:30 naphthol:tetralin:coal.
(d) 2-naphthol.

Adduction of 1-naphthol is a problem in runs with 1:1 solutions with tetralin, as shown by the high yields of preasphaltenes and asphaltenes compared with those of comparable fractions from runs with tetralin alone. This point is made more strikingly by examination of the oil yields, which are uniformly negative for the runs with mixed solvents. Some of the adducted material is held by hydrogen-bonding interactions, as shown by small peaks of the proper molecular weight in the GPC plots of the asphaltene fractions, but most of the naphthol is attached by other mechanisms.

The pattern of the oil yields from the 1:1 mixed solvent system is different from that described above for the runs with 1-naphthol alone and is more like that observed in mixtures of 1,2,3,4-tetrahydroquinoline (THQ) with the poor liquefaction solvent anthracene oil (Reference 11 and discussed later in this report). In that case, a minimum in the oil yield was observed at short residence times (5 min). But when THQ was mixed with a good solvent like SRC recycle solvent, no minimum was observed, the oil yield increasing with time. Since tetralin is a good solvent, the behavior of the naphthol/tetralin system was quite unexpected.

Adduction is a problem also in the runs with 20 or 40:70:30 naphthol:tetralin:coal, as shown by the increased yields of asphaltenes and preasphaltenes, as well as the low oil yields (the last down from 44 to 17% upon addition of 20 wt% 1-naphthol). With 40% 1-naphthol or 20% 2-naphthol, the oil yields are negative.

The conclusions, then, are that the presence of naphthol does not increase the conversion of coal above that obtained from a good hydrogen donor solvent alone. Not only that, but addition of this structural type is detrimental for recycle operation because it is lost from the solvent by adduction to the coal liquids.

Cresols. A series of runs was carried out to provide an indication of the effect on liquefaction capability of substitution on phenolic species. As shown in Table 12, o-, m-, and p-cresol are roughly equally effective in converting coal in reactions at 450°C, 30 minutes, when mixed 1:1 with tetralin.

## Table 12

### Coal Liquefaction with Single-Ring Phenolic Compounds[a]

| | Yield in wt% MAF Coal[b] | | | |
|---|---|---|---|---|
| Phenolic | Oils | Asph | Preasph | THF Solubles |
| o-Cresol | 36.4 | 29.0 | 5.9 | 71.2 |
| m-Cresol | 35.2 | 22.7 | 12.9 | 70.7 |
| p-Cresol | 32.6 | 22.7 | 10.9 | 66.2 |
| Phenol | 31.4 | 13.2 | 8.1 | 52.7 |
| 2,6-Dimethylphenol | 15.3 | 37.3 | 23.6 | 76.2 |

---

(a) 70:30 solvent:coal, 1:1 (wt) phenolic:tetralin, 450°C, 30-min residence time, 3.45 MPa hydrogen.

The extents of conversion, though, are considerably less than those obtained from 1-naphthol/tetralin under comparable conditions. This difference may well be due to the fact that naphthol is not near its critical point and so is predominantly liquid, while the cresols are probably in the dense gas phase (critical temperatures 424, 432, and 431°C for o-, m-, and p-cresol, respectively). The three cresols, however, are all much more effective in coal liquefaction that is the parent phenol, which has a critical temperature of 421°C. All of the single-ring phenolics in 1:1 combination with tetralin lead to product distributions very much like that available from tetralin alone; in no case was a negative oil yield observed.

A slightly higher degree of conversion is observed from a 1:1 mixture of 2,6-dimethylphenol and tetralin, but the yield is still not equivalent to that from tetralin alone. The preasphaltene and asphaltene yields are higher than that from the mono-substituted phenols, and the oil yield is lower. A possible explanation is some steric crowding of the hydroxyl group in conjunction with the formation of adducts through the two methyl groups, a reaction pointed out by Larsen (4).

## 2. Bench-Scale Liquefaction Experiments

Considering the results of the batch liquefaction experiments with phenolics and the past literature (1-3) indicating that phenolics were effective for liquefaction, a series of runs were made in the CSTR unit to evaluate the effect of adding phenolics to anthracene oil (AO) and SRC-II recycle solvents. The experiments were made at nominal space times of 4 and 15 minutes with a hydrogen atmosphere (total unit pressure of 10.3 MPa/1500 psig). Because 1- and 2-naphthol exhibited strong adduction tendencies in the micro-autoclave runs, emphasis was directed toward the use of m-cresol and phenol at a relatively low level of addition, namely 5 parts additive plus 65 parts base solvent for an overall 70/30 solvent-to-coal ratio. With the exception of the first run made with AO at 400°C, all of the runs were made at a reactor temperature of 450°C.

In all of the experiments, the product streams (gases, condensates, and slurry) were analyzed and a detailed elemental material balance was calculated. Again, it is noted that the extraction technique in combination with the material balance can give a "negative oil yield" of pentane solubles. This means that less pentane solubles are being recovered in the product than were originally fed as solvent.

The results of the CSTR runs are summarized in Table 13. First, the anticipated overall changes with changes of operating parameters occurred. Namely, SRC-II is a better solvent than AO at short reaction times as indicated by higher overall coal conversion, a lower level of preasphaltenes, and lower hydrogen consumption. With both solvents the yields of oils were negative. With an increase in space time to 15-19 minutes, overall conversions increased to about the same level (72-75%). The recoveries of preasphaltenes were essentially the same at about 5%, and the hydrogen consumptions were equal at 3.5 g/100 g MAF coal. However, a sizable negative yield of oils was observed in the AO run at 15 minutes. This was apparently due to a high yield of asphaltenes. While this observation appears to be anomalous, the product slurry was extracted a total of five times with essentially the same results.

With respect to the addition of phenolics, the direct addition of phenol to AO (4-min space time) was detrimental. While % solvation had a marginal increase, the yield of asphaltenes increased greatly over that of the run with AO alone. The product slurry was also very sticky and difficult to handle, which may account for some of the difficulty of pentane penetrating into the slurry sample and then extracting the oils. The yields of preasphaltenes were essentially the same for the runs with AO and AO plus phenol.

## Table 13

## Summary of CSTR Runs with Phenolic Additives

| Solvent/Additive | Space Time (min) | % Solvation[1] (g/100 g) | Hydrogen Consumption[2] (g/100 g) | Yields[2] (g/100 g) | | |
|---|---|---|---|---|---|---|
| | | | | Oils | Asphaltenes | Preasphaltenes |
| Anthracene Oil | 4.2 | 55.4 | 3.0 | -7.0 | 29.9 | 19.9 |
| +m-Cresol | 4.3 | 58.3 | 2.4 | 9.6 | 30.2 | 27.0 |
| +Phenol | 4.4 | 58.5 | 2.1 | -46.5 | 71.3 | 22.1 |
| +OH-CONC | 4.1 | 56.7 | 2.5 | -9.9 | 33.5 | 23.6 |
| Anthracene Oil | 15.2 | 74.7 | 3.4 | -35.5 | 82.9 | 6.7 |
| +m-Cresol | 19.1 | 80.2 | 4.3 | -2.1 | 55.3 | 3.7 |
| SRC-II Solvent | 4.7 | 61.3 | 1.8 | -5.3 | 41.8 | 14.0 |
| OH-Reduced SRC-II | 4.6 | 63.9 | 2.7 | 2.1 | 34.5 | 17.8 |
| SRC-II Solvent | 19.0 | 71.7 | 3.6 | 12.3 | 33.2 | 4.7 |
| +m-Cresol | 15.0 | 76.6 | 3.6 | 14.5 | 34.9 | 7.5 |

---

Notes: (1)Solvation is given as grams of tetrahydrofuran solubles/100 grams MAF coal.
(2)Yields are given as grams/100 grams MAF coal.

As also observed in Table 13, the addition of OH-concentrate, recovered from the ion exchange resin treatment of SRC-II solvent (see Subtask 1), to AO had little effect on the distribution of products. Considering the OH-concentrate has a moderate level of hydroaromaticity while AO is low and that the OH-concentrate had already effectively passed through a liquefaction reactor, the OH-concentrate may not react sufficiently with coal radicals to form additional asphaltenes.

The addition of m-cresol appeared to be of particular benefit to the AO runs. This addition resulted in an increase in the yield of oils along with a marginal increase in % solvation. In the case of m-cresol addition to SRC-II solvent at a 15-minute reaction time, there was a small increase in % solvation with nominal increases in each of the product fractions.

Due to a lack of feed sample, only a single CSTR run was made with the solvent recovered after treatment with IRA-904 resin. This solvent contained 1.9% oxygen, while the as-received SRC-II contained 2.8% oxygen. Even this partial removal of hydroxyls appears to be of benefit as observed by an increase of oil yield, a decrease of asphaltenes yield, and a marginal increase in % solvation (THF solubles).

## Conclusions

In the micro-autoclave coal liquefaction experiments conducted at 450°C with product extractions carried out to minimize the impact of a co-solvent effect on determination of total conversion, 1-naphthol has been found to be a surprisingly good solvent to convert coal to THF solubles. It is considerably poorer than tetralin but significantly better than the efficient hydrogen shuttling agent phenanthrene. Mixtures of 1:1 (wt) 1-naphthol:tetralin do not promote greater conversion of coal than does tetralin alone. Conversion is not increased when either 1- or 2-naphthol is added to a reaction mixture of tetralin and coal (70:30 by wt). Loss of solvent 1- and 2-naphthol by adduction to the coal liquids is a major problem, as indicated by a loss of oil yield in that less oil is recovered than originally fed as solvent. This occurs even in solutions containing substantial amounts of tetralin.

Series of coal liquefaction experiments were carried out at 450°C in a continuous feed stirred-tank reactor (CSTR) to observe the effect of adding phenolics to anthracene oil (AO) and SRC-II recycle solvents. At nominal space times of 4 and 15 minutes, the levels of conversion (THF solubles) were significantly higher with SRC-II recycle solvent than with anthracene oil. The addition of phenol to AO at a ratio of 5/65 resulted in a nominal increase in coal conversion to THF solubles, but the amount of asphaltenes more than doubled resulting in a sizable net loss of solvent. The addition of m-cresol to both AO and SRC-II solvents had a positive effect on coal conversion to both THF and pentane solubles (oils). The partial removal of an OH-concentrate from SRC-II solvent was carried out using Amberlyst IRA-904 ion exchange resin. The resin-treated oil was only marginally better than raw SRC-II recycle solvent for coal liquefaction.

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## B. Liquefaction with Nitrogen-Containing Compounds

Experiments with model compounds containing nitrogen heterocyclic species have demonstrated the usefulness of these compounds as donor solvents in coal liquefaction. In particular, interaction with oxygen-containing functional groups has been shown. While the interaction of such groups promotes liquefaction, it also results in a hydrogen-bonding effect that reduces the ability to recover the liquefaction products from the recycle solvent due to the resulting changes in vapor-liquid equilibria and extraction effectiveness. As in the previous case with phenolic compound addition, the work will be presented in manuscript form. Emphasis will be directed first to the micro-autoclave results (combining a portion of that previously presented in the Final Report of DOE Contract No. DE-AC22-80PC30080 with more recent results). Next the CSTR results will be discussed, and finally the supercritical water/nitrogen-compound results will be reviewed.

## Introduction

Coal liquefaction in a hydrogen-donor solvent is accomplished by a combination of the dissolution of low molecular weight species and the thermal cracking of larger species. The resulting free radicals from the cracking are stabilized by the abstraction of hydrogen from a donor solvent or from the coal or coal-derived liquids. Some of the best initial work in this area has been presented by Curran et al. (1a), Wiser (1b), and Neavel (1c).

Considering the various postulated coal structures (2), it would appear that nitrogen-containing donor solvents would be effective in the conversion of coal. First, these polar solvents should effectively swell coal and act as good solvents due to polar interaction with various oxygen-containing species within coal. Secondly, the fracturing of ether and thioether linkages occurs at relatively low temperatures (for example, dibenzyl ether (3) has a half-life of about 3 min at 450°C), and any interaction with a polar compound would appear advantageous due to the proximity of a donor.

A first step would be the study of the thermal cracking of selected compounds in the presence of either tetralin or tetrahydroquinoline (THQ). Cronauer et al. (3) and Panvelker et al. (4) demonstrated that the rate of cracking of dibenzyl was not influenced by the choice of solvent, but hydrogen was selectively abstracted from the THQ. This is particularly shown in Figures 12, 13, and 14. In addition, the rate of cracking of dibenzyl ether was not influenced by the choice of solvent primarily because hydrogen is moved by intramolecular rearrangement during thermolysis. In the reduction of acetophenone and benzaldehyde, the reaction with THQ present as a donor was faster than that with tetralin by a factor of more than 4. It was also shown that the rate of hydrogenation of quinoline to THQ was faster than that of naphthalene to tetralin in the presence of coal liquefaction residues; therefore, it is implied that the nitrogen heterocyclic compounds would be better hydrogen shuttlers than aromatic hydrocarbons.

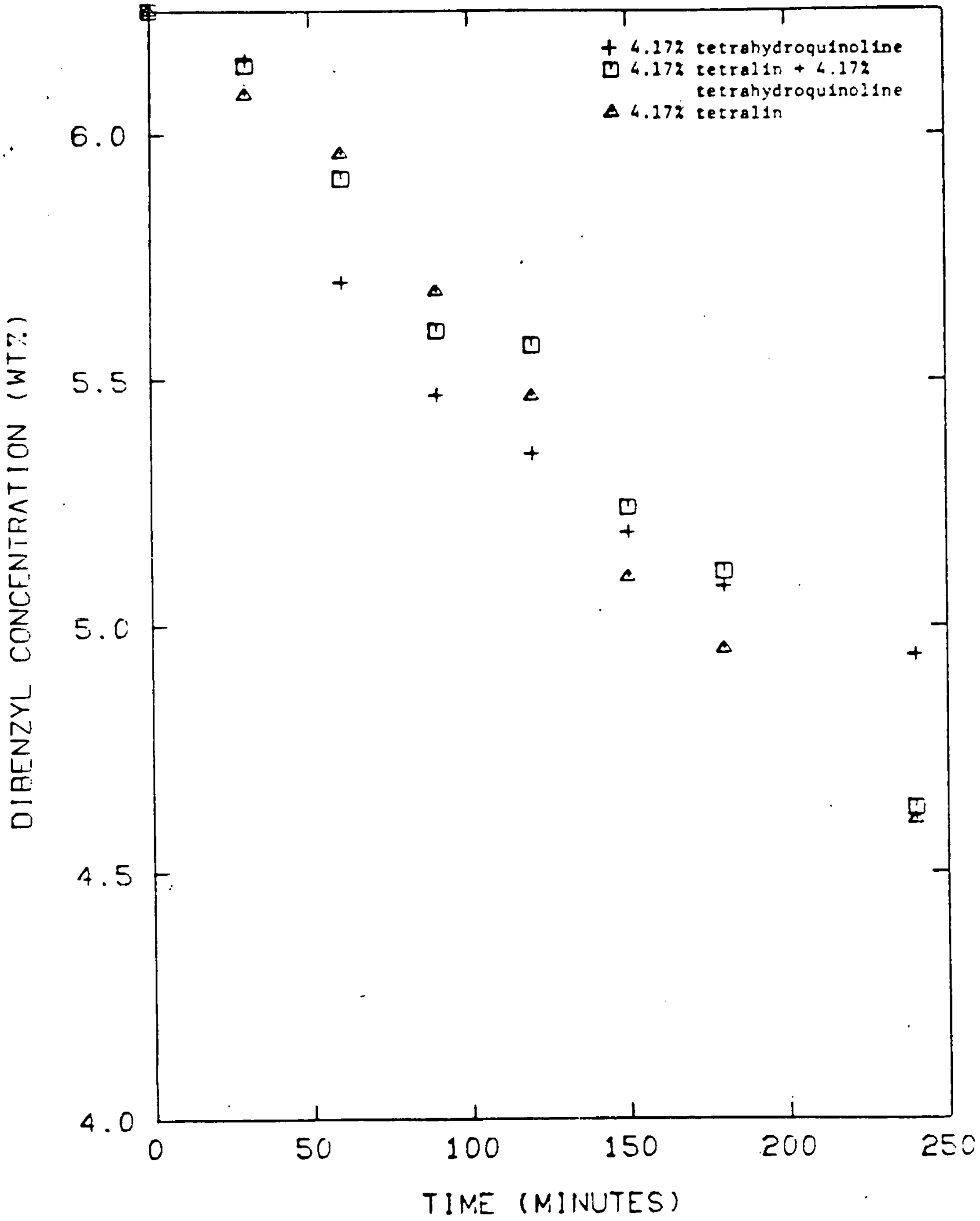


FIGURE 12 CONVERSION OF DIBENZYL IN THE PRESENCE OF LIMITING AMOUNTS OF DONOR SOLVENTS

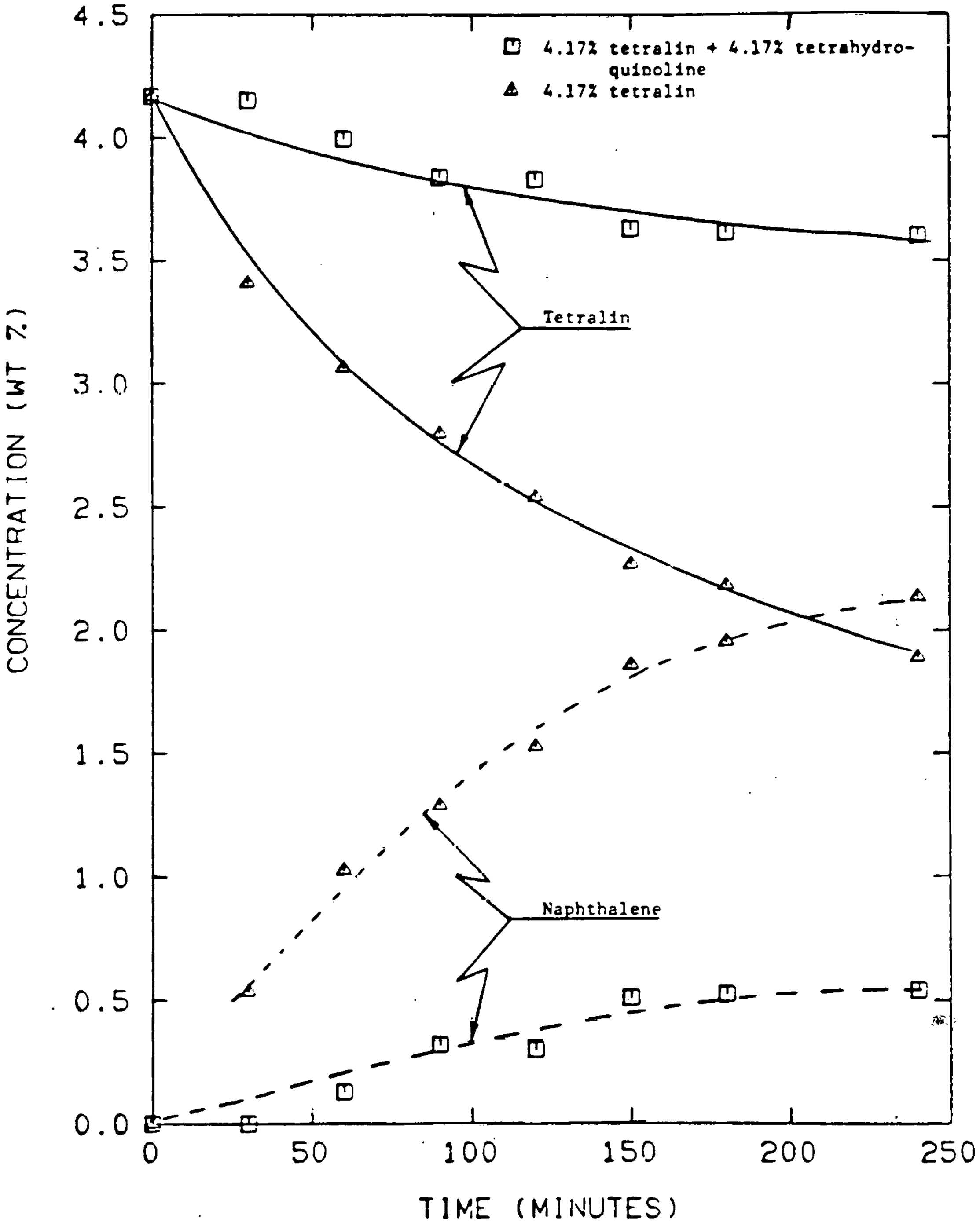


FIGURE 13 CONSUMPTION OF TETRALIN AND THE FORMATION OF NAPHTHALENE IN THE REACTION OF DIBENZYL

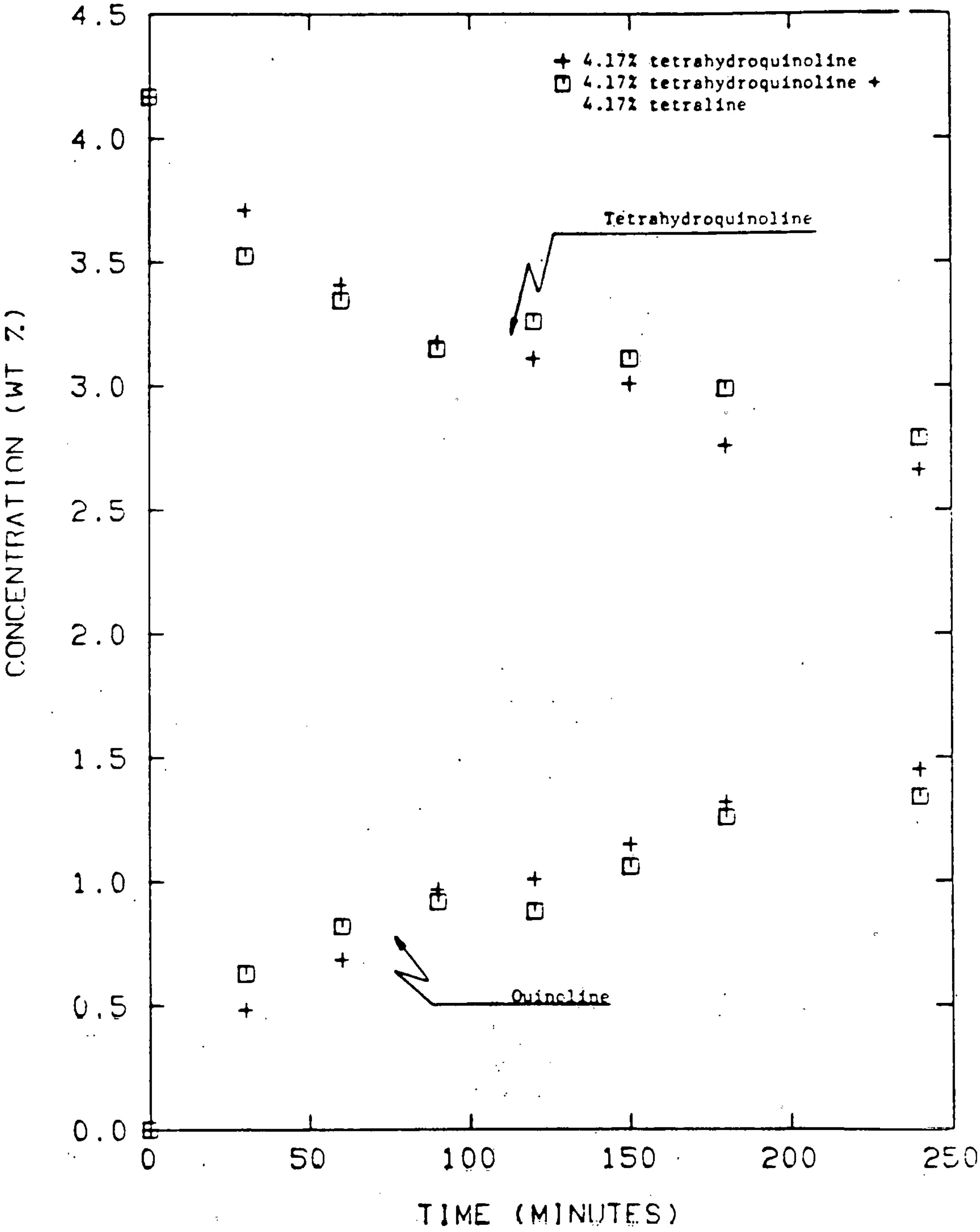


FIGURE 14 CONSUMPTION OF TETRAHYDROQUINOLINE AND THE FORMATION OF QUINOLINE IN THE REACTION OF DIBENZYL

THQ has been shown by Brucker and Kolling (5) and Hausigk et al. (6) to be an effective coal liquefaction donor solvent. However, a high level of nitrogen was observed in the heavy products. In our recent work [Panvelker et al. (7)], it was found that the addition of THQ to an effective donor solvent system, hydrogenated phenanthrenes, had essentially no effect on the product distribution. The addition of THQ was also ineffective in altering the yields of extractables when using SRC-II derived recycle solvent. However, the addition of THQ to a poor donor solvent, anthracene oil, had a sizable effect on the distribution of pentane solubles (oils) and asphaltenes (pentane insolubles/toluene solubles). As shown in Figures 15 and 16, there was a net loss of pentane solubles with a corresponding increase in asphaltenes. There appeared to be an increase in the net conversion of coal to tetrahydrofuran solubles, but this was within the range of data reproducibility. The apparent reason for the above sizable loss of yield appears to be the adduction of quinoline to the coal-derived liquids by hydrogen bonding with some formation of direct chemical bonding (i.e., C-C or C-N bonds). Reference is also made to the work of Collins et al. (8) concerning the retention of pyridine and similar solvents in coal.

## Experimental

The procedure used in the micro-autoclave runs is the same as that given in the previous section for the phenolic compounds. In addition, a sample of SRC-II solvent was distilled in a Podbielniak Hyper-cal unit (about 35 cm of Heli-pak packing) at a reflux ratio of 5/1. Ten wt% distillate cuts were recovered for use in a series of micro-autoclave experiments. Selected distillate samples were treated with Amberlyst-15 resin (3.3/1.0:oil/resin) to recover samples of reduced nitrogen content for subsequent liquefaction experiments.

Micro-autoclave experiments were also run using $^{13}C$-labeled THQ, tetrahydrocarbazole, and carbazole. The compounds were prepared by Professor E. J. Eisenbraun and his students at Oklahoma State University to contain about 99% $^{13}C$ label at the following positions:

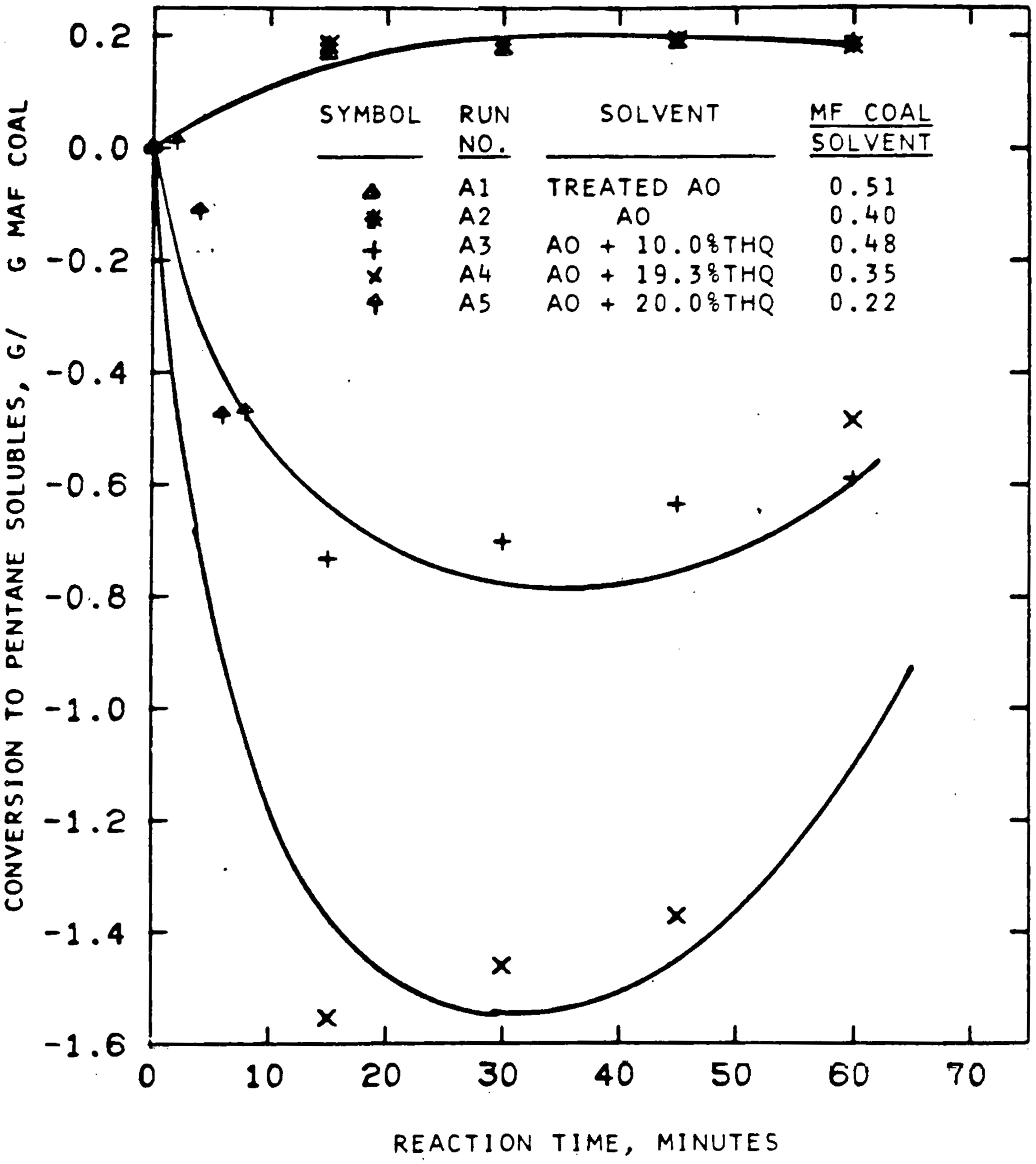


FIGURE 15 EFFECT OF THE ADDITION OF THQ TO ANTHRACENE OIL IN THE CONVERSION TO OILS

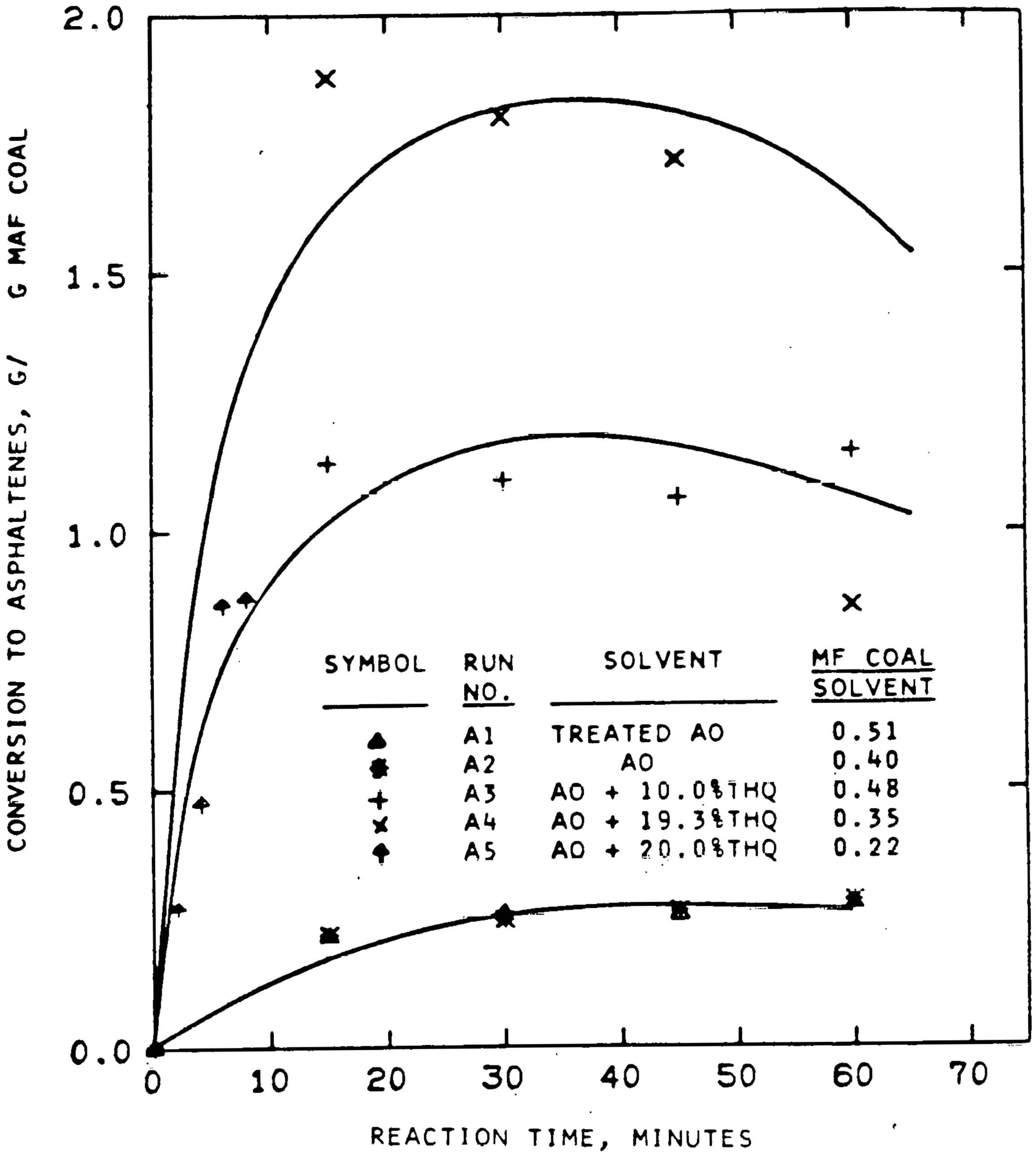
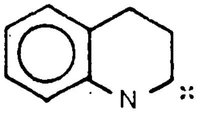
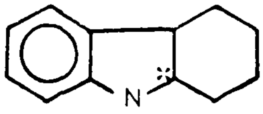


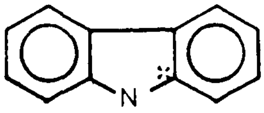
FIGURE 16 EFFECT OF THE ADDITION AF THQ TO ANTHRACENE OIL IN THE CONVERSION OF COAL TO ASPHALTENES



THQ



tetrahydrocarbazole



carbazole

The amount of $^{13}C$ in the product samples was determined by Global Geochemistry Corporation (Canoga Park, California). In the field of geochemistry, the level of $^{13}C$ is compared to a standard, and the range of $^{13}C$ concentrations is typically from 1.02% to 1.13%. Precision of measurement is of great importance. Isotopic compositions have generally been reported in the literature as δ values, the definition of which follows:

$$\delta^{13}C = \frac{R_S - R_R}{R_R} \times 1000\%$$

where $R_S$ and $R_R$ refer to the $^{13}C/^{12}C$ ratio in the sample and reference, respectively. The δ value is referred to as a deviation in parts per thousand (per mil). It is positive if enriched and negative if depleted. The common reference is PDB [Peedee Formation carbonate (belemnite)] with a value of 0.0112372. The mean $\delta^{13}C$ value of our coal sample was -23.16 with a standard deviation of ±0.065. This is equivalent to a $^{13}C$ level of 1.09769% with a standard deviation of ±0.00007%.

A series of fifteen runs was made in the continuous feed, stirred-tank reactor (CSTR) using two levels of space time (nominally 10 and 30 min), two base solvents [anthracene oil (AO) and SRC-II derived process solvent], and three nitrogen-containing solvents (quinoline, THQ, and the nitrogen concentrate from SRC-II solvent). The composition of the feed was 60:40 solvent:coal or 55:5:40 with the additives. The products were sequentially extracted with pentane, toluene, and tetrahydrofuran (THF) with the last two fractions (asphaltenes and preasphaltenes) being subjected to gel permeation chromatography (GPC) with THF as solvent.

## Results and Discussion

### 1. Direct Micro-Autoclave Experiments

The purpose of this aspect of the micro-autoclave study is to investigate the combination of coal liquefaction capability and tendency for solvent adduction of a group of nitrogen-containing species starting with tetrahydroquinoline (THQ) and progressing through phenanthroline. It is noted that THQ is an extremely labile solvent for hydrogen transfer, giving up its hydrogen atoms far more readily than tetralin, and the hydrogen loss ($THQ \rightarrow Q + 2H_2$) is not due solely to satisfy the demand by radical species. Specifically, when a 70:30 mixture of THQ and biphenyl was heated at 450°C for 30 min (3.45 MPa $H_2$ charge at ambient temperature), the resulting product mixture contained a THQ to Q ratio of 67/33. Biphenyl did not crack at these temperatures. With dibenzyl under similar conditions, the ratio was 48/52 with an estimated ratio of about 90/10 needed to satisfy the radicals from the dibenzyl → toluene reaction.

The results of the coal liquefaction experiments to provide information on the coal conversion capabilities of a variety of nitrogen-containing solvents are shown in Table 14. THQ is an excellent solvent for coal liquefaction (82% conversion to THF solubles in 30 min). However, use of THQ as a solvent results in a sizable increase in the nitrogen content of the products. We observed that the nitrogen content of the asphaltene fraction was more than four times higher than that of the corresponding fraction from liquefaction with tetralin.

Quinoline was a poorer coal liquefaction solvent than THQ by a factor of about three. The products had the expected high nitrogen content. Carbazole, which is not capable of hydrogen donation in the same mode as THQ (i.e., the tetrahydroaromatic-aromatic couple; perhaps including also the dihydroaromatic species), nonetheless appeared to be about one-third as effective as THQ in liquefying coal. Acridine was found to generate a negative coal conversion, meaning that the THF-insoluble product weighed more

## Table 14

## Coal Liquefaction with Nitrogen-Containing Solvents[a]

| Solvent[b] | Time (min) | THF Solubles | Coal Conversion[c] Oils | Asph | Pre-Asph | Wt% N[d] Asph |
|---|---|---|---|---|---|---|
| THQ | 30 | 82.3 | -16.5 | 94.9 | 3.8 | 4.70 |
| Q | 30 | 28.7 | -35.6 | 54.0 | 10.4 | 5.56 |
| C | 30 | 34.1 | -- | -- | -- | -- |
| A | 30 | -83.8 | -- | -- | -- | -- |
| Q | 60 | 37.2 | -50.4 | 81.6 | 6.0 | -- |
| A | 60 | -87.9 | -- | -- | -- | -- |
| P-N | 60 | -151.7 | -- | -- | -- | -- |

---

[a] Run conditions: 3.5 g solvent, 1.5 g coal, 34.5 MPa $H_2$ at room temperature.

[b] Solvents: Tetrahydroquinoline (THQ); Quinoline (Q); Carbazole (C); Acridine (A); Phenanthroline (P-N).

[c] Negative yields result when more of an individual fraction is recovered than original MAF coal feed; can be considered as a solvent loss.

[d] The corresponding value of the wt% nitrogen in the asphaltenes from a run with tetraliln was 1.29%.

than the feed coal. Whether this is due to reactions of the acridine with itself or to adduction reactions with the coal is not known; however, the anthracene results presented above suggest the latter is at least a possibility. The data do suggest that solvents with high concentrations of acridine-type structures are not desirable for coal liquefaction.

To expand upon these results, micro-autoclave runs were made with THQ solvent at reaction times of 0 to 30 minutes. The results of these runs and those of comparable runs with tetralin are given in Table 15. Even though overall conversion to THF solubles remained fairly constant with THQ, negative oil yields (pentane solubles) were observed along with high yields of asphaltenes. Nitrogen contents of the asphaltene and preasphaltene fractions were obtained to confirm the high level of THQ reaction with these heavy fractions. As reported in Table 16, the average nitrogen contents of the asphaltenes and preasphaltenes were 6.9 and 4.0 wt%, respectively.

Because of these high nitrogen contents, a study was made using gel permeation chromatography (GPC) to ensure that the THQ, or its reaction product--quinoline, was not physically entrapped in the heavy fractions. Considering the high level of solvent dilution in GPC, along with the long nominal bed residence time, the concentrations of these fractions in solvent were about 2 ppm. Therefore, they should be well dispersed, and they should appear as isolated peaks.

To provide a calibration for the determination of the amount of entrapped quinoline in asphaltene samples, series of GPC scans were obtained for mixtures of a selected asphaltene (micro-autoclave run at 10 min with THQ solvent) with added amounts of quinoline. The GPC plots of the asphaltene and the asphaltene plus 44% quinoline are given in Figure 17. The calibration figure is also given. Considering that the raw asphaltene contained residual quinoline (estimated at 7.1%), there is a linear correlation between the GPC peak area and the amount of added quinoline.

## Table 15

### Summary of Micro-Autoclave Liquefaction Results for Tetraline and THQ Runs

| Solvent | Reaction Time at 450°C (min) | Net Conversion (wt%) Pentane Solubles | Net Conversion (wt%) Toluene Solubles | Net Conversion (wt%) THF Solubles |
|---|---|---|---|---|
| Tetralin | 0 | 14.8 | 40.7 | 63.0 |
| Tetralin | 10 | 23.1 | 66.2 | 83.9 |
| Tetralin | 30 | 28.8 | 76.5 | 86.0 |
| THQ | 0 | -10.8 | 58.0 | 89.2 |
| THQ | 5 | -28.7 | 78.2 | 89.5 |
| THQ | 10 | -37.6 | 58.3 | 81.1 |
| THQ | 30 | -14.7 | 72.2 | 82.1 |
| (Note 1) | | -16.5 | 78.4 | 82.3 |

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Note 1: Previous work: FUEL, 1983, 62, 806-812.

## Table 16

### Nitrogen Results of Asphaltenes and Preasphaltenes of Micro-Autoclave Runs

| Solvent | Reaction Time at 450°C (min) | Nitrogen Content (wt%) | | Quinoline Area (GPC %) | |
|---|---|---|---|---|---|
| | | Asph. | Preasph. | Asph. | Preasph. |
| Tetraline | 30 | 1.1 | (1.2) | - | - |
| THQ | 0 | 7.3 | 3.3 | 4.18 | 1.24 |
| THQ | 5 | 6.4 | 3.6 | 2.63 | 1.54 |
| THQ | 10 | 6.8 | 4.9 | 7.05 | 2.84 |
| THQ | 30 | 6.9 | 4.1 | 0.0 | 0.0 |
| Avg. N-Content of THQ Runs | | 6.9 | 4.0 | 0.37* | 0.15* |

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*Calculated nitrogen content considering that quinoline contains 10.8 wt% nitrogen.

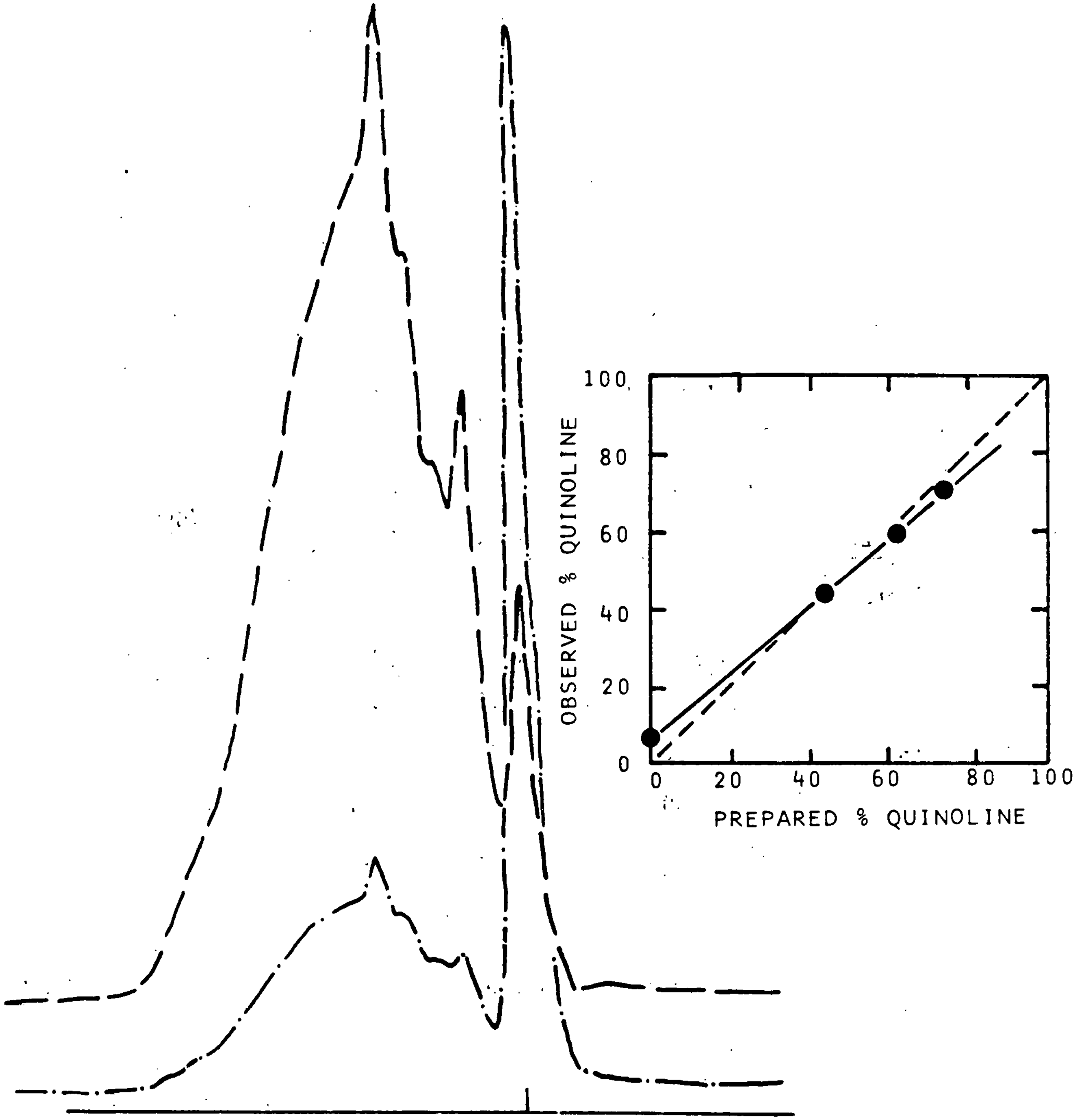


FIGURE 17 GPC PLOTS OF SAMPLES OF ASPHALTENE (MICRO-AUTOCLAVE, 10 MIN, THQ SOLVENT) AND ASPHALTENE WITH 44% QUINOLINE

The GPC plots of the asphaltene and preasphaltene fractions from the micro-autoclave runs with THQ solvent are shown in Figures 18 and 19, respectively. It is first noted that the asphaltenes have low levels of entrapped quinoline (and/or THQ). Considering the average quinoline GPC area and a 10.8 wt% nitrogen content in this solvent, only 0.37 wt% nitrogen is present in the asphaltenes as a result of entrapment. Therefore, about 1.1 wt% is due to coal-derived species, and the remaining 5.4 wt% is due to adducted solvent. In the case of preasphaltenes, the respective nitrogen contents are 0.15, 1.2, and 2.6 wt% for physical entrapment, coal-derived species, and adducted solvent, respectively.

As also shown in the GPC plots, there is a general trend of molecular weight reduction (longer retention time) with increased reaction time. In particular, the leading, high molecular weight shoulders of asphaltenes and preasphaltenes undergo reduction with increased reaction time.

## 2. Experiments with Labeled Solvents

To further confirm the adduction tendency of nitrogen-containing solvents, series of experiments were run using $^{13}$C-labeled THQ, carbazole, and tetrahydrocarbazole. By determining the absolute level of $^{13}$C in the various product fractions, the level of adducted compound was measured. The results in terms of yields and $^{13}$C levels are given in Table 17. For reference, the amount of $^{13}$C is given in terms of $\delta^{13}$C. This is a ratio with respect to a standard expressed in parts per thousand. See the Experimental Section for a detailed description.

Due to the somewhat limited quantity of labeled compounds, combination of solvents was used, and this must be taken into account in a discussion of the results. A repeat THQ/30 min run was made to prepare fresh samples for analysis. The yields followed expected trends. A subsequent run (No. 2) with THQ plus $^{13}$C-labeled THQ (60/10 with 30 coal) resulted in a somewhat different distribution of products, namely, a positive oil yield with a reduced asphaltene yield. This cannot be explained. Runs 3 and 4 were made with high levels of tetralin and low levels of $^{13}$C-THQ primarily to observe

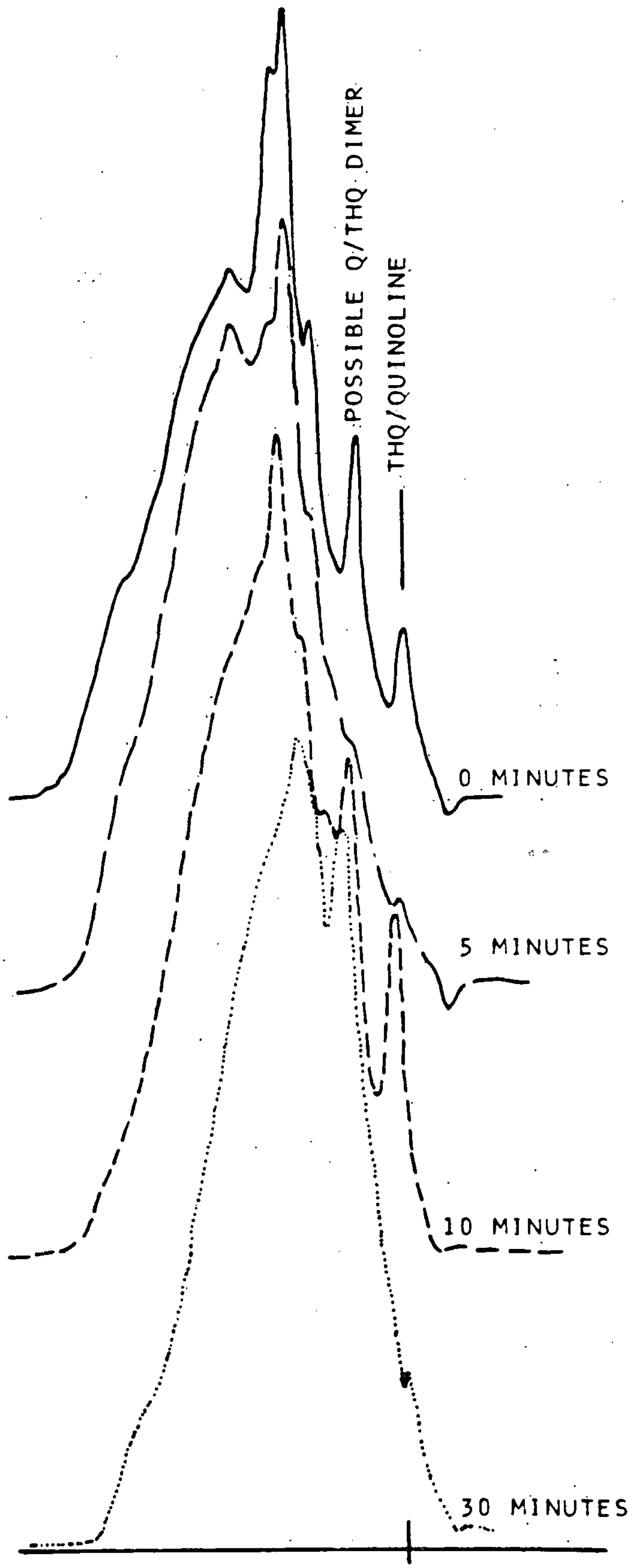


FIGURE 18 GPC PLOTS OF ASPHALTENES FROM THE MICRO-AUTOCLAVE RUNS WITH THQ SOLVENT

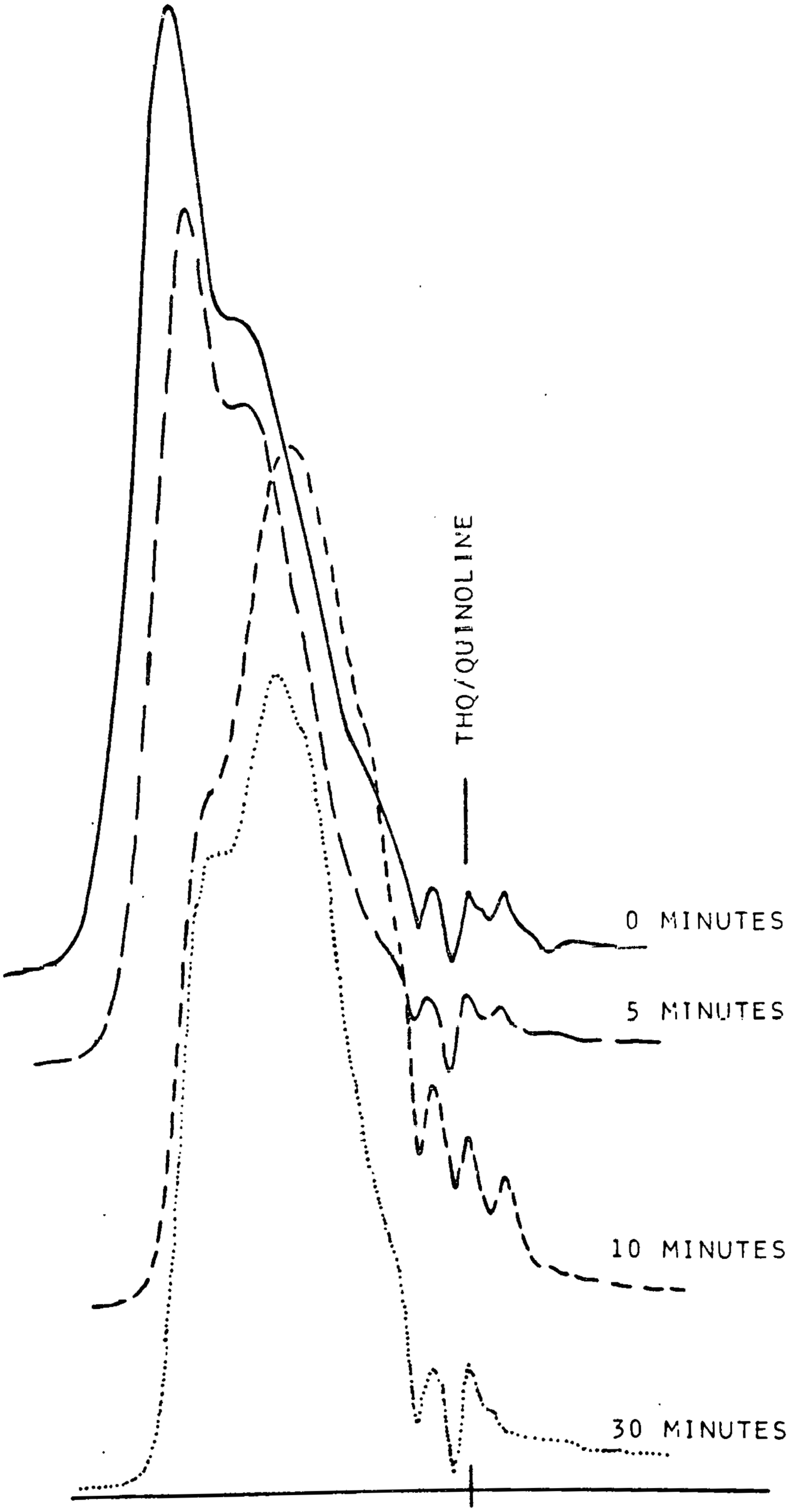


FIGURE 19 GPC PLOTS OF PREASPHALTENES FROM THE MICRO-AUTOCLAVE RUNS WITH THQ SOLVENT

## Table 17

## Micro-Autoclave Experiments with $^{13}C$-Labeled Solvents

Summary of Conversion Results:

| Run No. | Solvent(1) | Reaction Time at 450°C (min) | Net Conversion (wt%) | | | |
|---|---|---|---|---|---|---|
| | | | Pentane Solubles | Asphaltenes | Preasphaltenes | THF Insolubles |
| 1 | THQ | 30 | -17.0 | 94.1 | 4.7 | 18.1 |
| 2 | THQ*(2) | 30 | 18.7 | 58.1 | 7.7 | 15.5 |
| 3 | THQ* + Tet(3) | 0 | 15.5 | 36.7 | 25.7 | 22.1 |
| 4 | THQ* + Tet(3) | 30 | 27.1 | 43.7 | 7.5 | 21.6 |
| 5 | CARB + Tet(4) | 10 | <----65.0----> | | 15.4 | 19.7 |
| 6 | CARB* + Tet(5) | 10 | <----67.3----> | | 14.0 | 18.8 |
| 7 | HCARB* + Tet(6) | 10 | <----61.7----> | | 10.0 | 28.3 |

Summary of $^{13}C$ Levels; $\delta^{13}C$ Values:

| Run No. | Solvent | Reaction Time at 450°C (min) | Pentane Solubles | Asphaltenes | Preasphaltenes | THF Insolubles |
|---|---|---|---|---|---|---|
| 1 | THQ | 30 | - | -22.2 | (-222) | -21.9 |
| 2 | THQ* | 30 | - | 401.6 | 170.4 | 136.1 |
| 3 | THQ* + Tet | 0 | - | 838.3 | 96.0 | 76.9 |
| 4 | THQ* + Tet | 30 | - | 854.5 | 252.4 | 244.9 |
| 5 | CARB + Tet | 10 | - | - | -24.9 | -23.1 |
| 6 | CARB* + Tet | 10 | - | - | -8.9 | -9.9 |
| 7 | HCARB* + Tet | 10 | - | - | 66.3 | 54.9 |

---

Notes: (1) Solvent to coal ratio = 70:30, except as noted below.
(2) THQ* = 60 parts THQ plus 10 parts $^{13}C$-labeled THQ.
(3) THQ* + Tet = 60 parts tetralin plus 10 parts $^{13}C$-labeled THQ.
(4) CARB + Tet = 70 parts tetralin plus 30 parts coal + 10 parts carbazole.
(5) CARB* + Tet = 70 parts tetralin plus 30 parts coal + 5 parts carbazole plus 5 parts $^{13}C$-labeled carbazole.
(6) HCARB + Tet = same as (5) but 5 parts $^{13}C$-labeled tetrahydrocarbazole.

adduction tendencies. The product yields were consistent with those of tetralin. Because carbazole is a non-donor, two experiments were made with a coal/tetralin/carbazole feed level of 30/70/10; namely, Run 5 was made with common carbazole while Run 6 was made with a 50/50 blend of common and $^{13}$C-labeled carbazole. The yield distribution of these runs was comparable, but they had higher preasphaltenes yields than the prior runs of tetralin plus THQ. The carbazole run products were extracted with only toluene and THF due to a limited carbazole solubility in pentane. It is interesting that the single run with tetralin plus tetrahydrocarbazole resulted in a lower yield of oils plus asphaltenes (toluene solubles) and higher THF insolubles than the prior two runs with tetralin plus carbazole. Apparently this is due to adduction.

An analysis of the levels of adduction was obtained by observing the $^{13}$C levels of the product fractions. The reference level of the coal and products is in the $\delta^{13}$C range of -22 to -25 based on runs with unlabeled solvents. With the use of labeled THQ as solvent (60 parts THQ, 10 parts $^{13}$C-THQ, and 30 parts coal) in Run 42, the $\delta^{13}$C level of the asphaltenes was 401.6. This is equivalent to an adduction level of 47 molecules of THQ per 1000 asphaltene carbons, which would result in a nitrogen content in the range of 4.7 to 4.9%. This calculated nitrogen level is made considering that the analysis of the asphaltenes of Run 53 (tetralin only at 450°C, 30 min) had a nitrogen content of 2.6 wt% with an additional 47 THQ/1000 carbons. This is consistent with an observed nitrogen content of 4.7 wt% for a THQ run @ 450°C and 30 min. The levels of THQ adduction in the preasphaltenes and solids of this run are 17 and 14 molecules per 1000 carbons, respectively. Of course, this "adduction" reaction includes any reactions that could occur resulting in THQ showing up in an individual fraction. Such reactions include polymerization, coking, etc. (In the above results, the effect of $^{13}$C-THQ dilution was taken into account.)

With the use of $^{13}$C-THQ plus tetralin (10 parts/60 parts, respectively), high $\delta^{13}$C values were observed in the product fractions of the 30-minute run. Our past work in this project and that of DOE Contract

DE-AF22-80PC30080 has shown that THQ is more reactive than tetralin in transferring hydrogen and undergoing adduction reactions. Therefore, it is consistent that the level of $^{13}$C-THQ adduction in the asphaltene fraction was about 11 molecules/1000 asphaltene carbons since the labeled THQ only made up one-seventh of the feed solvent. (In the above case of THQ solvent alone, the adduction level was 47 after dilution was taken into account.) The levels of THQ adduction into the preasphaltene and solid fractions were sizable at levels of 3.1 molecules/1000 carbons. As shown in Table 17, the level of THQ adduction in the "0" minute run at 450°C using THQ plus tetralin solvent was somewhat different than that observed for the 30-minute run. While the adduction in the asphaltene fraction was essentially equal (namely, 10.4 molecules/1000 carbons), the levels of adduction in the preasphaltenes and solids were about one-third (namely, 1.3 and 1.0 versus 3.1). Apparently, there was insufficient time during the "0" minute heat-up period for the THQ to react to the same extent. As a generalization, this would be consistent with a portion of the solvent undergoing polymerization or coking reactions.

When $^{13}$C-labeled carbazole was introduced with the unlabeled tetralin feed, only low levels (~0.1) of adduction in the preasphaltene and solids fractions were observed. With the introduction of tetrahydrocarbazole, adduction levels of about 1 molecule/1000 carbons were observed in both the preasphaltene and THF-insoluble fractions. The modes of adduction of tetrahydrocarbazole and carbazole are much different with the former probably attaching through a free radical formed by hydrogen donation. In the case of THQ and quinoline, about equal levels of adduction are observed to occur, presumably through interaction with the nitrogen site.

### 3. Experiments Using Distillate Cuts

To evaluate both the effect of solvent boiling point and that of Amberlyst-15 ion exchange treatment of selected cuts for nitrogen reduction, a short series of micro-autoclave runs was made using SRC-II distillate cuts. As described in the Experimental Section, SRC-II solvent was distilled into eight distillate cuts of 10 wt% each. The distillation curve and cut points are given in Figure 20. Samples of cuts 2, 3, 4, 5, 6, and 8 were contacted with A-15 resin at a ratio of 3.3/1.0. The treated solvent was then used for some of the liquefaction runs.

The results of the liquefaction experiments are summarized in Figure 21 with the converting solid points designating the yields of the experiments with raw SRC-II distillate cuts. These points show some randomness with low conversion levels being observed for the Cut 1 and Cut 7 solvents. However, a high conversion level was observed for Cut 6. For the most part, conversion levels using ion exchange-treated solvents were essentially equal to those of the untreated solvents.

## 4. Bench-Scale Liquefaction Experiments

To expand upon the micro-autoclave results, series of runs were made in the CSTR unit to evaluate the effect of adding THQ, quinoline, or nitrogen concentrate to either anthracene oil (AO) or SRC-II recycle solvent. The feed slurry consisted of 40% Powhatan No. 5 coal and 60% solvent (or 55% solvent plus 5% additive). The experiments were made at reaction pressure and temperatures of 10.3 MPa and 450°C with nominal slurry space times of 10 or 30 minutes. As in the previous runs with phenolics, detailed material balances were calculated, and the results are summarized in Tables 18 and 19.

In the case of SRC-II solvent, there was no significant effect of solvent additive upon the product distribution at either reaction space time. With the increase of space time from 10 to 30 minutes, sizable increases in the yields of gases and THF solubles were observed with smaller increases in the yields of oils and toluene solubles.

When a comparison is made among equivalent runs with anthracene oil and SRC solvent (namely, neat and THQ added solvents), the yield of oils doubled when going from the poorer to better solvent (AO versus SRC, respectively). However, the yields of toluene and THF solubles were about equivalent.

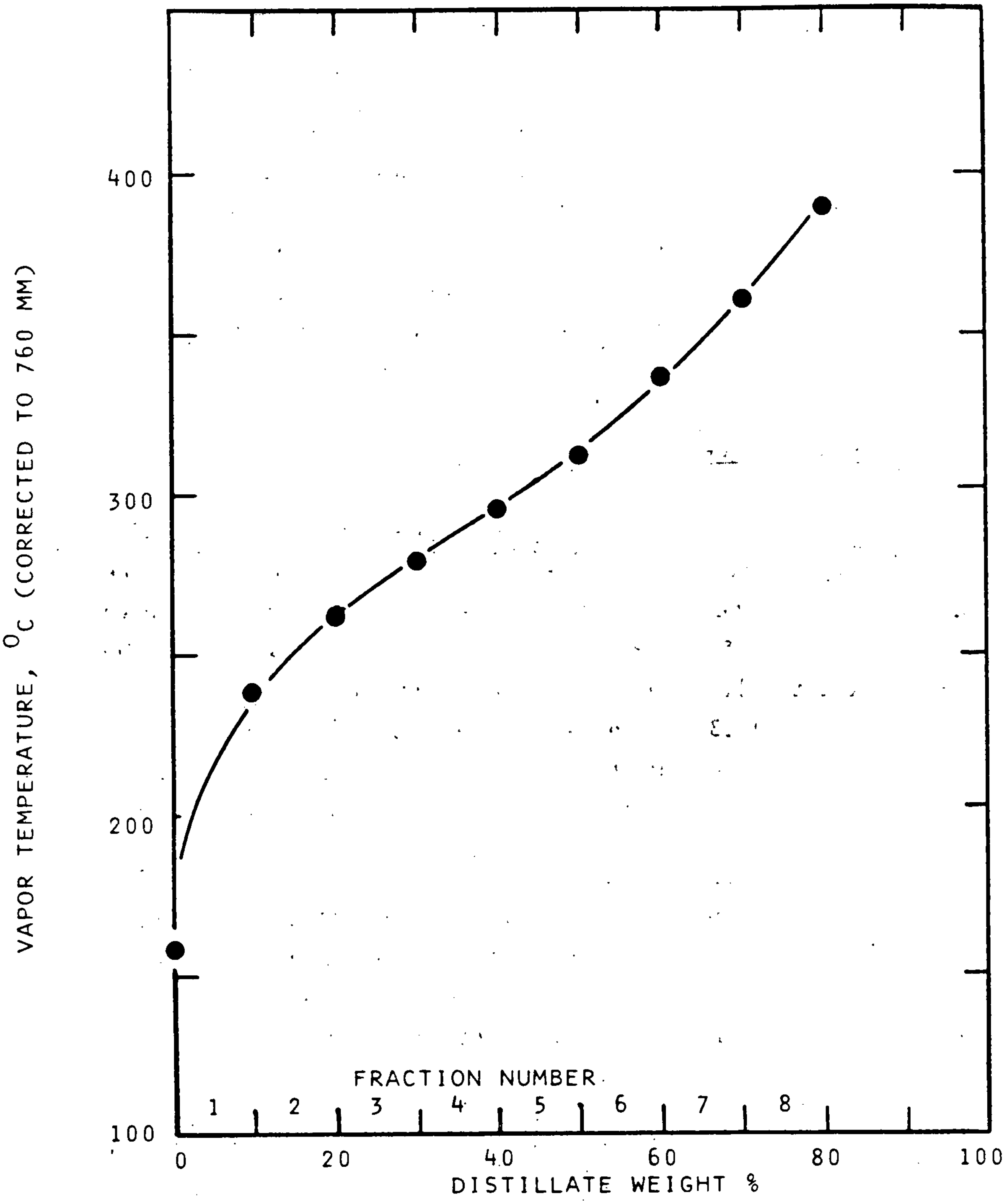


FIGURE 20 DISTILLATION CURVE OF THE SRC-II SAMPLE

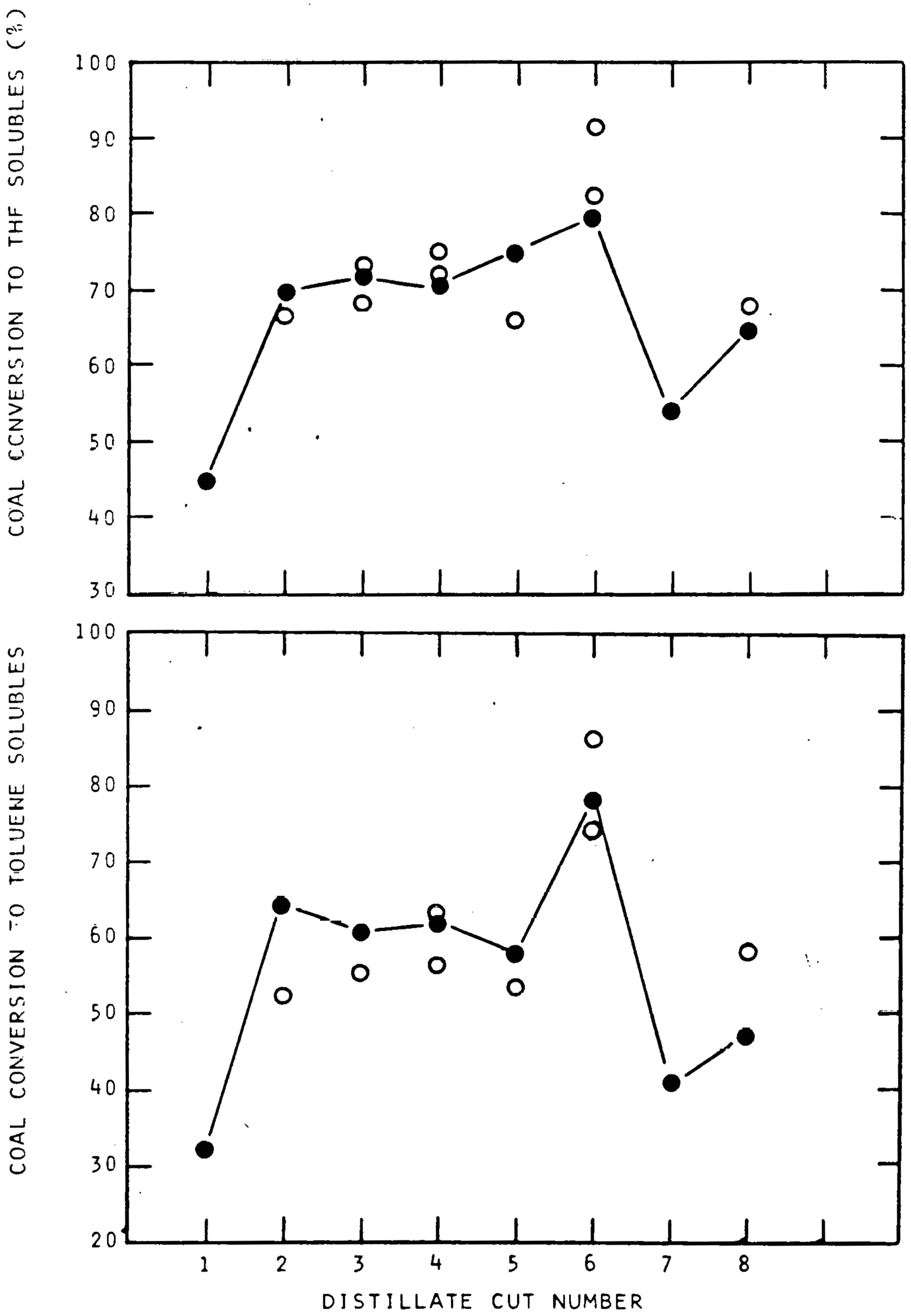


FIGURE 21 CONVERSION AS A FUNCTION OF DISTILLATE CUT NUMBER ( RAW SOLVENT, A-15 TREATED SOLVENT, POINTS ARE CONNECTED AS A MEANS OF CONVENIENCE, ONLY)

## Table 18

### Summary of Bench-Scale Liquefaction Results at a Space Time of 10-11 min(1)

| Solvent (Additive) | Net Conversion (% MAF)<br>$C_1$-$C_6$ Gases | Pentane Solubles | Toluene Solubles | THF Solubles |
|---|---|---|---|---|
| SRC (Avg.)(2) | 4.6<br>±0.3 | 15.6<br>±0.4 | 45.0<br>±3.5 | 66.5<br>±2.0 |
| AO | 3.2 | 5.7 | 49.4 | 68.4 |
| AO (THQ) | 3.0 | 11.2 | 48.9 | 73.2 |
| AO (Q) | 3.4 | -3.7 | 40.1 | 68.3 |
| AO (NC)(3) | 3.4 | 1.7 | 29.7 | 54.0 |

---

(1) Run conditions: 40% Powhatan No. 5 coal, 60% solvent (or 55% solvent + 5% additive), 450°C, 10.3 MPa pressure.

(2) Average of runs with the solvents: SRC, SRC (THQ), SRC (Q), and SRC (nitrogen concentrate).

(3) Results of single determination at time of run; duplicate results about four months later gave -25.3, 35.0, and 63.7% for pentane, toluene, and THF solubles, respectively.

## Table 19

### Summary of Bench-Scale Liquefaction Results at a Space Time of 28-32 min(1)

| Solvent (Additive) | Net Conversion (% MAF) | | | |
|---|---|---|---|---|
| | $C_1$-$C_6$ Gases | Pentane Solubles | Toluene Solubles | THF Solubles |
| SRC (Avg.)(2) | 8.2<br>±1.5 | 17.3<br>±1.5 | 47.9<br>±3.7 | 73.6<br>±5.4 |
| AO | 6.0 | 1.1 | 43.4 | 66.3 |
| AO (THQ) | 5.2 | 15.1 | 43.0 | 64.5 |
| AO (Q)(3) | 3.2 | 18.2 | 45.1 | 65.6 |
| AO (NC) | 6.5 | 16.1 | 43.9 | 73.5 |

---

(1) Run conditions: 40% Powhatan No. 5 coal, 60% solvent (or 55% solvent + 5% additive), 450°C, 10.3 MPa pressure.

(2) Average of runs with the solvents: SRC, SRC (THQ), and SRC (Q).

(3) A total of three determinations.

As also observed in Tables 18 and 19, the addition of nitrogen-containing additives had a sizable effect on the yield of oils in the AO series of runs. The addition of 5 parts THQ to 55 parts AO resulted in a sizable oil yield increase. The addition of quinoline and nitrogen concentrate resulted in marginal (but strongly interacting with time) oil yield increase. With all of these additions, there appeared to be little effect upon the yields of toluene and THF solubles.

Representative GPC plots of the SRC and AO asphaltenes are shown in Figures 22 and 23. The patterns for all the SRC products are superimposable; the presence and identity of the additive had little effect. The plot from an AO run without any additives is strikingly different, having two major components, a lower intensity band due to high molecular weight material and a high-intensity peak due to low molecular weight material. The presence of the THQ or quinoline additives resulted in a drastic change in the overall pattern; namely, the higher molecular weight peak of the AO run (alone) became more pronounced in the AO plus THQ or Q runs. It is noteworthy that no peaks are observed in either the SRC or AO runs corresponding to the additives. That is, there is no direct evidence of hydrogen bonding between the additive and the coal liquid.

The GPC plots of the preasphaltenes are shown in Figures 24 and 25 for the SRC and AO products, respectively. In the SRC series, all the plots have basically the same shape, although there are small variations in the low molecular weight shoulder, which increases in intensity in the order AO alone < AO + THQ < AO + Q. (The stabilizer in the THF used for the extraction, butylated hydroxytoluene, provided a convenient molecular weight marker.) The position of the pattern from the coal-derived materials shifted to longer elution times with the presence of the additives, indicating an upgrading of the product (lower MW). As was found to be the case with the asphaltenes, the pattern of the product from a run with AO alone was greatly different from that observed with SRC or from AO plus additives. Furthermore, the presence of THQ or Q resulted in a shift to higher molecular weight preasphaltenes. This may be a result of upgrading of the less refractory, lower molecular

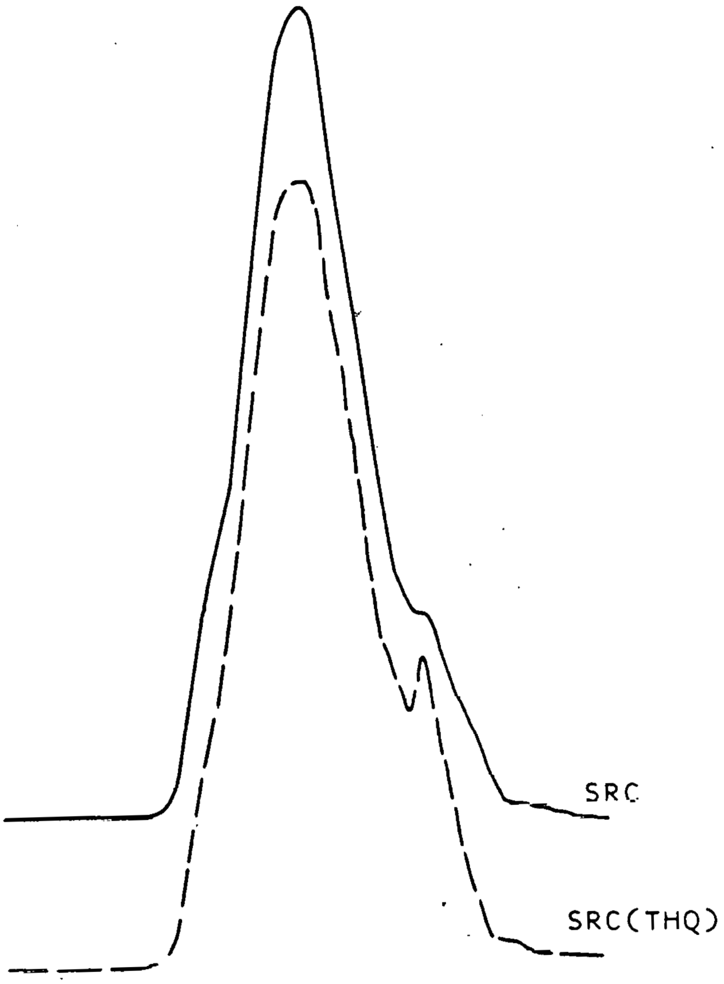


FIGURE 22 GPC PLOTS OF ASPHALTENES FROM THE 28-32 MINUTE SPACE TIME RUNS WITH SRC SOLVENT

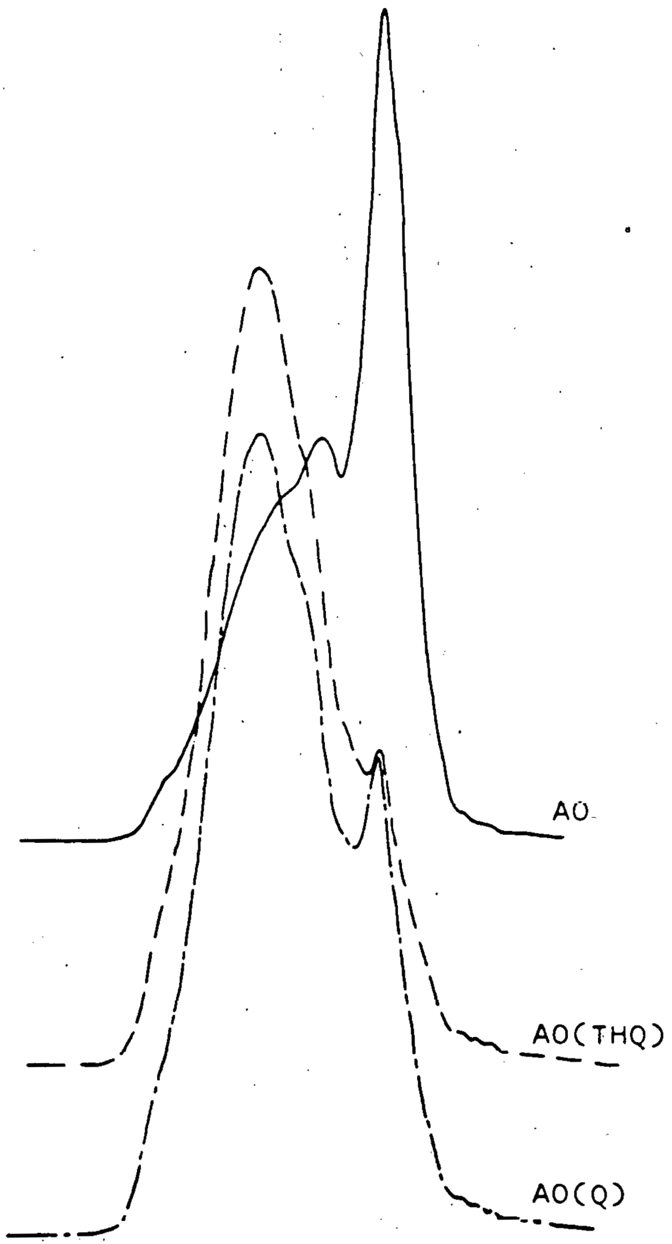


FIGURE 23 GPC PLOTS OF ASPHALTENES FROM THE 28-32 MINUTE SPACE TIME RUNS WITH ANTHRACENE OIL SOLVENT

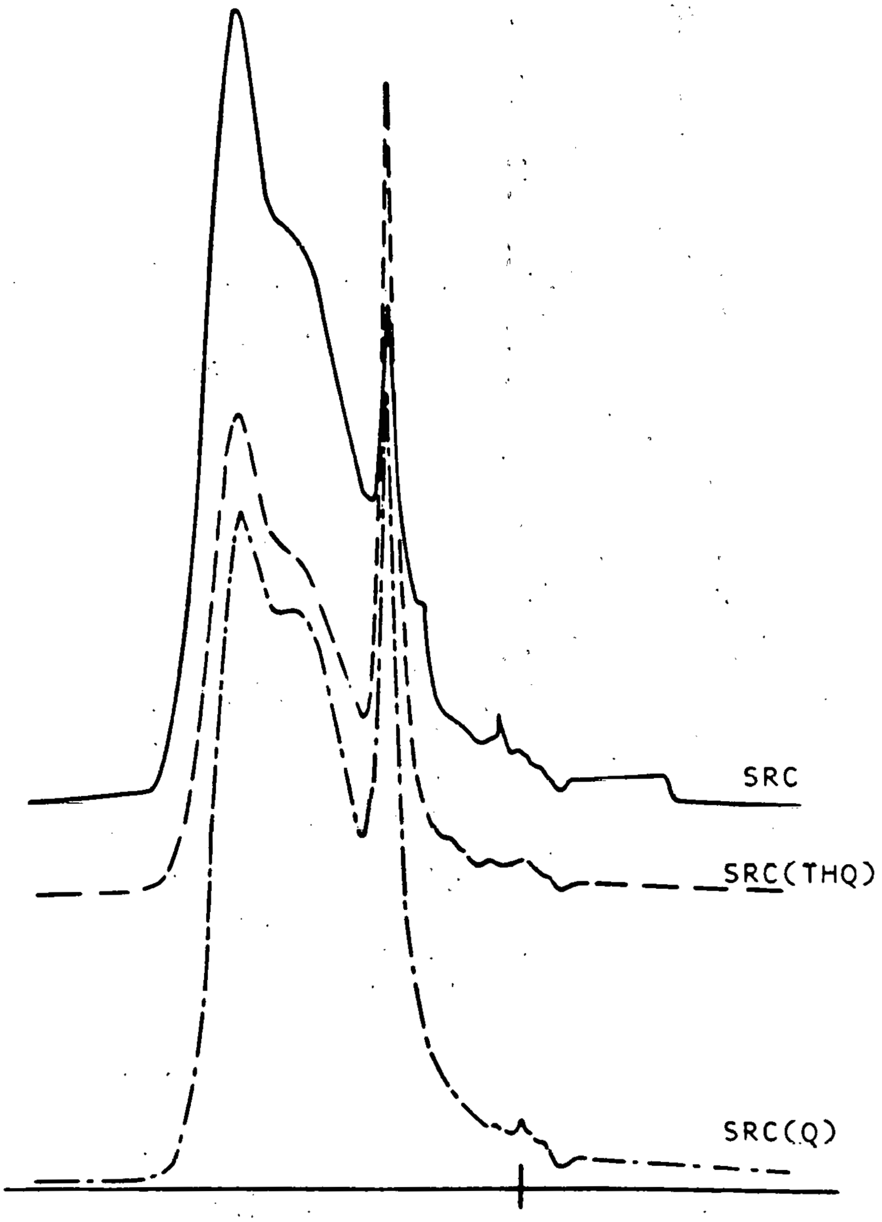


FIGURE 24 GPC PLOTS OF PREASPHALTENES FROM THE 28-32 MINUTE SPACT TIME RUNS WITH SRC SOLVENT

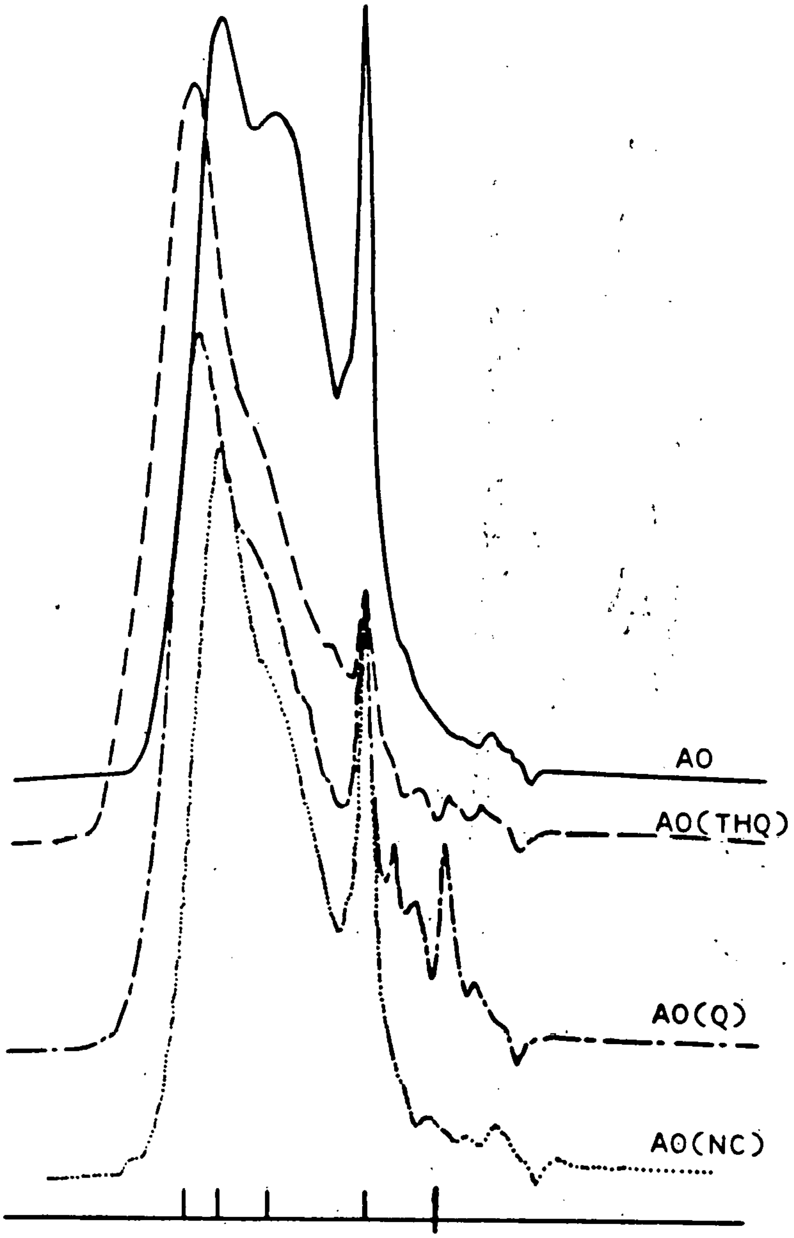


FIGURE 25 GPC PLOTS OF PREASPHALTENES FROM THE 28-32 MINUTE SPACE TIME RUNS WITH ANTHRACENE OIL SOLVENT

weight material with its removal from the preasphaltene fraction. Alternatively, some of the otherwise insoluble material may have become THF soluble by adducting the solvent. With nitrogen concentrates as the additive, the position of the main peak shifted slightly to lower molecular weight, indicating that some upgrading took place.

The results indicate that the presence and type of basic nitrogen additives in SRC-II recycle oil had no effect on the quality of the asphaltenes and only a slightly beneficial effect on the size of the preasphaltenes. In contrast, the presence of the additives in runs with anthracene oil appeared to result in the loss of the lower molecular weight materials from both the asphaltenes and the preasphaltenes.

The nitrogen analyses of the asphaltenes and preasphaltenes of the bench-scale liquefaction products are shown in Table 20. From the apparent lack of a nitrogen concentration increase, no adduction occurred. This is probably due to the vaporization of quinoline and THQ into the gas stream which quickly exited the reactor. This is in contrast to the micro-autoclave runs in which these components remain in the liquid phase during the extended reaction period.

## Conclusions

Hydroaromatics having nitrogen functionality should be good solvents for coal liquefaction considering their effective solvent power, ability to penetrate and swell coal, and their ability to readily transfer hydrogen, particularly in the presence of oxygen functionality. However, these benefits are overshadowed by the strong tendency of the nitrogen-containing species to adduct with themselves and coal-derived materials. As demonstrated in micro-autoclave experiments in which nitrogen compounds including tetrahydroquinoline (THQ), phenanthroline, acridine, etc., are used as solvents, high levels of asphaltenes are recovered. These asphaltenes have high nitrogen contents. The level of adduction is further demonstrated by observing the attachment of labeled species into both preasphaltene- and tetrahydrofuran-insoluble fractions.

## Table 20

### Nitrogen Contents of Asphaltenes and Preasphaltenes of Bench-Scale Products at a Space Time of 28-32 min

| Solvent (Additive) | Nitrogen Content (wt%) | |
|---|---|---|
| | Asphaltenes | Preasphaltenes |
| AO | 1.4 | - |
| AO (THQ) | 1.9 | 1.5 |
| AO (Q) | 1.9 | 1.1 |
| AO (NC) | 1.1 | 1.6 |
| SRC | 2.1 | - |
| SRC (THQ) | 1.8 | - |
| SRC (Q)(1) | 1.9 | 1.5 |
| SRC (NC)(1) | 1.8 | 1.2 |
| AVERAGE | 1.7 | 1.4 |

---

(1)Results are from products of runs of 10-11 min space times.

The use of THQ in CSTR units appears to be of some advantage in improving a poor donor solvent. However, it appears that this light solvent is readily stripped into the vapor space, thereby limiting the extent of adduction reactions.

Experiments undertaken with gel phase chromatography (GPC) show that essentially all of the solvents (i.e., THQ and quinoline) undergo some sort of chemical reaction with the coal-derived species. Specifically, only a small fraction of the increase of nitrogen content in the heavy fractions is due to retained unreacted solvent, which can be isolated in the GPC scan.

## III. SUBTASK 3a: Extraction of Coal Using Supercritical Fluid Mixtures

To complement the above work, experimentation was undertaken in collaboration with the Chemical Engineering Department of the University of Pittsburgh to study coal liquefaction using supercritical water in combination with nitrogen-containing solvents. This work has been completed and is presented herein in the format of a manuscript for publication.

### Abstract

Powhatan No. 5 and Bruceton coals were reacted/extracted for 15-60 min at 380°C and 30 MPa, in supercritical aqueous mixtures containing 10 to 20 wt% tetrahydroquinoline (THQ), quinoline, or tetralin. The THQ mixtures produced the highest conversion, up to 74%, to THF-soluble products. In order of decreasing effectiveness in producing THF solubles were the tetralin-water, quinoline-water, and pure water solvents. Addition of hydrogen to the quinoline-water solvent increased yields slightly but not to the level obtained using THQ.

The yields of THF solubles in all instances depended upon the concentration of solvent in the mixture with the 10% THQ and 10% tetralin giving the maximum yields for these systems. Quinoline-water mixtures

containing 10% quinoline produced a minimum yield for that system. High levels of chemical adduction of the nitrogen-containing solvents with the coal-derived products were observed.

## Introduction

A sizable amount of research on producing liquid chemicals and fuels from coal has been performed over the last 20 years, due in part to concern over petroleum shortages and the consequential need for alternate energy and chemical feedstock sources. Several types of coal liquefaction processes have been developed through the pilot plant stage, ranging from pyrolysis to direct and indirect hydrogenation of coal. The solvent Refined Coal (SRC-I and -II), the Exxon Donor Solvent, and the H-Coal processes are among the more completely developed donor solvent processes.

Supercritical extraction of coal is now undergoing a high level of activity. Supercritical extraction involves the thermal breakdown of coal and subsequent hydrogenation reactions, but the liquefaction is enhanced by the greater solvent power of the supercritical fluid. Depending on the solvents used, supercritical extraction of coal can be successfully performed at low temperatures (350-400°C), moderate-to-high pressures (8-30 MPa), and in batch or continuous modes. This method shows potential, although most studies of supercritical coal extraction have been limited to basic thermodynamic and kinetic research.

A number of studies have been performed over the past decade using supercritical (SC) water as a solvent for coal liquefaction. Stewart and Dyer(1) patented a process for the thermal cracking of coal in the presence of SC water. They obtained conversions of 20-25% by reacting a bituminous coal at 400-500°C for 1-5 min. Modell (2) used SC water in reactions with glucose, cellulose, maple sawdust, or coal slurried with sulfur, and their results showed that supercritical water may prevent the formation of char, which is a significant and generally undesirable by-product of coal pyrolysis reactions.

Ross et al. (3) reacted samples of high- and low-ash Illinois No. 6 bituminous coal with SC water alone and in combination with CO, $H_2$, and/or KOH. They showed that the SC water-CO combination is more effective in terms of coal conversion than SC water-$H_2$, particularly for the high-ash content coal. It was also shown that for the SC water-CO systems, even small amounts of added KOH greatly improved the conversion (if CO was not present, the effect of KOH addition was much lower). Barton (4) added catalyst (stannous chloride or molybdenum trisulfide) and $H_2$ to a SC water-coal system and achieved up to 54% conversion (pyridine solubles) after reacting at 400°C for 96 to 234 min.

Deshpande et al. (5) used supercritical water at its critical density in a series of autoclave studies, reacting separately Bruceton bituminous coal, German brown coal, and glucose with SC water at 377°C for 15-60 min. Conversions of 58% and 75% were obtained for the Bruceton and German coals, respectively (THF solubles, MAF basis). The results indicated that the SC water must be at or near its critical density to be effective as a hydrogen-donor liquefaction solvent; increases in water density produced increased conversions.

Only a few solvent mixtures have been used for supercritical coal liquefaction and extraction of coal at supercritical conditions. Kershaw (6) reacted several commercially available hydrocarbon mixtures with a South African bituminous coal at 450°C, and as he had done with pure solvent, he obtained correlations which related the degree of extraction to the mixture critical temperatures, boiling points, and density. Martin (7) continuously extracted a British coal with a SC fluid consisting of toluene with either tetralin or THQ added in the 380-440°C temperature range. He showed that the addition of tetralin or THQ increased the coal conversion by as much as 10%, especially at the highest temperatures.

## Experimental

Two Pittsburgh Seam bituminous coals (Powhatan No. 5 and Bruceton) and an Illinois No. 6 coal were used in the experiments. Their proximate and ultimate analyses are given in Table 21. Except where noted, Powhatan No. 5 was used for all runs.

### 1. Supercritical Coal Extraction Procedure

The experimental apparatus is shown in Figure 26 and consists of a 1-L stainless steel autoclave equipped with a Magnedrive stirrer and a coal injection system. The reactor is charged with 340 g of water and is heated at 3-4 K/min. Once the reaction temperature is reached, ambient coal is injected into the reactor using high-pressure argon (hydrogen was used instead of argon for runs 35, 36, and 41). The average weight of injected coal was 14 g. Reaction times are measured from the time at which the coal is injected.

All experiments were run at 380°C and 30 MPa unless otherwise noted. In addition to the water, a second solvent was added in either 10 wt% (38 g) or 20 wt% (76 g) amounts prior to heating and coal injection.

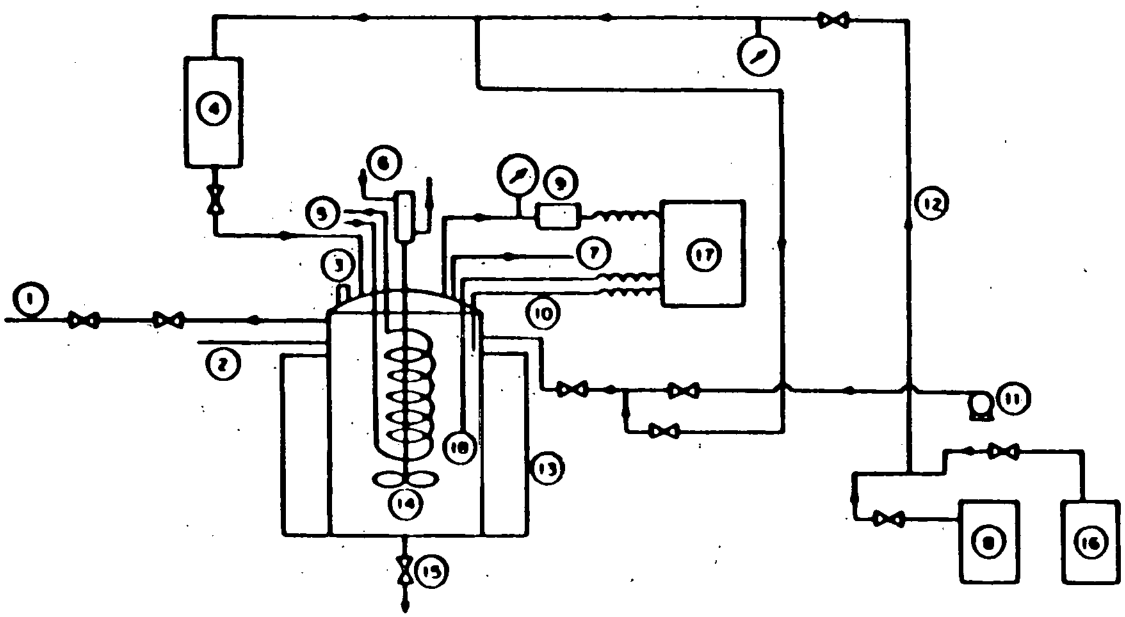
The liquid and solid contents were collected from the reactor and placed in a Soxhlet extraction thimble and dried for 1-2 days at 100°C with a nitrogen gas sweep. The thimble was then placed in a Soxhlet unit and extracted with toluene until the extractant was clear (about 2 days). After drying again for 1-2 days, the product was weighed and similarly extracted with tetrahydrofuran (THF) for 1 day, dried, and weighed a final time. The weight of the dried product after toluene extraction and after THF extraction is designated toluene and THF insolubles, respectively.

The conversion parameters, based on the extraction results, are defined below.

# Table 21

## Characterization of Coal Samples

| Coal Analysis (Moisture-Free) | Powhatan No. 5 | Bruceton | Illinois No. 6 |
|---|---|---|---|
| Carbon | 72.3 | 78.6 | 67.5 |
| Hydrogen | 5.1 | 5.3 | 4.8 |
| Nitrogen | 1.5 | 1.6 | 1.2 |
| Oxygen (Diff.) | 7.8 | 8.2 | 6.6 |
| Sulfur | 3.6 | 1.4 | 4.0 |
| Ash | 9.7 | 4.9 | 15.9 |
| | 100.0 | 100.0 | 100.0 |



① GAS SAMPLE LINE
② RUPTURE DISC TO HOOD
③ LIQUID SAMPLE PORT
④ COAL BOMB
⑤ COLD WATER (FOR STIRRER)
⑥ COLD WATER (FOR MAGNETIC HEAD)
⑦ VENT LINE TO HOOD
⑧ HELIUM CYLINDER
⑨ PRESSURE TRANSDUCER
⑩ THERMOCOUPLE
⑪ PUMP
⑫ GAS LINE
⑬ FURNACE
⑭ AGITATOR
⑮ DRAIN VALVE
⑯ ARGON CYLINDER
⑰ DATA LOGGER
⑱ REACTOR

FIGURE 26 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL UNIT

Gases, Oils, and Asphaltenes (GOA), %

$$= 100 \times \left(\frac{\text{coal injected (g)} - \text{toluene insolubles (g)}}{\text{coal injected (g)}}\right) \quad (1)$$

Total Conversion, %

$$= 100 \times \left(\frac{\text{coal injected (g)} - \text{THF insolubles (g)}}{\text{coal injected (g)}}\right) \quad (2)$$

Preasphaltenes, % = % Total Conversion - % Toluene Solubles (3)

All weights are on a MAF basis. It is also assumed that all toluene solubles are likewise soluble in THF.

### 2. Micro-Autoclave Coal Extraction Procedure

To provide a direct comparison with the above, a series of coal liquefaction experiments were carried out in a micro-autoclave reactor of 1 cm I.D. and 15 cm long, placed vertically in a fluidized-bed sand bath. Various run times were used at a reaction temperature of 380°C with either pure tetrahydroquinoline or tetralin as solvent. The experimental unit, operating procedure, and Soxhlet extraction procedure are described in Reference 8. The conversion results are given in terms consistent with those defined above.

## Results and Discussion

### 1. Effect of Coal Type on Extraction with Supercritical Water

Different coals react differently under identical reaction conditions depending upon their structure, the amount and type of ash, and their carbon content. Powhatan No. 5, Illinois No. 6, and Bruceton bituminous coals were reacted with supercritical water under similar reaction conditions; the results are given in Table 22. The total conversion to gases and THF-soluble products for each coal is shown in Figures 27 and 28.

## Table 22

## Conversion and Product Distribution for Runs with Coals in Supercritical Water

| Run No. | Reaction Time (minutes) | Coal | % Total Conversion | Yield % |  |
|---|---|---|---|---|---|
|  |  |  |  | GOA | Preasphaltenes |
| 39 | 5 | Powhatan | 10.8 | 8.9 | 7.9 |
| 10,29* | 15 | Powhatan | 19.8 | 14.6 | 5.2 |
| 8A,15* | 30 | Powhatan | 16.2 | 14.3 | 1.9 |
| 9 | 60 | Powhatan | 19.4 | 17.3 | 2.1 |
| G44 | 60 | Illinois | 29.1 | 27.5 | 1.6 |
| G17 | 15 | Bruceton | 36.3 | -- | -- |
| G16 | 30 | Bruceton | 53.4 | -- | -- |
| G18 | 60 | Bruceton | 58.4 | -- | -- |

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*Average of two runs.

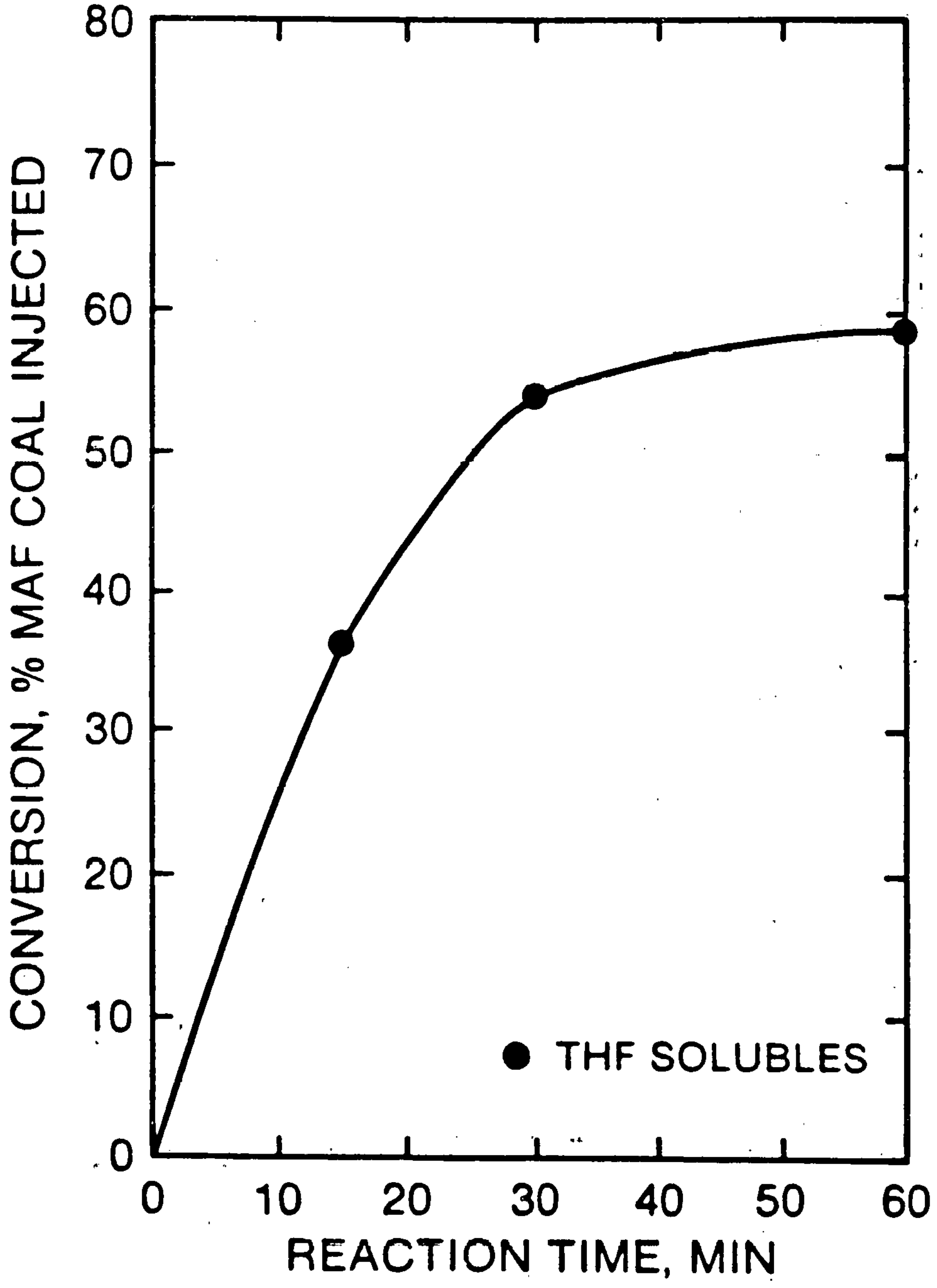

FIGURE 27 EFFECT OF REACTION TIME ON THE CONVERSION OF BRUCETON COAL TO TOTAL THF-SOLUBLE PRODUCTS

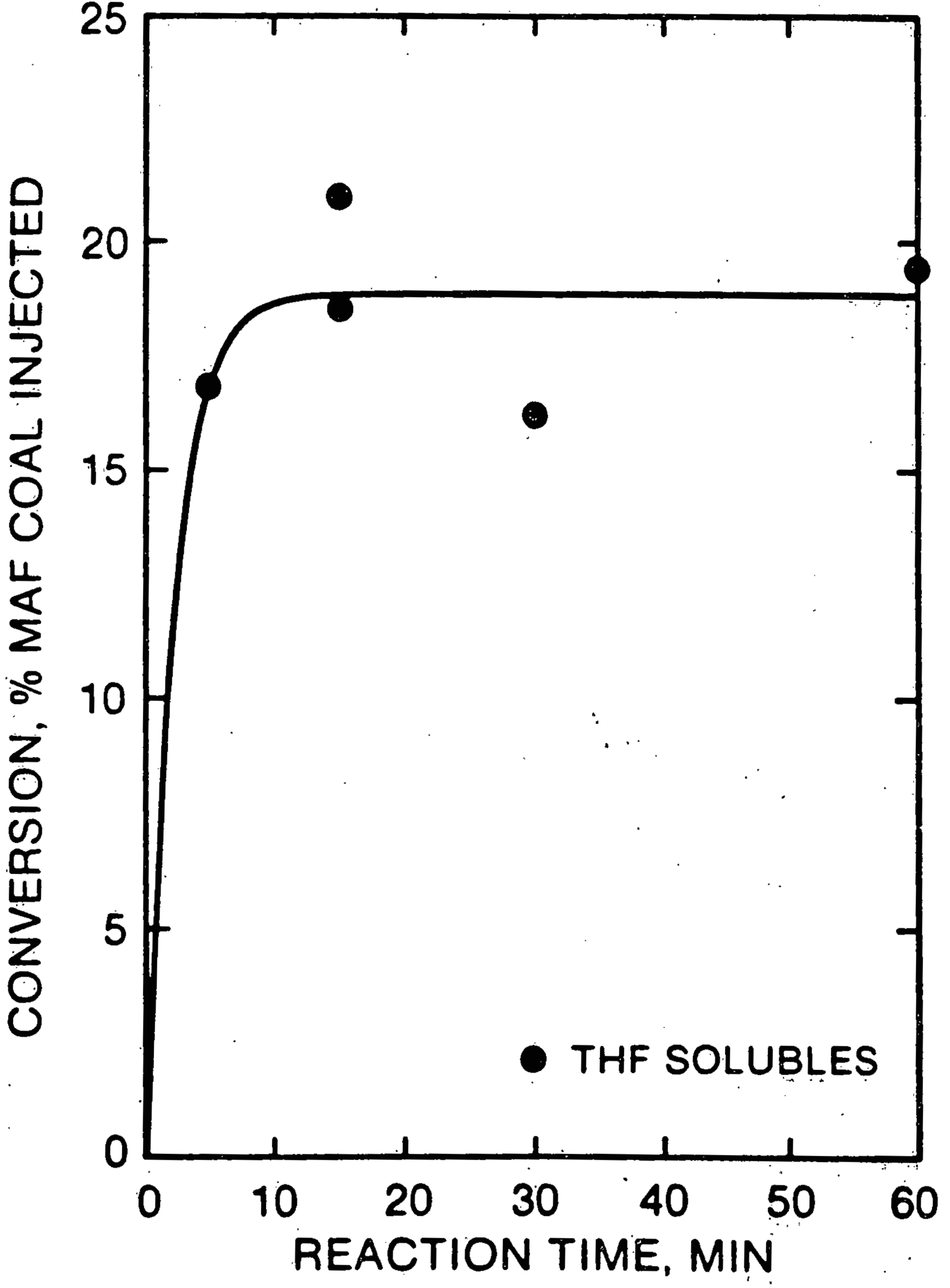

FIGURE 28 EFFECT OF REACTION TIME ON THE CONVERSION OF POWHATAN COAL TO TOTAL THF-SOLUBLE PRODUCTS

It is clear that there is a significant difference in the conversion of the three coals. This is expected since the coals have different THF solubilities prior to extraction, namely, about 9% for Bruceton coal, about 3% for Illinois No. 6 coal, and less than 1% for Powhatan No. 5 coal. It can also be seen that Powhatan No. 5 coal reaches its equilibrium conversion of about 18% in 30 min, while Bruceton coal reaches its equilibrium conversion of about 58% after 60 min. The single run with Illinois No. 6 coal had a conversion of 29% at a 60 min reaction time.

## 2. Effect of Mixed Solvent Characteristics on Coal Conversion

To study the effect of mixed solvent characteristics on conversion to THF-soluble products, different organic solvents such as tetrahydroquinoline, quinoline, tetralin, and piperidine were mixed with water and were used for extraction in their supercritical state. The resulting conversions and product distribution for THQ, quinoline, piperidine, and tetralin are compared in Table 23. All extractions are believed to have taken place in a uniform supercritical solvent phase.

In the case of tetrahydroquinoline, quinoline, and tetralin, dilute mixtures (10% by wt and 1-3% by mole) were used because of the critical temperature of these organic solvents are much higher than that of water and higher weight fractions (of the order of 30%) may have caused a subcritical extraction at the reaction temperature of 380°C. Piperidine has a critical temperature much lower than that of water (594K versus 647K). Hence a higher weight fraction (54% by weight and 20% by mole) was used for extraction. The coal extracted using piperidine was Bruceton bituminous coal.

It can be seen that the conversion strongly depends on the type of the organic solvent in the aqueous mixture. For 10 wt% mixtures, the highest conversion is obtained for tetrahydroquinoline (65%) which is an effective hydrogen donor, and the lowest conversion was obtained using quinoline. Tetralin gave intermediate conversion (34%). The values given in parentheses are for a reaction time of 30 min. In the case of piperidine which is a

## Table 23

## Conversion and Product Distribution for Runs with Powhatan No. 5 Coal and Water Plus Solvent

| Run No. | Reaction Time, (minutes) | Wt% Solvent in Water | % Total Conversion | Yield % GOA | Yield % Preasphaltene |
|---|---|---|---|---|---|
| 28 | 30 | 10% Tetralin | 34.0 | 27.6 | 6.4 |
| 26 | 30 | 20% Tetralin | 29.8 | 21.1 | 8.7 |
| 27 | 2 | 10% Quinoline | 0.6 | -8.9 | 9.5 |
| 11,34* | 15 | 10% Quinoline | 14.4 | 6.7 | 7.7 |
| 17 | 30 | 10% Quinoline | 13.8 | 10.2 | 3.6 |
| 14 | 60 | 10% Quinoline | 8.6 | 6.3 | 1.9 |
| 19 | 18 | 20% Quinoline | 9.8 | 3.6 | 6.2 |
| 21,32* | 30 | 20% Quinoline | 20.4 | 18.4 | 2.0 |
| 25 | 60 | 20% Quinoline | 21.8 | 16.2 | 5.6 |
| 37 | 2 | 10% THQ | 11.0 | -26.9 | 37.9 |
| 40 | 5 | 10% THQ | 19.6 | 4.3 | 15.3 |
| 16,33* | 15 | 10% THQ | 48.3 | 33.9 | 14.4 |
| 18 | 30 | 10% THQ | 64.5 | 53.7 | 10.8 |
| 31 | 60 | 10% THQ | 79.4 | 57.9 | 21.5 |
| 24 | 2 | 20% THQ | 14.2 | -6.7 | 20.9 |
| 30 | 15 | 20% THQ | 33.0 | 24.0 | 9.0 |
| 22,23* | 30 | 20% THQ | 47.5 | 23.2 | 24.3 |
| 38 | 60 | 20% THQ | 64.1 | 44.5 | 19.6 |
| G33** | 15 | 54% Piperdine | 16.8 | -- | -- |

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* Averages of two runs.
** Bruceton bituminous coal.

one-ring hydrogen donor containing nitrogen, the level of conversion was only 17%. However, the reaction time was 15 min compared to that of 30 min used with the other mixtures.

As a comparison to the above results, selected coal liquefaction experiments were made in a micro-autoclave unit using either THQ or tetralin at a reaction temperature of 380°C. The experimental approach is somewhat different in the micro-autoclave runs in that the reactants are charged to a small reactor (about 10 cc) and then lowered into a preheated fluidized sand bath. The reactants come to temperature in about 2.5 min, which is thereafter defined as "0" time. As pointed out in previous work (8), some liquefaction occurs during this short heat-up time.

The results of the micro-autoclave runs with Powhatan coal are summarized in Table 24. The conversion of coal to THF solubles is about 35% during the heat-up period for both the THQ and tetralin solvents. This level is higher than that observed for the 2- and 5-min periods of the runs with 10% THQ in water. It is noted that the ratio of coal to THQ is about equal in both the autoclave and supercritical water runs due to the high solvent charge in the latter case. While the levels of total conversion at a 30-min reaction time are about equal for the THQ and the 10% THQ in water experiments, the conversion with tetralin alone appears to be better than that in a mixture with supercritical water. The primary advantage of using supercritical water is that of reducing the levels of heavy reaction intermediates, namely preasphaltenes, in these experiments. As observed in the results of Tables 22 and 23, less preasphaltenes (namely about one-fourth) are being recovered in the products of the supercritical water runs. This implies that the coal-derived, radical-containing species are well-dispersed and recombination is greatly reduced, or perhaps, the solvent system may react with these coal-derived species. A study of these reactions is beyond the scope of the present project.

## Table 24

### Conversion and Product Distribution Micro-Autoclave Runs and Powhatan No. 5 Coal

| Run No. | Reaction Time, (minutes) | Solvent* | % Total Conversion | Yield % GOA | Yield % Preasphaltene |
|---|---|---|---|---|---|
| C1 | 0 | THQ | 35.2 | 14.5 | 20.7 |
| C2 | 30 | THQ | 67.7 | -20.7 | 88.4 |
| C3 | 0 | Tetralin | 33.1 | 24.0 | 9.1 |
| C4 | 5 | Tetralin | 39.9 | 25.0 | 14.9 |
| C5 | 30 | Tetralin | 53.8 | 29.4 | 24.4 |

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* Average feed consisted of 15 g coal plus 3.6 g solvent; after charging the reactor was pressurized with 500 psi $N_2$ (cold) prior to the run.

### 3. Effect of Solvent Concentration on Conversion to THF-Soluble Products

To study the effect of solvent concentration on conversion to THF-soluble products, solvent concentrations of 0, 10, and 20 wt% were used for tetrahydroquinoline, quinoline, and tetralin. The values of conversions and product distributions are tabulated in Table 23. Figure 29 shows the total conversion after 30 min for 0, 10, and 20 wt% solvent mixtures of THQ, tetralin, and quinoline with water and the quinoline/water/$H_2$ system.

It can be seen that, for solvents which are hydrogen donors like tetrahydroquinoline and tetralin, higher levels of conversion are observed at 10% than at either 0 or 20% concentrations, while the reverse is true for non-donors such as quinoline (Figure 30). This is particularly demonstrated in Figure 30 for 10 and 20% THQ mixtures with conversion reported over a wide range of reaction times.

It is probable that these hydrogen donors form adducts with coal at a rate in proportion to the concentration of the hydrogen donor. If these adducts are not THF-soluble products, the conversion would decrease due to the solvent being adducted to coal. Conversely, the presence of a hydrogen donor helps in stabilizing the coal radicals leading to reduced retrogressive reactions with an apparent increase in conversion. These competing effects lead to a maximum in conversion at low concentrations of the hydrogen donor. Apparently, concentrations near 10% (or ratios of coal-to-donor solvent of about 1:2) are sufficient to stabilize the coal radicals; further increases in concentration result in greater adduct formation with lower yields.

For quinoline-water mixtures, there also appears to be adduct formation. This will be discussed further in the following section dealing with GPC and nitrogen analysis.

It is clear that at least two and probably four competing processes are predominating. Among the possibilities are:

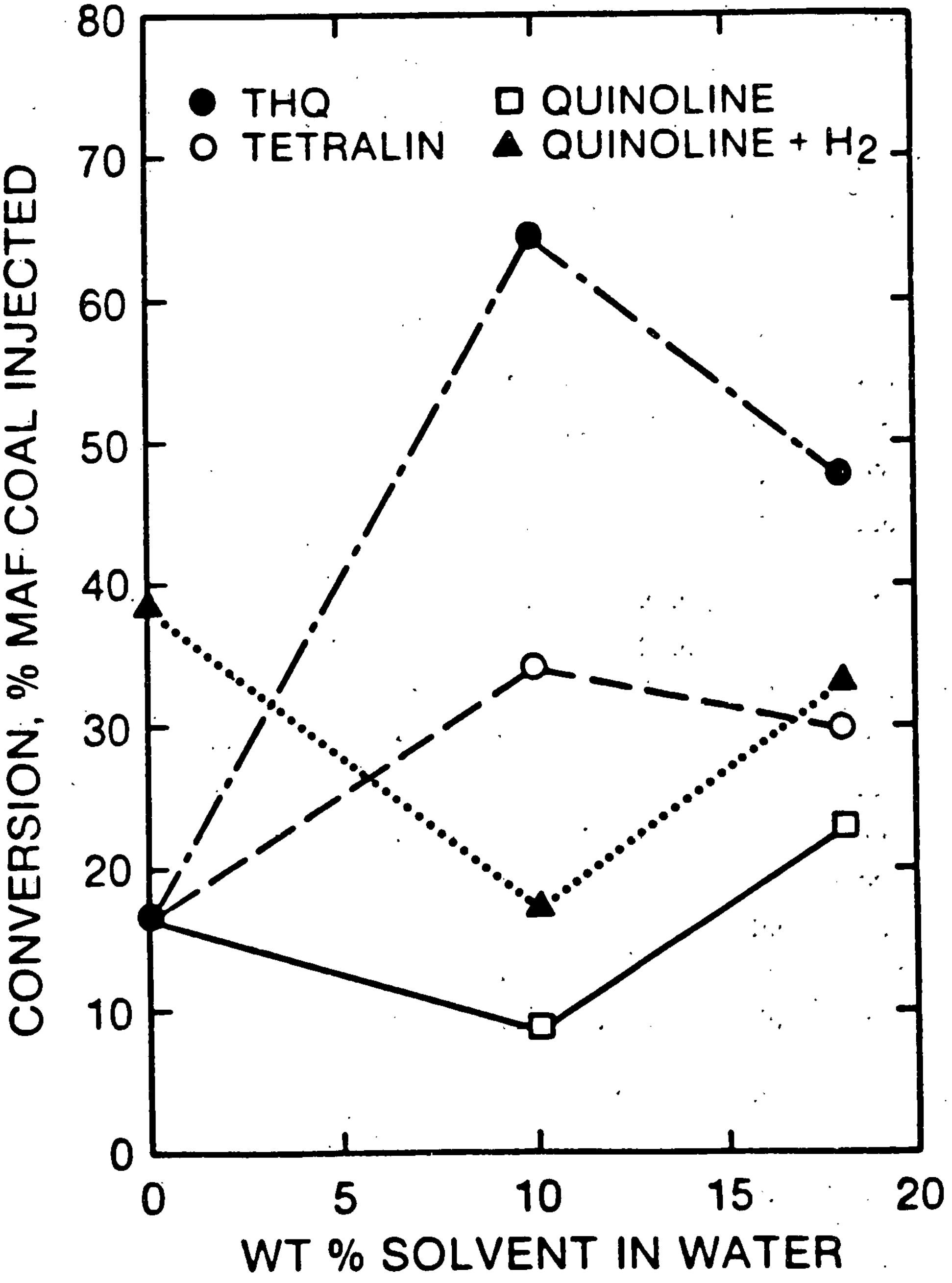

FIGURE 29 EFFECT OF SOLVENT CONCENTRATION ON COAL CONVERSION TO TOTAL THF-SOLUBLE PRODUCTS

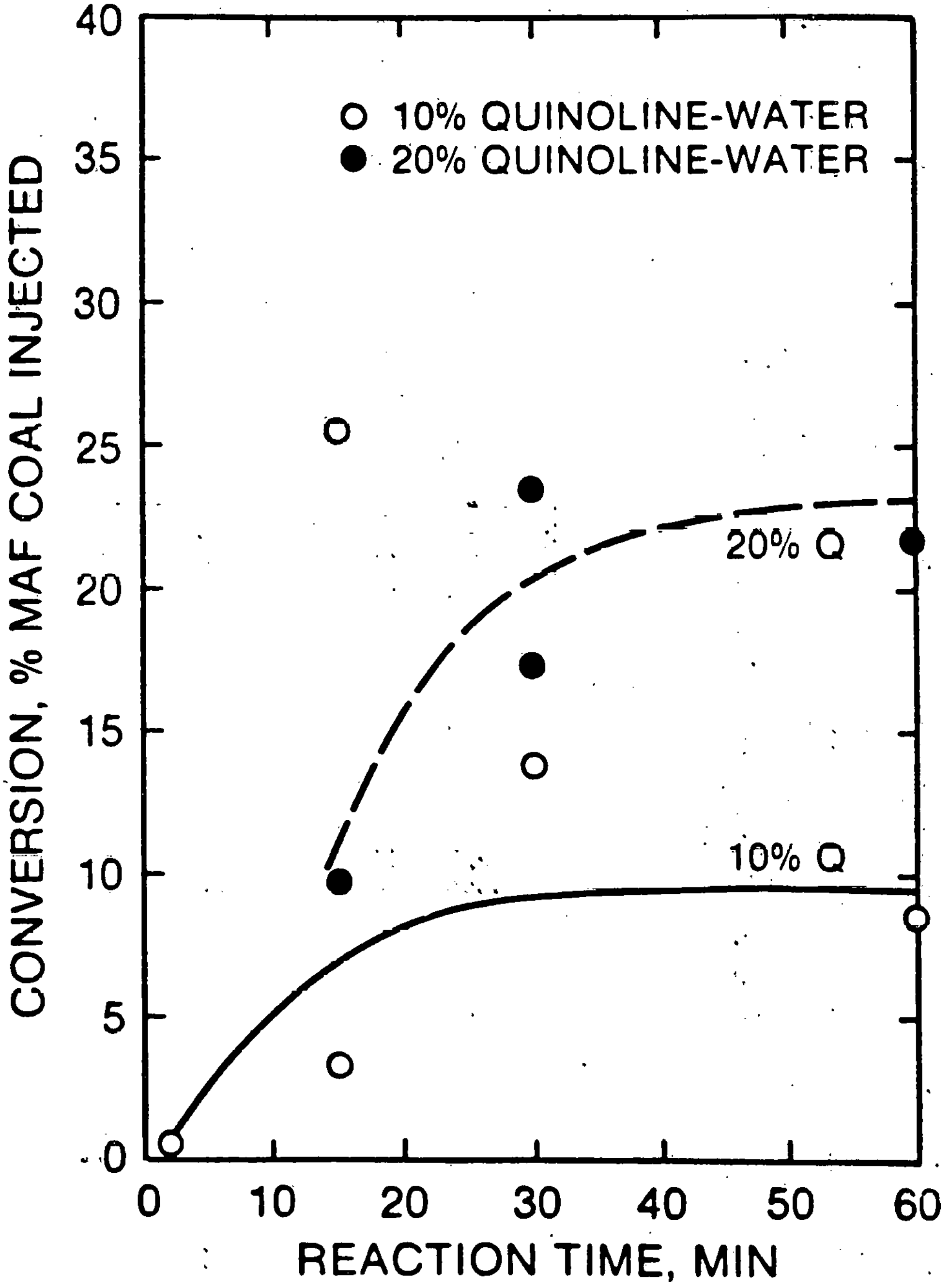

FIGURE 30 EFFECT OF REACTION TIME ON COAL CONVERSION TO TOTAL THF-SOLUBLE PRODUCTS FOR 10 AND 20% THQ-WATER MIXTURES

1. Coal dissolution--favored by good organic solvents.
2. Coal pyrolysis with capping of free radicals or reactive intermediates--favored by hydrogen donor and the presence of supercritical water.
3. Adduction--depending on the type of donor solvent.
4. Coal pyrolysis with retrogressive reactions--more extensive in the presence of a nonhydrogen donor.

Process 1 appears to occur in a short time (<15 min) as shown in Figures 27 and 28 and by the micro-autoclave results. With excess solvent, process 2 proceeds even at low concentration and appears to be fairly independent of concentration. Hence the effect of having a hydrogen donor present is not enhanced by going from 10% to 20% in water. However, process 3 increases with concentration causing a decrease in conversion as hydrogen donor concentration increases. Process 4 appears to be happening with quinoline mixtures, since as time increases, the conversion decreases for the 10% quinoline in water mixture.

### 4. Effect of Hydrogen Addition on Conversion to THF-Soluble Products

$H_2$ is used in coal liquefaction processes to improve the H/C ratio in the final product by capping the coal radicals. These capped radicals contribute to the higher conversion to lower boiling fraction materials. Therefore, in 3 runs, $H_2$ was used instead of argon to inject the coal into the supercritical phase. The systems under study were water and water-quinoline mixtures which had no hydrogen-donating capacity. The results of these experiments are summarized in Table 25.

It can be seen that the $H_2$ addition results in higher conversions compared to those when no $H_2$ is present. For water, coal conversion to THF solubles increases from 16.2% to 37.9% with an increase in the yield of preasphaltenes from 1.9% to 11.5%. For the 10% quinoline/water mixture, the conversion only increases from 13.8 to 16.7%, while for 20% quinoline/water

## Table 25

## Conversion and Product Distribution for Runs with Solvent Mixtures with $H_2$ Used to Inject Coal

(Reaction Time of 30 min)

| Run No. | Solvent | Wt% Solvent in Water | % Total Conversion | Yield % GOA | Yield % Preasphaltene |
|---|---|---|---|---|---|
| 41 | Water | 100% | 37.9 | 26.4 | 11.5 |
| 35 | Quinoline | 10% | 16.7 | 5.9 | 10.8 |
| 36 | Quiniline | 20% | 32.6 | 31.0 | 1.6 |

mixture, it increases from 20.4 to 32.6%. With $H_2$ addition, the amount of preasphaltenes increases from 3.6% to 10.8% for the 10% quinoline/water mixture, while that obtained using the 20% quinoline/water mixture remains almost the same with or without $H_2$. The use of a hydrogen atmosphere results in the increased capping of coal-derived radicals as denoted by increased yields of lighter fractions.

### 5. Effect of Reaction Time on Conversion to THF-Soluble Products

The reaction time has an important effect on the conversion and the product distribution in any chemical process. It is interesting to note that the time dependence is greater for the more effective solvents in the aqueous supercritical systems. With quinoline as the solvent, time seems to have a negative effect. The kinetics for pure water, 10% and 20% quinoline, and 10% and 20% THQ systems were investigated by varying the reaction time from 2 to 60 min. The results of these runs are listed in Table 23. Figures 30 and 31 depict the total conversion to THF-soluble products as a function of time and solvent concentration for the quinoline-water and THQ-water systems, respectively.

In the case of water, the conversion to THF-soluble products remains almost constant after a reaction time of 15 to 30 min, but the % preasphaltenes in the product decrease from 5.2% to 1.9% when the reaction time is increased from 15 min to 30 min. The composition of products is almost unchanged when the reaction time is increased from 30 min to 60 min.

For 10% quinoline in water, the conversion decreases with an increase in reaction time, while for 20% quinoline the conversion increases with reaction time. It is not clear why this occurs, but it may be related to adduct formation.

As shown in Figure 28 for the runs with 10% and 20% THQ in water, coal conversion to THF solubles increases with reaction time. Figures 29 and 30 show the time dependence of GOA and preasphaltene yields, respectively.

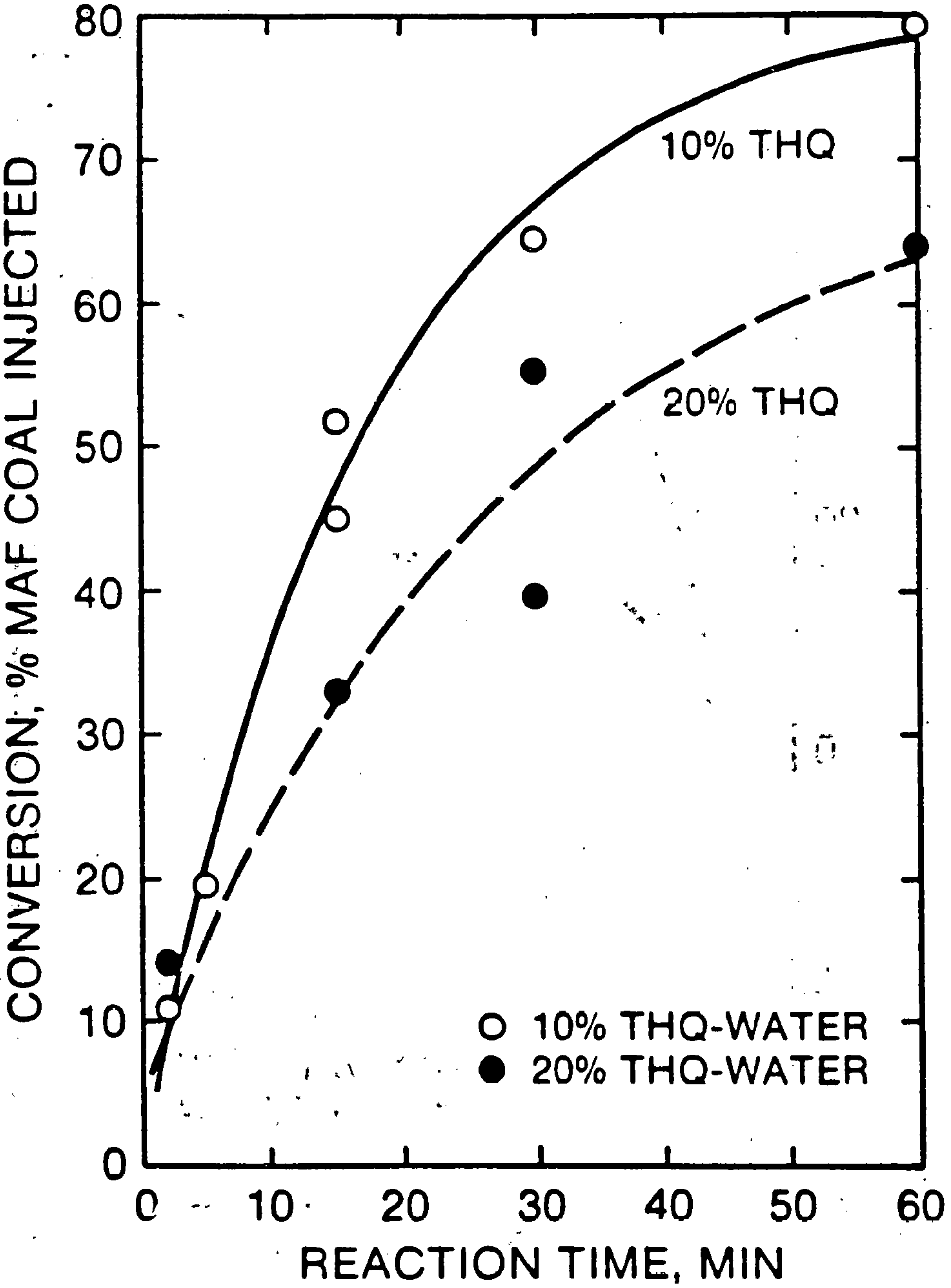

FIGURE 31 EFFECT OF REACTION TIME ON COAL CONVERSION TO TOTAL THF-SOLUBLE PRODUCTS FOR 10 AND 20% THQ-WATER MIXTURES

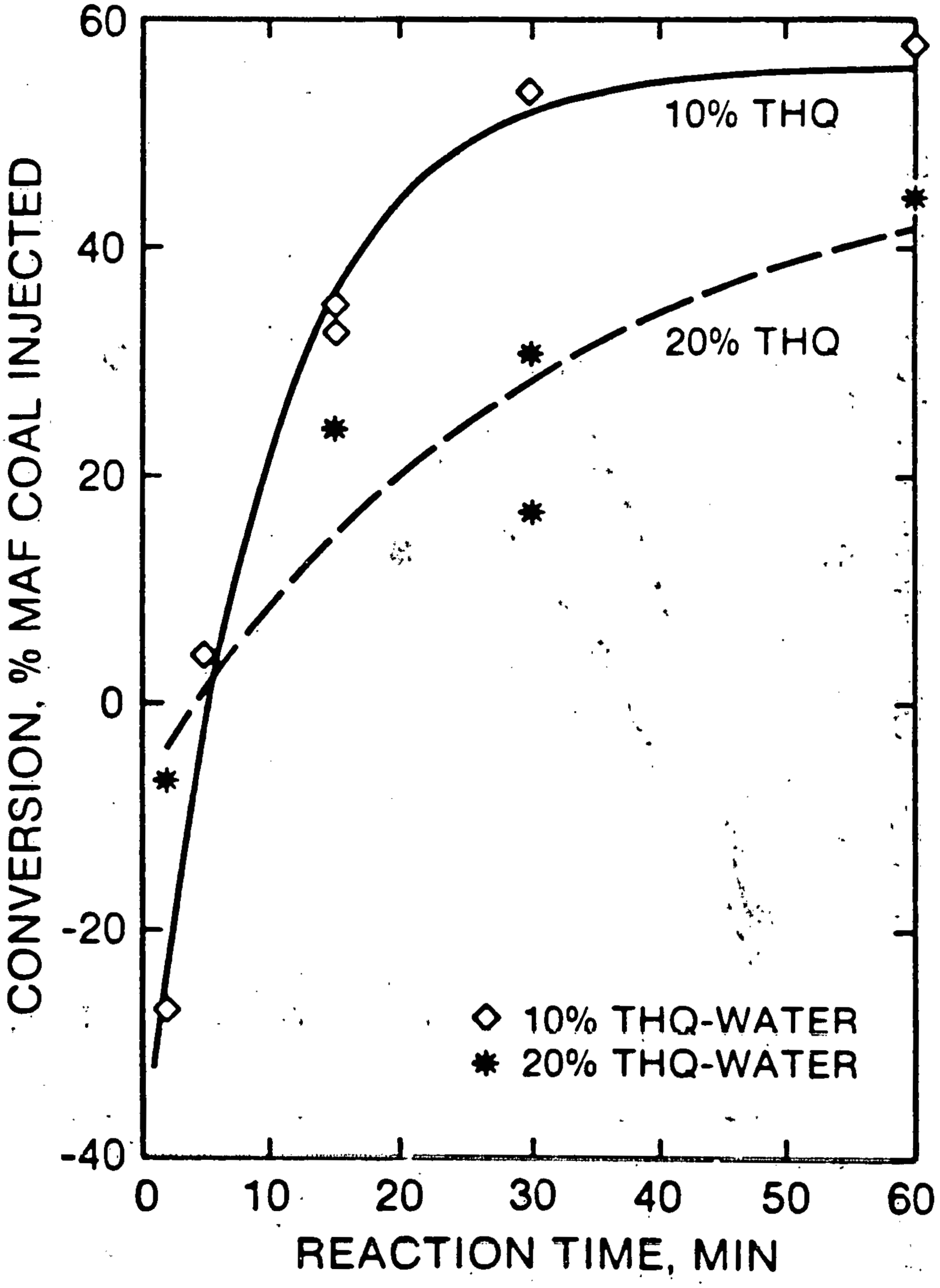

FIGURE 32 EFFECT OF REACTION TIME ON COAL CONVERSION TO GOA'S FOR 10 AND 20% THQ-WATER MIXTURES

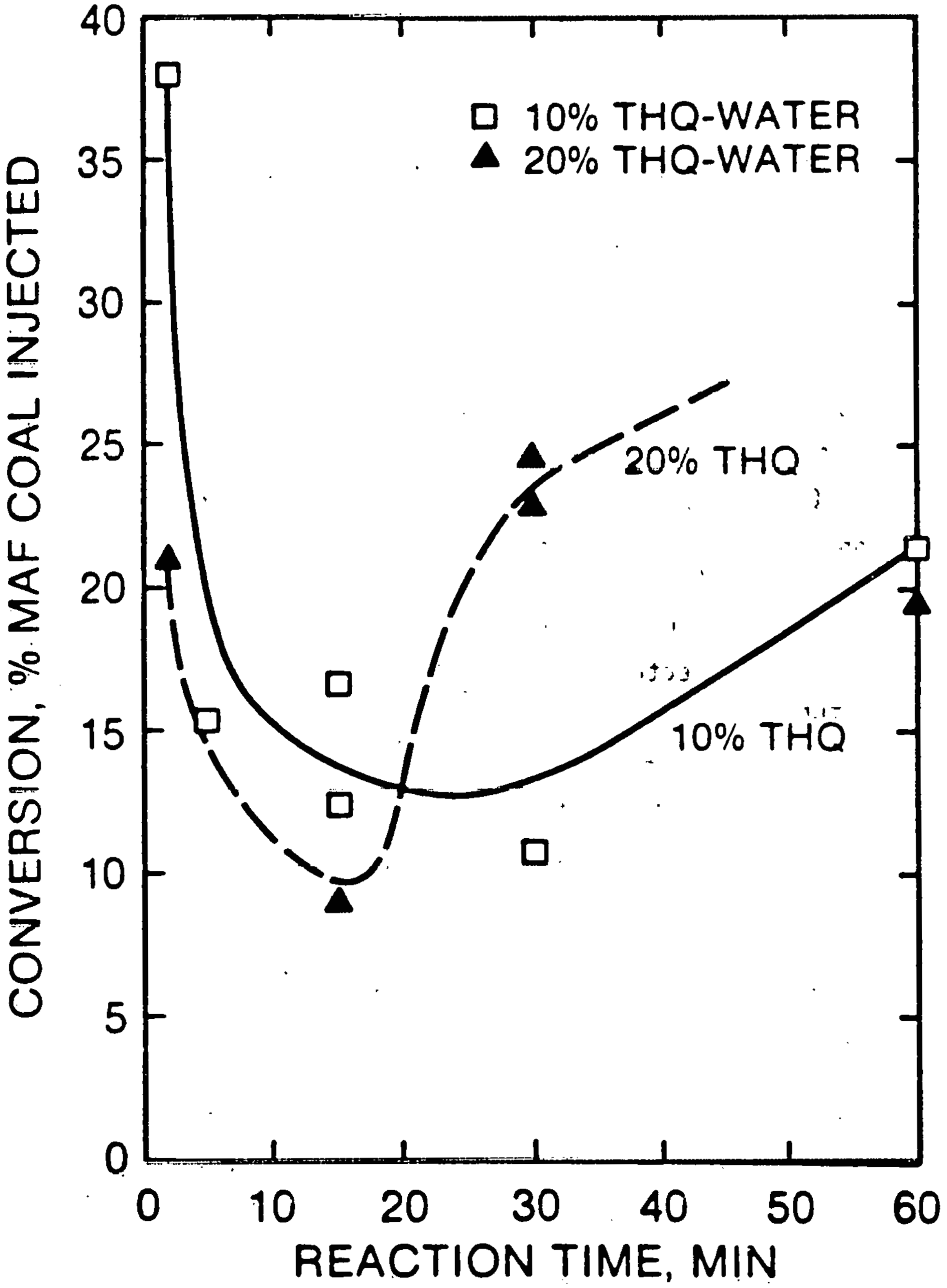

FIGURE 33 EFFECT OF REACTION TIME ON COAL CONVERSION TO PREASPHALTENES FOR 10 AND 20% THQ-WATER MIXTURES

It is clear that adduct formation occurs at short reaction times as denoted by "negative yields" of GOA at reaction times up to about 5 min. The "negative yields" indicate a net loss of solvent during this period. At longer times, a portion of these compounds are converted to toluene solubles. The degree of adduction appears to be initially greater for the 10% THQ/water system; however, the reactions are such that the yield of GOA's is soon higher for the 10% THQ/water system than for the 20% THQ/water system.

### 6. Adduction as Confirmed by Nitrogen Analyses

The nitrogen contents of the toluene-soluble and preasphaltene fractions from selected runs made with water, 10% THQ, 10% quinoline, and 10% quinoline plus $H_2$ are given in Table 26. The products from the 100% water runs contain 0.9 to 1.4% nitrogen, while those from the runs with THQ or quinoline contain 3.5 to 6% nitrogen.

To check that the nitrogen contents primarily reflect chemically adducted solvents, selected samples were analyzed by gel phase chromatography (GPC) using THF as the carrier. Considering the sampling procedure and the nominal time distribution in the Waters GPC unit, the samples are well dispersed at a concentration of about 2 ppm. For reference, free quinoline is observed at a scan time of about 24.15 min.

The GPC scans of selected oil plus asphaltene (OA) samples are given in Figure 34. The scan of the OA sample from the 100% water run (15 min) has a somewhat symmetric distribution with a nominal peak molecular weight of 560 (polystyrene standards). The scan of the OA sample of the 10% THQ in water run is somewhat similar but extending to an area of lower molecular weight. The level of quinoline is estimated as 5.1%, which amounts to only 0.5% of the 5.2% nitrogen in the OA's. A second peak of higher molecular weight may be a dimer and would account for about the same level of nitrogen. The OA sample of the 10% quinoline in water run is much different than the above in that about 45% of the sample appears to be free quinoline. This is consistent with a light tan color of this sample. Obviously, the use of a nitrogen compound such as quinoline is detrimental in this type of supercritical coal extraction.

## Table 26

### Nitrogen Analyses of Selected Oil Plus Asphaltene and Preasphaltene Samples

| Run No. | Reaction Time (minute) | Solvent | Nitrogen Content (wt%) | |
|---|---|---|---|---|
| | | | Oil + Asphaltenes | Preasphaltenes |
| 9 | 60 | Water | 0.93 | 1.42 |
| 10 | 15 | Water | 1.10 | 1.23 |
| 16 | 15 | 10% THQ | 5.19 | 3.48 |
| 18 | 30 | 10% THQ | 5.70 | 3.63 |
| 17 | 30 | 10% THQ | 5.62 | 5.24 |
| 35 | 30 | 10% THQ/$H_2$ | 6.37 | 5.42 |

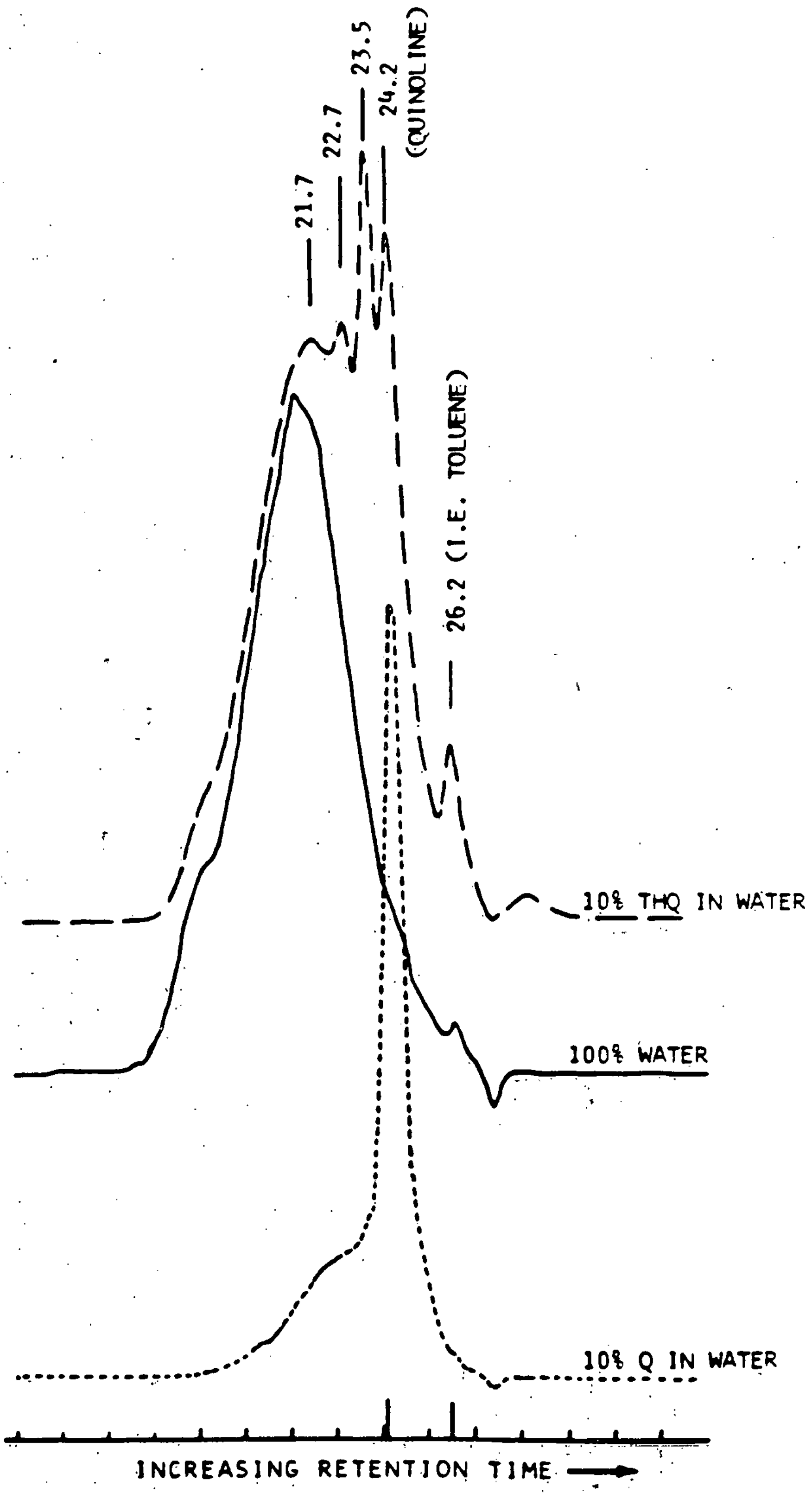

FIGURE 34 GPC SCANS OF SELECTED SAMPLES OF OILS PLUS ASPHALTENES

The GPC scans of samples of preasphaltenes are shown in Figure 35. The GPC scans of the PA's of the 100% water and 10% THQ in water are similar, with the latter showing a minor (<1%) amount of free quinoline. The GPC scan of the PA of the 10% quinoline in water run is markedly different than the others in that it is of lower molecular weight, and it appears to have a double peak totalling about 15% quinoline. This would account for about 1.6% of the 5.2% nitrogen in the PA. It is unusual that quinoline would be present in this sample in that it had been stripped at 80°C for at least one day before and after a two-day extraction with toluene.

In summary, a high level of nitrogen is observed in the heavy, coal-derived products of the THQ/water runs as a result of chemical adduction and not physical entrapment. The use of quinoline plus water results in poor yields with high levels of both chemical adduction and apparent physical entrapment.

## Conclusions

In the supercritical extraction of Pittsburgh Seam coal (Powhatan No. 5 Mine), a hydrogen donor-water mixture with hydrogen donor in dilute concentration (10 wt%) is an effective solvent for high levels of conversion. Higher concentrations of donor may not be beneficial. The addition of a hydrogen atmosphere increases the conversion for solvents which are not good hydrogen donors, although it is not as effective as that of using a good hydrogen donor. The use of nitrogen-containing solvents (quinoline and tetrahydroquinoline) results in high levels of solvent adduction as indicated by high nitrogen levels in the heavy product fractions. Reaction times of about 1 h are needed to approach equilibrium conversions when using hydrogen-donor water mixtures. However, a reaction time of 1/2 h is sufficient for nonhydrogen donors, but these give lower conversions. The reactivity of coal depends strongly on the coal type as confirmed by the observed differences in levels of conversion of Bruceton and Powhatan (both Pittsburgh seam) coals and Illinois No. 6 coal.

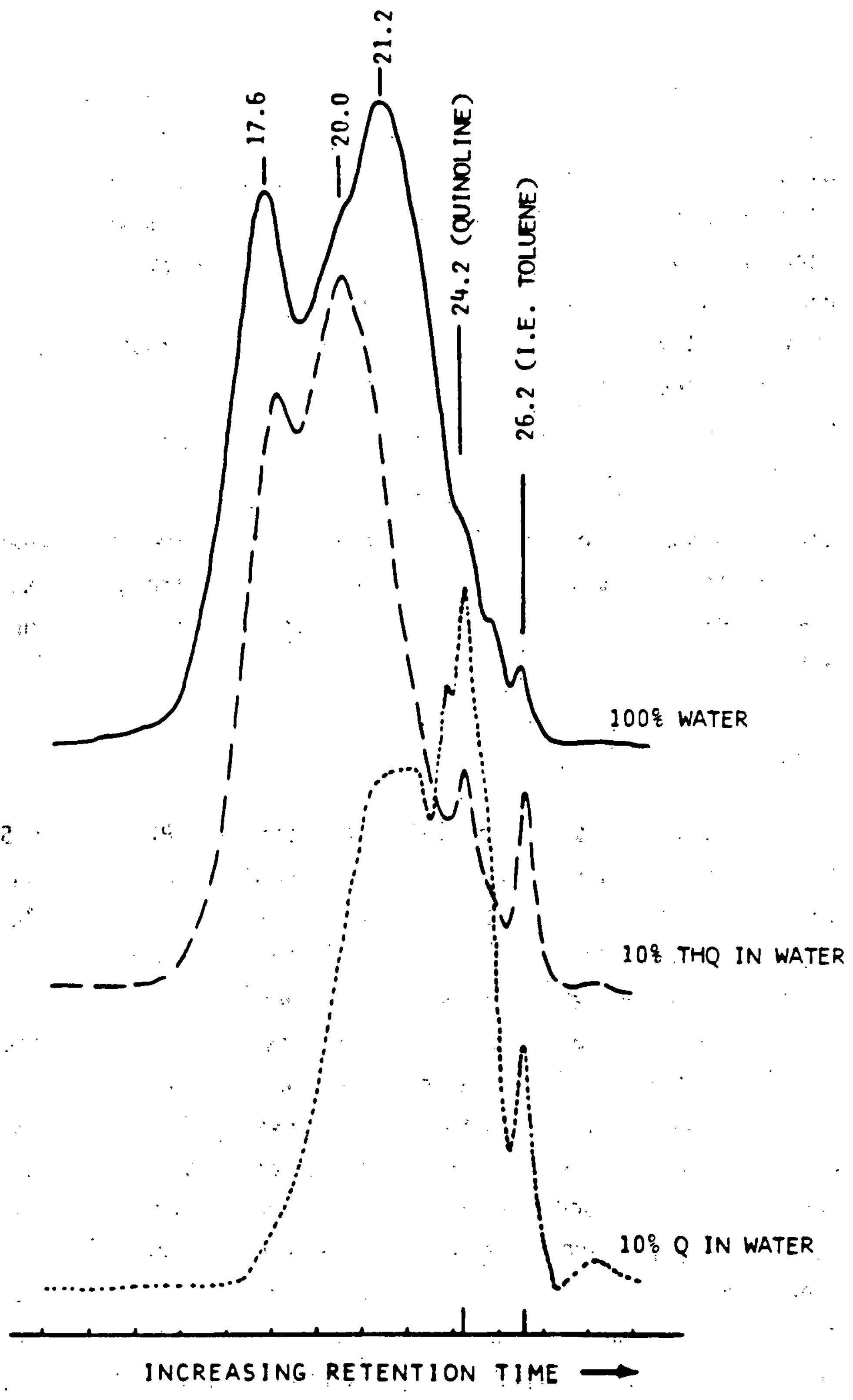

FIGURE 35 GPC SCANS OF SELECTED SAMPLES OF PREASPHALTENES

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## IV. SUBTASK 5: New Research Concepts

In developing possible new reaction concepts to liquefy coal, the following points need to be taken into account:

1. The most effective conversion of coal to first stage products occurs in hydroaromatic solvents of low heterofunctionality (to avoid adduction).

2. Catalysts are important in the upgrading steps following the initial conversion of coal; these catalysts should be recoverable without extensive treatment or, alternatively, directly disposable.

3. No advantage appears likely for the use of supercritical solvents during the initial stages of liquefaction; however, supercritical systems may be of advantage during the early stages of product upgrading.

4. The reduction of heterocompounds in recycle solvents would be of advantage to reduce adduction reactions. This may be accomplished by either catalytically hydrogenating the recycle solvent (such as in the EDS process scheme) or by adsorbing out these species using activated solids (for example using solids of high acid functionality).

In summary, a somewhat idealized process would consist of: (1) a first stage of short residence time using a recycle solvent of low polar functionality and high donor capacity, (2) a second stage reactor into which is introduced a major amount of critical solvent along with a catalyst (presumably a disposable one or the reactor may contain a fixed bed of catalyst in an arrangement to avoid plugging), (3) a pressure letdown vessel(s) to precipitate/agglomerate the ash along with heavy fractions, and

(4) a system to reduce the level of polar solvents from the recycle solvent system. It may be advantageous to hydrogenate the recycle solvent system.

In the above concept, past experience with various process options is combined with new concepts. It appears unlikely that radically different concepts will develop for the donor solvent liquefaction of coal. As has occurred in the past, new developments will occur as a result of new concepts being added to a combination of existing technologies.

WPC#4087

*U. S. GOVERNMENT PRINTING OFFICE: 1984-746-081/10046