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International Coal Refining Company
Allentown, Pennsylvania

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APRIL-JUNE 1981

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UNITED STATES DEPARTMENT OF ENERGY

Office of Solvent-Refined Coal Products
under Contract DE-AC05-78OR03054

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RECYCLE SOLVENT CHARACTERIZATION

**F. K. Schweighardt,* I. S. Kingsley,*
A. Z. Kamzelski,** and D. M. Parees****

The role of recycle solvent in solvent-refined coal (SRC-I) liquefaction, although well-studied, is not completely understood. In the SRC-I process, the conversion of bituminous coal to solids and liquids depends on a solvent to solvate the coal and to transfer gaseous hydrogen to the coal or its intermediate conversion products. Because the molecular composition of the solvent's functional groups may influence the extent of coal conversion, APCI has been analyzing recycle solvents from SRC-I pilot plants to determine as completely as possible the chemical composition of a typical SRC-I recycle solvent. The resulting data on chemical and physical properties will be used to develop a solvent quality index, which will aid in determining the potential of a solvent to maintain conversion at the rates and in the proportions designed for the SRC-I Demonstration Plant. Recycle solvents can also be defined as a boiling-point fraction: they are process-derived materials that boil between ~450 and 850°F.

This report covers our progress during the last quarter. We compared physical and chemical properties of six recycle solvents and found that the weight percent of hydrogen adjacent (α) to aromatic rings, the phenol and saturate contents, and the amount of solvent boiling above 600°F appear to correlate with results from solvent quality tests done at the SRC-I Pilot Plant in Wilsonville, Alabama on similar solvents.

After reviewing all the data, we selected solvent F (Wilsonville recycle solvent generated from Dotiki Mine Kentucky #9 coal) as a typical solvent for detailed molecular characterization. Four distillate fractions, initial boiling point (IPB)-450°F, 450-550°F, 550-650°F, and 650°F-end point, and the total sample were subfractionated into primary functional groups: saturates and aromatics, phenolics, and nitrogen bases. Individual compounds were identified in each fraction by gas chromatography and mass spectrometry. We also attempted using high-resolution mass spectrometry for compound identification, with moderate success; we found that this technique consolidates all the isomers and provides a better overview of compound classes.

Our results show that the majority of the solvent distilled between 475 and 525°F and contained C₁- and C₂-alkylnaphthalenes. Dowtherm (diphenyl ether and biphenyl) was found as a contaminant (2-8 wt %) in both the total sample and its distillation fractions.

COMPARISON OF SIX RECYCLE SOLVENTS

Six solvents were studied: solvents A, C, F, and G were derived from Kentucky #9 Dotiki Mine coal (from runs 206, 211, 179, and 211, respectively, at the Wilsonville Pilot

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Plant); solvent B is a hydrotreated creosote oil; and solvent J was obtained from run 1967 at the Ft. Lewis SRC-II Pilot Plant in Washington. We compared the solvents' physical and chemical properties by:

- profiling the total solvent as received;
- batch-distilling the samples to quantify boiling ranges;
- separating the solvents' functional groups.

The following analytical procedures were used to characterize both the total sample and its fractions: elemental analyses for carbon, hydrogen, oxygen, nitrogen, and sulfur; number-average molecular weight; American Society for Testing and Materials (ASTM) method D2887, simulated distillation by gas chromatography; proton nuclear magnetic resonance spectroscopy (^1H NMR); gas chromatography (GC); gas chromatography/mass spectrometry (GC-MS); near-infrared (near-IR); APCI specific gravity; refractive index; heating value; and viscosity.

Chemical and Physical Profile of Total Sample

By elemental analysis, we determined the distribution of carbon, hydrogen, oxygen, nitrogen, and sulfur in each of the solvents. These weight percents are listed in Table 1.

Vapor-pressure osmometry (methylene chloride, 29°C) was used to determine the number-average molecular weights (± 10) for each solvent, as follows:

Solvent					
A	B	C	F	G	J
209	210	210	196	210	235

Each sample was analyzed by proton magnetic resonance (^1H NMR; 200 MHz, CD_2Cl_2 solution, 25°C , 5-mm NMR tubes), with tetramethylsilane as an internal standard adjusted to 0 ppm. The weight percent distribution by chemical shift is detailed in Table 2. In the proton spectrum, H_{ar} are the protons directly attached to aromatic rings (chemical shift of 6-9 ppm), H_α are the protons on carbons directly attached to aromatic rings (2-4 ppm), and H_β are the remaining protons (0-2 ppm). Hydroxyl and amine protons are included as aromatics.

Distribution of oxygen and nitrogen heteroatoms strongly influences a recycle solvent's overall polarity and thus its solvating power. By using near-infrared spectroscopy, we determined the weight percent distribution of oxygen and nitrogen (as OH and NH or NH_2). These values were combined with the oxygen and nitrogen weight percents from elemental analysis (Table 1) to give the weight percent distribution of these heteroatoms (Table 4). Subsequent infrared data indicated there were no carbonyl ($\text{C}=\text{O}$) peaks in any of the solvent's spectra; thus, the remaining oxygen forms were ether linkages ($-\text{O}-$) and the nitrogen forms were basic $-\text{N}=$, NH , and NH_2 .

The six solvents exhibited a broad range of physical properties, which may be related to their process history. Table 5 summarizes the specific gravities, refractive indexes, Btu contents, and viscosities.

Boiling-Point Ranges

Each solvent is a complex mixture of components. One way to examine such mixtures is to separate the solvents into boiling-point fractions. We used ASTM method D2887, simulated distillation by gas chromatography. The sample is introduced into a GC column, which separates hydrocarbons in boiling-point order and generates a chromatogram that relates peak intensity to GC retention time. The times are then converted into boiling points using a calibration curve, and peak areas are related to percent concentrations. We could only determine the area percents of the fractions at this time (Table 6). Thus, the data should be interpreted only as a relative measure to profile all the solvents.

Functional Group Separation

We used column chromatography to separate the recycle solvents into functional groups representing three common classes of compounds: saturates (alkanes), neutral aromatics (aromatics and hydroaromatics), and polar components (phenols and nitrogen bases). Ten grams of each solvent was subjected to a 100-g silica/alumina adsorption column and eluted in sequence with n-pentane, methylene chloride in pentane, and methylene chloride/methanol/HCOOH to obtain the three fractions (Kingsley and Schweighardt, 1981). Table 7 summarizes the analytical results.

Solvent Quality

The quality of different recycle solvents can be compared by using the short-term Wilsonville Pilot Plant microautoclave test (Lamb and Kingsley, 1981). Using this test, we measured the following weight percents of tetrahydrofuran solubles:

Solvent					
A	B	C	F	G	J
58	89	73	70	77	66

The percent tetrahydrofuran conversion is related to the quality of a standard solvent by calibration curves. These results are not considered an absolute measure of solvent performance, but they are useful in distinguishing "good" from "bad" solvents, in terms of both the presence of coke formation (which indicates a hydrogen-starved condition) and the overall process of producing SRC and remaining in solvent balance.

The results of the microautoclave test and all of our analytical tests seem to correlate somewhat (see Table 8). As microautoclave test values increase from 58 to 77, the number of hydrogens located on carbon atoms adjacent (α) to aromatic rings increases, the hydroxyl content increases, the percentage of saturates (alkanes) decreases, and the boiling point

temperature at which 80% material is distilled increases. The absolute hydrogen content appears to be unrelated to the microautoclave numbers. Generally, results for solvent B, non-process-derived, and for solvent J, derived from another coal in the SRC-II process, do not follow this pattern; only the boiling-point and saturates content correlate to the microautoclave test results of the other solvents.

DETAILED CHARACTERIZATION OF RECYCLE SOLVENT F

After reviewing all the analytical data, we selected solvent F, derived from Kentucky #9 Dotiki Mine bituminuous coal during run 179 at Wilsonville, as a typical recycle solvent for extensive molecular characterization. Our decision was based on several factors: solvent F is available in sufficient quantity; its physical and chemical properties best represent the average of all the other solvents studied; its microautoclave test value (70) typifies a "good" solvent during long-term processing; and it has been used as a slurry solvent in many coal process development unit runs at APCI without any coking.

We vacuum-distilled solvent F into four fractions: 350-450, 450-550, 550-650, and 650-850°F. The weight percent yields of these fractions are diagrammed in Figure 1. After distillation, a synthetic blend of the fractions was made on a weight percent basis; we analyzed the blend as well as the original "as-received" solvent.

The area percent boiling point distribution of solvent F, determined by simulated distillation by gas chromatography, is somewhere between that of a #2 and a #6 petroleum fuel oil. A comparison of the carbon, hydrogen, oxygen, and nitrogen distributions of this solvent and fuels oils is shown in Figure 2. The coal-derived solvent F contains more oxygen and nitrogen, far less hydrogen, and almost the same amount of carbon on a weight percent basis.

The elemental distribution within each of solvent F's four distillate fractions reveals some interesting information (Figure 3). As the boiling point increases, the carbon content generally increases, but the hydrogen content decreases. This may indicate the presence of large polynuclear aromatic rings (three-five rings). The oxygen content decreases from 4 to 2 wt % across the distillation range. Because oxygen can be either hydroxyl (OH) or ether (-O-) bonded, we will be able to determine the chemical nature and distribution of oxygen by near-infrared measurements. The nitrogen content increases across the distillation range and appears to concentrate (1.5%) in the 650-850°F fraction. As the boiling point increases, so does the number-average molecular weight:

<u>Solvent F</u>	<u>IBP-450°F</u>	<u>450-550°F</u>	<u>550-650°F</u>	<u>650°F-end point</u>
196	136	175	215	250

(from MS anal.)

To check the efficiency of the 15-plate distillation of the solvent into four fractions, we analyzed each boiling-point fraction using simulated distillation by gas chromatography (Figure 4). The amount of distillation tailing between fractions is small (<5%) and acceptable for detailed chemical characterization.

Proton magnetic resonance data (200 MHz, 25°C, CD₂Cl₂ solution) for the distillates are presented in Table 9. From these data and the elemental distribution data (Figure 2), we calculated the absolute weight percent distribution of hydrogen (Table 10).

The distillate fractions show a unique distribution of oxygen and nitrogen heteroatoms; hydroxyl and amine contents were measured with near-infrared (Table 11).

Each distillate fraction was separated into functional groups by silica gel/alumina column chromatography (Figure 5). The greatest percentage of phenolics was found in the 350-450°F fraction, nonpolar predominated in the 450-550 and 550-650°F fractions, and nitrogen bases were found in the 650-850°F fraction.

Table 12 summarizes physical properties of solvent F and its distillation fractions, including specific gravities, refractive indexes, heating values, and viscosities.

We used capillary gas chromatography (CGC) and mass spectrometry (MS) to identify individual compounds in solvent F, its primary functional groups, and the four distillate fractions. Whenever possible, CGC conditions were kept constant from sample to sample (Table 13 summarizes the CGC conditions). When the mass spectrometer was used, the sample was introduced by a gas chromatograph (GC/MS). The gas chromatograph attached to the mass spectrometer is not identical with the instrument used for CGC profiles, but it was optimized to perform nearly identically. Nominal GC/MS conditions are listed in Table 14. Unless stated otherwise, Tables 13 and 14 define the GC and GC/MS operating conditions for solvent F and all its fractions.

GC/MS Analysis of Total Sample

The total sample was analyzed by gas chromatography according to the conditions in Table 13. The resulting chromatogram (Figure 6) has been marked to identify major peaks (defined in Table 15). The 28 principal components were identified by comparison with GC retention times of model compounds (using the same column and under identical conditions). The most likely components present within each peak are identified.

The complexity of the gas chromatogram for the total solvent sample can be simplified best by using a mass spectrometer as a detector to the capillary gas chromatograph. Identification is then accomplished by matching MS fragmentation patterns with standards in a mass spectrometer computer library. An isomer is identified absolutely only if a standard has been used to reference a GC retention time with the MS fragmentation pattern. Figure 7 shows the GC/MS total ion chromatogram for the total distillate; peaks are identified by scan number in Table 16. This table and other tables of GC/MS data identify the compound and indicate whether another isomer is possible or if a second component is present.

The major components in solvent F are 2-methylnaphthalene and phenanthrene (scans 512 and 1081, respectively). Scans 622 and 656 represent biphenyl and diphenyl ether, the major components in Dowtherm. Dowtherm is the heat exchange medium used at Wilsonville, which contaminates the recycle solvent by as much as 0-4 wt %. Biphenyl may be coal-derived because other analyses of solvent samples not in contact with Dowtherm contain 0.5-1% biphenyl, but diphenyl ether has not been found in concentrations exceeding 0.1%.

Examination of Table 16 reveals that there are few hydroaromatic components. Hydroaromatics are important for the transfer of gas-phase hydrogen to coal and its liquefaction intermediates, but the absolute steady-state hydroaromatic concentrations needed are unknown. In Table 8 we noticed that hydrogen and H_{α} concentrations (absolute weight percents) appear to differ from the Wilsonville microautoclave test results. What we may be observing is a steady state of hydroaromatics, formed from the process, whose equilibria depend upon still undetermined variables. To gain an insight into which equilibrium can

be established, we need to know more about the chemical content of the solvent. Thus, the remaining portion of this report provides a detailed chemical analysis of recycle solvent F. The distribution of functional groups and a detailed chemical analysis of compounds will help to further define the composition.

GC/MS Analysis of Functional Groups

Saturate Fraction. Solvent F saturates were separated by column chromatography and analyzed by gas chromatography according to the conditions in Table 13 (see Figure 8). Major hydrocarbons identified are C_{15} 's, followed by approximately equal amounts of C_{14} 's and C_{16} 's; GC response was observed through C_{31} . In Figure 8 the peaks between the major species represent various isomers, cycloalkanes, and trace contaminants. Table 17 gives the selected relative area percents of nearly 50% of the saturate sample, and the absolute weight percent of each component in the original sample.

Aromatic/Neutral Fraction. The major functional group (59 wt %) in solvent F is the aromatic fraction. The GC chromatogram of this fraction is shown in Figure 9, and a companion mass spectral total ion chromatogram (GC/MS) of the same sample using the conditions in Table 14 is shown in Figure 10. The two chromatograms, although not identical in relative response, give nearly identical retention times for peak matching.¹ The components (GC/MS scan numbers) of the neutral polynuclear aromatic hydrocarbons are identified in Table 18.

To quantify the major aromatic species in Figure 9, the GC chromatogram was processed through a Spectra Physics SP-4100 computer, printing out only those peaks with area percents above 0.5. The results are presented in Figure 11. The retention times, relative area percents, and compounds in this fraction are summarized in Table 19.

Phenolic Fraction. At nearly 32 wt %, the phenols are the second largest group in solvent F. As a polar functional group, the phenols contribute to the solvent's solvating power. They may also operate as hydrogen-transfer agents, but this is unproven. The phenolic species determined by GC/MS (Figure 12) are listed in Table 20. The primary separation of phenols from solvent F showed contamination from neutral aromatics, carbazoles, and some nitrogen bases. Thus, direct caustic extraction may be a more efficient way to isolate the phenols. The data in Table 20 highlight the major hydroxyl species that could be tentatively identified at this time.

Nitrogen Base Fraction. We used the following procedure to increase the nitrogen base concentration 100-fold before GC/MS. The nitrogen bases ($-N=$) were isolated by passing dry HCl gas through a benzene solution of the total distillate. All material that precipitated was washed with benzene and then back-titrated with ammonia to free the nitrogen base in benzene solution. This procedure concentrates nitrogen bases but does not cleanly separate the bases from all other functional groups.

Many compounds in the nitrogen-containing classes, including the alkylquinolines, alkylisoquinolines, and naphthalenamines, have the same molecular weight series. However, the methylquinolines and isoquinolines have boiling points in the range 252-264°C, whereas 1-naphthalenamine boils at 301°C and 2-naphthalenamine boils at 306°C. The first two

¹All quantitative data presented in this report are derived from capillary gas chromatography with a flame ionization detector. Compounds are identified from the total ion chromatogram by using the Finnigan 4000 GC/MS computer library or fragmentation patterns at 70 eV in the mass spectrometer.

classes will not be separated by gas chromatography (and some species will produce very similar mass spectral patterns), but the naphthalenamines will be distinguishable from the alkylquinolines having the same molecular weight because of their higher boiling points. Methylquinolines and a naphthalenamine are unambiguously assigned to scans 483-566 and 754, respectively, in the GC/MS (Figure 13). Scan numbers for the nitrogen base components are identified in Table 21.

High-Resolution MS Analysis of Functional Groups and Total Solvent

Solvent F and its functional group fractions were sent to the Midwest Center for Mass Spectrometry at the University of Nebraska in Lincoln. Our objective was to determine if high-resolution MS could replace GC/MS for compound identification and for organization of the data to reveal trends in molecular composition. Twenty-five individual analyses were completed, including work at high and low ionizing energy (10 and 70 eV) and resolution studies at 10,000, 20,000, and 40,000.

A number of difficulties were encountered in the test study. The high-resolution system had the following major problems:

- Elemental formula (Z-number) tables omitted alkanes, so data on this class of compounds are unavailable.
- The percentage of total ion current assignable to mass windows of the elemental formulas in the Z-number tables was frequently very small; thus, a large portion of the sample was unaccounted for.
- The sensitivity at high resolution (40,000) was extremely low. Detection limits were not determined.
- A large percentage of ion current was assigned to incorrect structures, and did not change consistently as the resolution changed.

Computer programs were used to assign all the ion intensity in a given scan to the elemental formula having the highest mass value in a resolution window. Presently, the data are being analyzed on a scan-by-scan rather than total scan (by summing all the data) basis before ion intensities are assigned. This allows some ions that represent compounds volatilizing at different times to be identified in the same resolution window.

Table 22 summarizes the analyses completed on solvent F, and Table 23 defines the computer search categories used in each of the mass spectral runs listed in Table 22. As defined, the computer search allows for all possible isomers and combinations of elements.

As a first attempt, this broad-based reduction of data led to problems in component identification. Because we can select limits to compound structures based upon elemental distribution, future studies should provide a more tailored search, leading to a more rapid data reduction.

Table 24 lists the elemental distribution of solvent F and its subfractions that was used for high-resolution mass spectral analysis. Note that the heteroatoms are concentrated in the phenols (O = 7.11 wt %) and nitrogen bases (N = 5.32 wt %); sulfur, showing no special preference, is distributed throughout all the fractions.

High-resolution, mass spectral, three-dimensional computer plots were made of the samples listed in Table 22. Fifty-four plots were made (available upon request). Each plot

provides a wealth of information about the distribution of compounds, their relative MS intensity, and the series number (hydrogens/molecule). The information is complex and requires further study before trends are confirmed for any molecular series. In general, the data are read to find the major species present, its elemental formula, and the relative intensity of the component in a series. By changing the resolution from 10,000 to 40,000, we can discern different elemental compositions for the same nominal mass. The higher resolution permits one to determine if oxygen is present or if the component is made up of one carbon and four hydrogens or other elemental combinations giving an equivalent mass of 16.

The total, as-received solvent F sample was profiled for carbon, hydrogen, oxygen, and nitrogen. The resolution was adjusted to differentiate 1/10,000 and 1/40,000 changes in formula weight.

In the hydrocarbon saturate plots, oxygen and sulfur were identified at high resolution as part of the hydrocarbon fraction. Ether oxygen bonds and disulfide bonds would behave in this manner and elute with saturates and alkanes.

The aromatic/neutral fraction had the most complex molecular composition. Oxygen components were identified as ethers and dibenzofuran; sulfur compounds were identified as dibenzothiophene. Nitrogen compounds were present in the aromatic fraction as substituted carbazoles. Table 25 (summarizing data for this fraction) shows some selected data under different conditions. As expected, the total number of ion counts decreased as resolution increased. All samples were 0.25 μ L, with a 30-sec scan time. Because the analysis was done from the solids probe, data were lost from ions not being scanned. The only ions detected will be from species volatilizing from the probe during the portion of the relatively slow scan when these ions are focused at the detector. Ions of different masses created simultaneously will be lost.

When the resolution increased from 10,000 to 20,000, the percentage of the ion total assignable to structures in the Z-tables also increased, but it decreased at 40,000 resolution. Also, it is likely that many of the assigned masses are wrong. The high percentages of ion counts assigned to oxygen-containing species at 20,000 and 40,000 resolution must be in error. In the complete data tables, many examples of unrealistic formulas appear, including species with little or no hydrogen and 10-20 carbons and species such as C_5O_3 . These are allowed formulas, presently. However, real, expected major components in the aromatic fraction do appear. $C_{16}H_{10}$ is pyrene and fluoranthene and $C_{14}H_{10}$ is anthracene and phenanthrene. We do not know whether the shifts in relative size of these and other ions as the resolution changes (i.e., an intensity assigned to a formulation at low resolution is removed at a higher resolution) are justified. GC/MS data indicated that the major components were naphthalene ($C_{10}H_8$), methylnaphthalenes ($C_{11}H_{10}$), phenanthrene, and pyrene/fluoranthrene. This compares poorly with the major ions at 40,000 resolution shown in Table 25.

The phenol fraction was contaminated with polynuclear aromatic hydrocarbons. There appear to be a number of compounds identified having two or more heteroatoms. Positive identification was made for only a few of these materials.

The nitrogen bases were examined for dual functionality: oxygen (OH) and nitrogen (N-base) in the same molecule. We observed many compounds that appear to fit the elemental distribution of $C_xH_yO_aN_b$. As in the phenol fraction, contamination and inadequate identification hindered further analysis.

This preliminary use of ultra-high-resolution mass spectrometry to profile coal-derived recycle solvents was moderately successful. GC/MS appears to be superior to the high-resolution MS for compound (isomer) identification. The high-resolution MS does, however,

consolidate all the isomers and provides a more concise computer printout and better overview of compound classes. In comparing one sample with another by MS, we can determine whether the two-ring naphthalene series has been reduced to one, two, three, or more alkyl groups under the process conditions employed. Hence, cracking and splitting of complex polynuclear aromatics can be differentiated. On the other hand, to trace hydrogen donors in recycle solvents, by determining the relative hydroaromatic/aromatic equilibrium of specific compounds, GC/MS would be superior. We conclude that the most important need in using complex GC/MS and MS data to profile compositional change as a function of process change is the acquisition of adequate computer data reduction sub-routines.

GC/MS Analysis of the Boiling-Point Fractions

We determined the distribution of the primary functional groups in each boiling-point fraction by capillary gas chromatography. The data printout from the chromatogram of each of the four functional groups (Figures 8, 9, 14, and 15) was divided by retention time into 5-min windows, i.e., 0-5, 5-10, . . . 45-50 min. The area percents in each window were then totaled.

Weight percent totals were multiplied by the percent of the total sample that each functional group represented to obtain an adjusted weight percent (Table 26). The total functional group distribution is: 4% saturates, 61% aromatics, 32% phenols, and 3% nitrogen bases. The adjusted weight percents were then plotted vs. retention times to show the distribution graphically (Figure 16).

To compare this weight percent distribution with the boiling-point distribution of the total sample, simulated distillation data were generated using three methods of calibration: saturates, aromatics, and aromatics with their response factors. First, we took the accumulated weight percents (line 10 of Table 26), which were obtained from the four functional group chromatograms, and converted their retention times to boiling points using an equation developed earlier (Kingsley et al., 1981):

$$\text{boiling point} = \frac{27.65 + \text{retention time}}{0.083}$$

Using the data in Table 26, we determined the boiling-point range at which the maximum amount of each functional group would distill. Most of the total sample (23.9 wt %) distills between 454 and 574°F. Saturates are most concentrated (19.4 wt %) between 541 and 574°F. Aromatics and phenols show similar trends, 15.6 and 22.9 wt % distilling between 454 and 541°F, respectively. The nitrogen bases are concentrated (15.8 wt %) in the highest temperature range, 634-695°F.

The following discussion describes the functional groups found in each distillate fraction.

Low-Boiling (<450°F) Material. We have included the low-boiling fraction as part of our discussion on coal-derived distillates because it completes the distribution of the organic fraction boiling below the SRC fraction (850°F+). The low-boiling material collected from a pilot plant was separated from the accompanying product water using Whatman Phase paper to concentrate the organic layer.

Figure 17 is the GC/MS total ion chromatogram and Table 27 summarizes the chemical composition of the condensate (IBP to ~450°F). Figure 18 shows the distribution of major organic components in the IBP-350°F fraction. The primary components are toluene, nonane, naphthalene, 2-methylnaphthalene, diphenyl ether, biphenyl, and pentadecane.

350-450°F Distillate of Solvent F. Neutral Hydrocarbons. Neutral aromatics and saturates were separated from the total 350-450°F distillate fraction by column chromatography. The GC/MS total ion chromatogram is shown in Figure 19 and the components identified are listed in Table 28. The major species present are 2-methylnaphthalene, 2- and 5-methyltetralin, naphthalene, and tetralin.

Phenolic Fraction. Figure 5 shows that the 350-450°F fraction contained the largest percentage of phenolics. The phenol compounds found in this boiling range are shown in Table 29. The major species are one-ring phenols substituted with C₁-C₄ alkyls.

The phenolic fraction was chromatographed under the GC conditions in Table 14 and the components were detected by mass spectrometry (see Figure 20 for the GC/MS total ion chromatogram). Notice that there are less than 15 major components. Scan 325, the major species, is a 3,5-dimethylphenol, which was identified by matching with the retention time determined by GC analysis. Scan numbers from Figure 20 are identified in Table 30.

Nitrogen Bases. The nitrogen bases were also analyzed by GC/MS. Figure 21 is the GC chromatogram of the bases, and Table 31 identifies the components determined by mass spectrometry. The major compounds are substituted anilines and pyridines. No free pyridine was found, but free aniline was found to represent nearly 6% of this fraction.

A high degree of alkyl substitution on the nitrogen bases is expected. For denitrogenation to occur, the ring containing nitrogen in the condensed nitrogen base, e.g., quinoline, must first be hydrogen-saturated. Next, an additional mole of hydrogen is required to form a substituted aniline, which is relatively stable. If a highly complex nitrogen polynuclear aromatic is present, or if the quinoline species itself is highly substituted, alkylpyridines will form. These proposed mechanisms agree with our experimental findings (see Table 31).

450-550°F Distillate. Saturates and Polynuclear Aromatic Hydrocarbons. The 450-550°F distillate fraction (40.9 wt %) constitutes the largest portion of material from recycle solvent F. Within this distillate, the neutral hydrocarbons are the largest subfraction, and the GC/MS of this fraction was the least complex in the number of identifiable compounds (total ion chromatogram is shown in Figure 22 and compounds are identified in Table 32). Biphenyl and diphenyl ether (scans 570 and 603, respectively) are due primarily to the heat-exchange medium, Dowtherm, used at Wilsonville Pilot Plant. Scanning Table 32 we find that 2-methylnaphthalene is the major component. This subfraction contains the most hydroaromatics, substituted C₁- and C₂-tetralins, and acenaphthylenes that were identified.

Phenolic Fraction. The phenolic compounds were the most numerous heteroatom components identified in the 450-550°F fraction. A large number of C₁-C₅ alkyl isomers substituted on phenol and indanol comprise the entire fraction. Figure 23 shows the total ion chromatogram of this fraction, and Table 33 summarizes the 39 compounds identified and their relative area percentages. The fraction contains several of quinolines due to contamination from the chromatographic separation.

Nitrogen Bases. The nitrogen bases from the 450-550°F distillate fraction were chromatographed on the GC/MS to give the total ion chromatogram in Figure 24. The distribution of components is rather narrow compared to the other nitrogen-base fractions. We observed a number of major peaks, which are identified in Table 34. Pyridines and quinolines (C₁-C₂ alkyl isomers) were widely distributed on the GC column. Note that scans 379 and 512

represent unique tetrahydroquinoline structures, with hydrogen substitution at the 5,6,7,8 and 1,2,3,4 positions, respectively:

At first, both of these compounds appear to be of nearly equal concentration. As discussed in the section on 350–450°F nitrogen bases, however, denitrogenation prefers the 1,2,3,4-tetrahydroquinoline structure for ultimate loss of a ring nitrogen. Hydrogenation at positions 5,6,7,8 may be considered as a side reaction that uses 2 moles of hydrogen inefficiently. The resulting compound might not leave that distillate fraction because of its stability.

550–650°F Distillate. Aromatic and Saturate Neutrals. To date, the aromatic/saturate neutrals are the only components analyzed by GC/MS in the 550–650°F fraction. Figure 25 shows the total ion chromatogram and Table 35 summarizes the compounds identified. The major species, scan 929, is phenanthrene. Scans 729, 786, and 864 are C₁–C₂ alkylbiphenyls. As discussed previously, the presence of biphenyl is expected during coal liquefaction; the presence of alkyl biphenyls confirms this component as the most likely link to subsequent dealkylation. We did not observe any diphenyl ether derivatives (alkyl) in this distillate fraction; these would be present if the parent diphenyl ether was due to the coal rather than Dowtherm leaks at the pilot plant.

Summary. The change in molecular composition throughout the distillate range can be dramatically demonstrated by proton and carbon magnetic resonance spectra (Figures 26–30). The proton spectra (upper portions) show a distinct progression of resonances from C₁–C₄ alkyl-substituted one- and two-ring aromatics. IBP-450 and 450–550°F distillate fractions have sharp peaks, resolved splitting, and large aliphatic contributions between 2 and 5 ppm. Model compound spectra of di- and trimethylnaphthalenes, phenols, and benzenes closely resemble these distillates.

The higher boiling fractions show less detail; peaks are shifted to the lower field in the aromatic region (6–10 ppm), and the aliphatic protons (0–4 ppm) are less pronounced. NMR spectra of polynuclear aromatics with C₁–C₂ methyl substituents resemble the NMR spectra of the 550–650°F fractions. The multiplet of signals at 8.8 ppm in Figure 30 is identical to the signals from phenanthrene as a model compound.

A molecular profile of solvent F was generated from the GC and GC/MS data. We quantified each component identified as a one-, two-, three-, or four-ring aromatic, without regard to the degree of alkyl substitution. Figure 31 summarizes the ring distribution of recycle solvent. The molecular structures identified were the most abundant species in each category. Forty-five percent of solvent F contains two-ring aromatics (naphthalenes).

We also calculated the aromatic ring distribution for individual distillate fractions. Figure 32 shows that the 450–550°F fraction is 75% naphthalene-type material. Notice that the ring distribution for one-, three-, and four-ring aromatics covers two distillate ranges, but the two-ring aromatics span the entire boiling range. This is due to the heteroatom (O, N) and alkyl (CH₃) substitutions that are possible.

We can further quantify the distribution of organic compounds derived from coal by examining the estimated product slate from the 30,000 ton-per-day SRC-I plant. Yields are based upon direct SRC-I conversion, no upgrading, and an 18% distillate yield (MAF coal). Figure 33 graphically demonstrates the large volume of compound types that may be avail-

able from processing bituminous coal. ~420°F naphthalene would be produced as a non-substituted aromatic at 45,000 lb/yr, while all other alkylnaphthalenes would yield nearly 465,000 lb/yr.

Our analysis indicates that we should further examine the nature of the hydroaromatic/aromatic equilibrium, distribution of boiling points around 80% distilled, and the functional group compositions of the solvent in order to establish a physical/chemical basis for solvent quality. Future efforts will combine the analytical data with extensive microautoclave testing to screen coals and solvents for coal liquefaction.

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Table 1

Elemental Distribution^a of Recycle Solvents

Element	Wt % for					
	A	B	C	F	G	J
C	87.1	91.8	87.3	87.7	86.8	87.3
H	8.6	7.2	8.3	8.2	8.8	8.3
O ^b	3.0	0.4	3.1	2.8	3.2	3.0
N	1.0	0.6	0.9	0.8	0.6	0.8
S	0.3	0.04	0.5	0.4	0.6	0.6

^aData are normalized only if summation of mass is greater than 100 $\pm$ 1%.^bDirect determination, coulometrically titrated.

Table 2

¹H NMR Distribution of Recycle Solvents

	Wt % for					
	A	B	C	F	G	J
H _{ar}	32.7	37.2	32.2	37.4	30.4	32.3
H _{α}	30.1	29.5	30.9	30.7	31.9	33.5
H _{β}	37.3	33.2	36.7	32.0	37.7	34.2

Table 3

Distribution of Hydrogen

	Wt % for					
	A	B	C	F	G	J
H _{ar}	2.8	2.7	2.7	3.1	2.7	2.7
H _{α}	2.6	2.1	2.6	2.5	2.8	2.8
H _{β}	3.2	2.4	3.0	2.6	3.3	2.8

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Table 4

Distribution of Oxygen and Nitrogen Heteroatoms

Heteroatom	Wt % for					
	A	B	C	F	G	J
OH	43	3	47	46	56	55
-O-	57	97	53	54	44	45
=N-	98	91	100	86	86	79
-N-H	2	9	~0	14	14	21
NH ₂	~0	~0	~0	~0	~0	~0

Table 5

Physical Properties of Recycle Solvents

	Solvent					
	A	B	C	F	G	J
Specific gravity	1.002	1.114	1.020	1.025	1.015	1.047
Refractive index	1.3052	1.6656	1.3056	1.3048	ND ^a	1.5982
Btu	17,300	17,400	17,200	17,200	ND	17,100
Viscosity, 38°C (cP)	7.75	520	1.26	10.1	12.4	31.1
Viscosity, 50°C (cP)	5.75	152	8.1	6.9	8.0	16.8

^aND, not determined.

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Table 6

Boiling-Point Distribution (°F) Using ASTM Method D2887

Area %	Solvent					
	A	B	C	F	G	J
1	421	436	386	400	409	400
10	441	620	440	442	448	446
20	462	656	470	469	475	477
30	475	674	490	485	496	508
40	484	691	518	510	523	537
50	507	711	544	437	550	568
60	533	730	581	572	587	595
70	565	747	614	604	622	628
80	604	773	658	651	667	670
90	662	804	718	712	729	719
95	709	823	768	767	778	760
FBP ^a	804	873	859	868	868	827

^aFBP, final boiling point.

Table 7

Functional Group Separation of Recycle Solvent

	% in solvent					
	A	B	C	F	G	J
Saturate	8.2	0.2	5.6	5.9	3.4	3.3
Aromatic	58.6	77.2	56.6	58.6	60.6	51.4
Polar	33.2	22.6	37.8	35.5	36.0	45.3

Table 8

Correlation of Microautoclave Results to
Physical/Chemical Properties

	Solvent					
	A	F	C	G	J	B
Micro-autoclave	58	70	73	77	66	89
Wt % H	8.6	8.2	8.3	8.8	8.3	7.2
H _α by NMR	30.1	30.7	30.9	31.9	35.5	29.5
Wt % H _α	2.6	2.5	2.6	2.8	2.8	2.1
Wt % OH	43	46	47	56	55	3
80% distilled	604	712	718	729	670	773
% saturates	8.2	5.9	5.6	3.4	3.3	0.2

Table 9
¹H NMR Distribution of Distillates

	Solvent F	IPB-450°F	450-550°F	550-650°F	650°F- end point
H _{ar}	37.4	32.9	40.3	36.9	34.5
H _α	30.7	31.4	28.2	24.8	28.6
H _β	32.0	35.7	31.5	38.2	36.9

Table 10
 Weight Percent Hydrogen Distribution in Solvent F

	Solvent F	IPB-450°F	450-550°F	550-650°F	650°F- end-point
H _{ar}	3.1	3.0	3.4	3.0	2.6
H _α	2.5	2.9	2.4	2.0	2.2
H _β	2.6	3.3	2.7	3.1	2.8

Table 11
 Near-Infrared Measurements of Solvent F

	Solvent F	IPB-450°F	450-550°F	550-650°F	650°F- end point
% O as OH	46	68	39	35	45
% O as -O-	54	32	41	65	55
% N as NH	14	~0	16	19	22
% N as NH ₂	~0	~0	~0	4	8
% N as -N=	86	100	84	77	70

Table 12
Physical Properties of Distillate F Fractions

	Solvent F	IBP-450°F	450-550°F	550-650°F	650°F- end-point
Specific gravity	1.025	0.962	0.993	1.033	1.063
Refractive index	1.3048	1.5338	1.5802	ND ^a	1.644
Heating value (Btu/hr)	17,200	17,200	17,250	ND	16,900
Viscosity, 38°C (cP)	10.13	6.63	6.88	10.83	1674
Viscosity, 50°C (cP)	6.99	6.7	6.25	7.32	353

^aND, not determined.

Table 13
Capillary Gas Chromatography Conditions

Column type	SE-52 prepared by Alpine West Laboratories
Column length	15 m
Detector	Flame ionization
Carrier gas, flow	Helium, 2.2 cm ³ /min
Injector temp	250°C
Detector temp	275°C
Detector range	× 1
Make-up flow	30 cm ³ /min
Temp program	50-250°C at 4°C/min
Sample size	0.2 µL nominal
Splitter	55:1
Phase thickness	0.25 µm

Table 14
Gas Chromatography Conditions on the GC/MS

Column type	SE-54 J + W fused silica
Column dimensions	14.5 m x 0.25 mm i.d.
Detector	Finnigan 4000 mass spectrometer; EI ^a 70 eV
Carrier gas, flow	Helium, 2.1 cm ³ /min
Injector temp	250°C
Detector temp	250°C
Interface (GC-MS)	250°C
Temp program	50°C hold 1 min; 4°C/min to 250°C
Sample size	0.2 µl
Splitter	50:1
Phase thickness	0.25 µm

^aEI, electron impact.

Table 15

Major Compounds in Solvent F

Peak no. ^a	Compound	Peak no.	Compound
1	Methylphenol	15	Dibenzofuran
2	Tetralin	16	Trimethylnaphthalene
3	Naphthalene	17	Fluorene
4	Tetrahydromethylnaphthalene	18	n-C ₁₆
5	Tetrahydromethylnaphthalene	19	9,10-Dihydrophenanthrene
6	An ethylmethylphenol	20	Phenanthrene
7	2-Methylnaphthalene	21	Anthracene
8	1-Methylnaphthalene	22	n-C ₁₈
9	Biphenyl	23	Methylphenanthrenes
10	An ethylnaphthalene	24	Fluoranthene
11	Diphenyl ether	25	Pyrene
12	n-C ₁₄	26	n-C ₂₁
13	Dimethylnaphthalenes	27	Methylpyrene
14	Acenaphthene	28	n-C ₂₇

^aNumbers correspond to those in Figure 6.

Table 16

Compounds Identified by GC/MS in Total Sample of Solvent F

Scan no.	Library search result ^a	Compound	Comments
228	F = 970	2-Methylphenol	
252		3- and 4-methylphenols	
317	802/980	A 2,3-dihydromethylindene	4- or 5-methyl isomer
338	F = 950	A dimethylphenol	
343	F = 996	1,2,3,4-Tetrahydronaphthalene	(Tetralin)
368	959/999	Naphthalene	
392	F = 990	A dimethylphenol	
402	F = 967	Dodecane	Plus a C ₃ -alkylphenol
410	898/998	1,2,3,4-Tetrahydro-2-methylnaphthalene	
422	848/948	1,2,3,4-Tetrahydro-1-methylnaphthalene	
436	F = 987	Quinoline	Plus a tetrahydromethylnaphthalene or a 2,3-dihydrodimethyl-1H-indene
455	F = 975	A tetrahydromethylnaphthalene	Or a 2,3-dihydrodimethyl-1H-indene
474	903/996	1,2,3,4-Tetrahydro-5-methylnaphthalene	Or 6-methyl isomer
482		An ethylmethylphenol	
495	F = 940	A 2,3-dihydrodimethyl-1H-indene	Plus a C ₃ -alkylphenol
512		2-Methylnaphthalene	
530	911/982	1-Methylnaphthalene	
543	822/986	1,2,3,4-Tetrahydro-2,6-dimethylnaphthalene	May be -2,7-dimethyl- isomer or possibly another
549	F = 892	A trimethylbenzenemethanol	Plus a sec-butylphenol (F = 935)
556	F = 889	A 1,2,3,4-tetrahydrodimethylnaphthalene	Plus a trimethylbenzenemethanol?
573		A methylpropylphenol	Or a sec-butylphenol; plus a tetrahydro-C ₂ -alkylnaphthalene
578	751/962	2,3-Dihydro-1H-inden-1-ol	MM = 134; or a vinylbenzenemethanol or a dimethylbenzaldehyde? Plus?
586	F = 988	5-Methylquinoline	
595		See 573	Plus a naphthalenamine? Plus a tetrahydroethylnaphthalene?
613	F = 959	1,2,2a,3,4,5-Hexahydroacenaphthylene	
622	908/975	1,1'-Biphenyl	
636	870/999	2-Ethyl-naphthalene	
656	909/978	Diphenyl ether	
662	829/979	Tetradecane	
668	940/993	A dimethylnaphthalene	
672	F = 930	A dimethylnaphthalene	Plus a tetrahydro-C ₃ -alkylnaphthalene
690	F = 960	See 668	
702		C ₅ -Alkylphenol	Plus a dimethylquinoline? Ion at 135 may indicate pyrazine
713	F = 954	2-Isopropylnaphthalene	Plus C ₅ -alkylbenzene
745	945/989	1,2-Dihydroacenaphthylene	(Acenaphthene)
753		A propylnaphthalene	Plus a methylbiphenyl
762	F = 985	A methyl-1,1'-biphenyl	

Table 16 (continued)

Scan no.	Library search result ^a	Compound	Comments
774	821/974	An isopropyl-naphthalene	Or an ethylmethyl-naphthalene
784	881/991	Dibenzofuran	Plus pentadecane
798	810/975	A trimethyl-naphthalene	
803		An ethylmethyl-naphthalene	Possibly an isopropyl-naphthalene
811	F = 850	A dihydrotrimethyl-naphthalene?	MW = 172
816	F = 917	1-Butyl-naphthalene	MW = 184; plus MW = 188, see scan 840
824	815/990	A trimethyl-naphthalene	Plus 2-methyl-1-propyl-naphthalene (824/971)
840		A tetrahydrobutyl-naphthalene?	MW = 188; plus a methylethyl-naphthalene? MW = 170
847	F = 945	1-tert-Butyl-naphthalene	Plus MW = 200?
862	827/928	9H-Fluorene	
874	880/964	1-(2-Propenyl)-naphthalene	Part of the spectrum matches this best and part matches methyl-1,1'-biphenyls better. They are similar in other regions
882	822/955	A methyl-1,1'-biphenyl	However, see comment at scan 874
890	F = 905	A methyl-9H-fluorene	Plus a methylbiphenyl (F = 880)
906		Hexadecane	Plus a methyl-dibenzofuran
922	857/976	4-Methyl-dibenzofuran	
931	723/954	9H-Xanthene	Spectral match not as good as usual. A methyl-dibenzofuran or (1,1'-biphenyl)-4-carboxaldehyde are also possibilities
936	800/900	A C ₂ -alkylbiphenyl	
941		A tert-butyl-naphthalene	Plus a methyl-dibenzofuran? Plus MW = 198, a C ₅ -alkyl-naphthalene?
947	F = 980	A C ₂ -alkylbiphenyl	
961		An alkane	
970	769/954	1,1'-(1,2-Ethenediyl)-bisbenzene	
978		An alkane	
984	877/996	9,10-Dihydrophenanthrene	
990	F = 963	A methyl-9H-fluorene	
1000		See 990	Plus a C ₂ -alkylbiphenyl
1010		A butylmethyl-naphthalene	Plus a methyl-9H-fluorene (F = 966)
1020	F = 906	Heptadecane	
1027		An alkane	Plus a C ₂ -alkylbiphenyl?
1035		A C ₃ -alkylbiphenyl	Or something similar to 1,2-dimethyl-4-(phenylmethyl)benzene
1047	F = 942	Dibenzothiophene	And a dimethylbiphenyl, F = 900. These components are of about equal concentrations
1054	F = 925	A dimethyl-1,1'-biphenyl?	Plus MW = 196 (a C ₃ -biphenyl?)
1067		An alkane	
1081	907/971	Phenanthrene	
1087	F = 973	A benzoquinoline?	
1128		Octadecane	
1137		An alkane	Plus a C ₄ -alkylbiphenyl? MW = 210, loss of methyl and ethyl apparent
1143	F = 971	9H-Carbazole	
1152	F = 909	A methyl-dibenzothiophene	

Table 16 (continued)

Scan no.	Library search result ^a	Compound	Comments
1161		A C ₄ -alkylbiphenyl?	MA = 210. There are other possibilities, also
1169		A C ₃ -alkylbiphenyl?	MW = 196
1174	F = 930	See 1152	
1196	849/984	A methylphenanthrene	
1202		See 1196	
1212		See 1196	
1219		See 1196	Plus MW = 210, possibly a methylpropylbiphenyl
1223	F = 916	See 1196	Plus MW = 210 and 204
1230		Nonadecane	
1254	725/993	1,2,3-10b-Tetrahydrofluoranthene (could be a tetrahydropyrene)	Plus MW = 181? Which may be something similar to 9H-fluoren-2-amine
1275	812/977	2-Phenylnaphthalene	
1290	F = 948	9-Ethylphenanthrene	Or 2-ethyl isomer
1300	F = 966	4-Phenylbicyclohexyl	
1305	F = 950	A dimethylphenanthrene	4,5-Dimethyl isomer; M/Z = 191 is the base ion
1314		See 1305	2,3-, 2,5-, 2,7-, 3,6-, 9,10-dimethyl isomers are possibilities. M/Z = 206 is the base ion
1330		Eicosane	
1353	945/994	Fluoranthene	
1398	936/995	Pyrene	
1409		1-Phenylnaphthalene	MW = 204, plus benzo[k]xanthene, MW = 218
1424	811/991	Heneicosane	
1466	F = 913	An 11H-benzofluorene	
1509	F = 921	A methylpyrene	Or an 11H-benzofluorene
1516		Docosane	Plus 4,5,6-trihydrobenz[de]anthracene, MW = 218
1530	F = 930	A methylpyrene	
1536		See 1530	
1604		Tricosane	
1689		Tetracosane	
1699	895/986	Benz[a]anthracene	Benzo[c]phenanthrene elutes first and has the same molecular weight and a similar mass spectrum
1770		Pentacosane	
1849		Hexacosane	
1925		Heptacosane	

^aValues given in this column are a measure of the quality of match between the unknown spectrum and a computer library spectrum. The first value is the purity and the second is the fit. If only fit is given, it will be preceded by F =. Purity is a measure of the total overlap or match between ions in the unknown and library spectra, and fit is a measure of how much of the library spectrum is present in the unknown spectrum. The routines that calculate these numbers are quite complex. The numerical values range from 0 to 1,000. 1,000 is a perfect match and is rarely achieved for various reasons. Even values as low as 800 are useful when used with care. There are many situations that can cause low purity values, e.g., some are high backgrounds caused by column bleed or overlapping components. In these cases, fit becomes more useful. The spectra are examined for accuracy of the library match or for ions that are not in the standard, but could mean an important change in interpretation.

Table 17

Distribution of Saturates (Alkanes) in Solvent F

Carbon no.	Saturate (% relative)	Solvent F (wt %)
C ₁₃	7.2	0.4
C ₁₄	4.2	0.2
C ₁₅	7.6	0.4
C ₁₆	6.5	0.4
C ₁₇	5.8	0.3
C ₁₈	4.9	0.3
C ₁₉	3.6	0.2
C ₂₀	3.1	0.2
C ₂₁	2.3	0.1
C ₂₂	1.8	0.1
C ₂₃	1.3	0.1
C ₂₄	0.8	0.08
C ₂₅	0.7	0.04
C ₂₆	0.5	0.03

Table 18

Polynuclear Aromatic Hydrocarbons Identified by GC/MS in Solvent F

Scan no. ^a	Library search result ^b	Compound	Comments
340	847/994	1,2,3,4-Tetrahydronaphthalene	(Tetralin) MW = 132
365	953/999	Naphthalene	MW = 128
407	881/997	2-Methyl-1,2,3,4-tetrahydronaphthalene	MW = 146
471	869/995	5-Methyl-1,2,3,4-tetrahydronaphthalene	Or 6-methyl- isomer
505	F = 962	2-Methylnaphthalene	MW = 142
525	928/990	1-Methylnaphthalene	
539	F = 970	A dimethyltetrahydronaphthalene	Plus something with ions at 104 and 117
592	814/994	6-Ethyl-1,2,3,4-tetrahydronaphthalene	Or possibly another isomer
616	937/991	1,1'-Biphenyl	MW = 154
632	881/997	2-Ethyl-naphthalene	MW = 156
645	810/990	A dimethylnaphthene	Plus a methylbiphenyl
649	916/985	Diphenyl ether	MW = 170
659	F = 965	Tetradecane	MW = 198
663	898/991	A dimethylnaphthalene	
666	890/990	See 663	
686	F = 990	A dimethylnaphthalene	Plus minor amount of MW = 168 (a methylbiphenyl?) MW = 174 (a C ₃ -alkyltetralin)
711	842/977	2-Isopropylnaphthalene	MW = 170
739	923/975	1,2-Dihydroacenaphthylene	MW = 154, plus an alkane
750		An n-propylnaphthalene	Plus a methylbiphenyl (847/976)
759	F = 975	A methylbiphenyl	MW = 168
769	805/966	1-Isopropylnaphthalene	
778	876/996	Dibenzofuran	MW = 168
783		Pentadecane	MW = 212
795		A trimethylnaphthalene	
799		An ethylmethylnaphthalene? ^c	
821		See 795	
838		See 795	Plus a C ₄ -alkyltetralin? (MW = 188)
856	898/968	9H-Fluorene	MW = 166
870	888/960	1-(2-Propenyl)naphthalene	Possibly a methylbiphenyl instead, but the match significantly better with the compound shown
878	F = 925	A methylbiphenyl	Plus a methyl dibenzofuran?
881	F = 878	2-Butylnaphthalene	MW = 184
885	F = 942	9-Methyl-9H-fluorene	MW = 180
903		Hexadecane	Plus a methyl dibenzofuran
918	831/963	A methyl dibenzofuran	(1,1'-Biphenyl)-4-carboxaldehyde produces the spectrum
944	819/984	2-Ethyl-1,1'-biphenyl	
959		Alkylcycloalkane	Plus MW = 196 (C ₃ -alkylbiphenyl or C ₂ -alkyldibe

Table 18 (continued)

Scan no. ^a	Library search result ^b	Compound	Comments
981	907/922	9,10-Dihydrophenanthrene	MW = 180
1017		Heptadecane	MW = 240
1043	848/967	Dibenzothiophene	MW = 184 and a dimethylbiphenyl (F = 910) plus unknown with large ions at 141, 154, and 178
1050		Unknown	MW = 196, prominent 195
1074	945/995	Phenanthrene	MW = 178
1127		Octadecane	MW = 254
1152	F = 910	A methyl dibenzothiophene	MW = 198
1201	865/975	A methylphenanthrene	2- or 3-methyl isomer according to relative retention times of reference; MW = 192
1214		4H-Cyclopenta[def]phenanthrene?	MW = 190
1219		A methylphenanthrene?	9-Methyl isomer according to reference
1224	F = 945	A methylphenanthrene	4- or 1-methyl isomer according to reference
1232	809/975	Nonadecane	MW = 268
1256	F = 803	1,2,3,10b-Tetrahydrofluoranthene	Plus another tetrahydro isomer leading to large ion at 202? MW 206; mixture possible; a tetrahydropyrene instead is also possible
1277	845/946	2-Phenyl naphthalene	MW = 204, this is distinguishable from a dihydrofluoranthene or -pyrene
1291	F = 960	An ethylphenanthrene	9- of 2-ethyl isomer according to reference; MW = 206
1307		See 1291	
1316	F = 980	3,6-Dimethylphenanthrene	Possibly the 2,7 isomer
1332		Eicosane	MW = 282; contrary to some past experience, current work is producing molecular ions for long-chain hydrocarbons that are about 1% of the base ion
1339	F = 930	See 1316	
1354	927/982	Fluoranthene	MW = 202
1400	927/990	Pyrene	
1411	793/942	4,5-Dihydropyrene?	Few hydroaromatics elute, after the parent compound, so this may not be correct; MW = 204
1427	F = 960	Heneicosane	MW = 296; no visible molecular ion
1469	744/897	A methylpyrene	Or methylfluoranthene, or a 11H-benzofluorene; MW = 216
1490	797/917	See 1469	
1512	F = 920	See 1469	
1519		Docosane	MW = 310
1532		See 1469	There are three possible methylpyrene isomers. At least one of these four peaks (1469, 1490, 1512, 1532) must be another structure such as those suggested in the 1469 comment. Benzofluorenes precede methylpyrenes (a, then b). The methylpyrenes elute with 4- and 2- together, then the 1-methyl isomer; see Lee et al., 1979

Table 18 (continued)

Scan no. ^a	Library search result ^b	Compound	Comments
1607		Tricosane	MW = 324
1691		Tetracosane	MW = 340
1702	890/958	Chrysene	Benz[a]anthracene, triphenylene, and naphthacene elute in the same region and have the same spectra
1773		Pentacosane	MW = 354
1852		Hexacosane	MW = 368
1928		Heptacosane	MW = 382 (1901 is a noise spike)
2001		Octacosane	MW = 396
2073		Nonacosane	MW = 410

^aScan numbers for specific components from this appendix cannot be compared with the numbers for other samples such as F217N and F217P because a different capillary column flow rate was used for this work.

^bValues given in this column are a measure of the quality of match between the unknown spectrum and a computer library spectrum. The first value is the purity and the second is the fit. If only fit is given, it will be preceded by F =. Purity is a measure of the total overlap or match between ions in the unknown and library spectra, and fit is a measure of how much of the library spectrum is present in the unknown spectrum. The routines that calculate these numbers are quite complex. The numerical values range from 0 to 1,000. 1,000 is a perfect match and is rarely achieved for various reasons. Even values as low as 800 are useful when used with care. There are many situations that can cause low purity values, e.g., some are high backgrounds caused by column bleed or overlapping components. In these cases, fit becomes more useful. The spectra are examined for accuracy of the library match or for ions that are not in the standard, but could mean an important change in interpretation.

^cQuestion marks indicate strong questioning of a particular compound choice, although it probably has much in common with the exact compound.

Table 19

Aromatic/Neutrals in Recycle Solvent F
(Keyed to Figure 11)

GC retention time	Compound	Relative area %
6.89 ^a	Tetralin	0.2
7.41	Naphthalene	2.6
9.99	2-Methyltetralin	1.5
10.84	2-Methylnaphthalene	8.1
11.30	1-Methylnaphthalene	2.7
13.65 ^b	Biphenyl	4.9
14.54 ^b	Diphenyl ether	8.9
14.81	Dimethylnaphthalene	2.8
16.71	1,2-Dihydroacenaphthalene	2.8
17.73	Dibenzofuran	3.2
19.7	9H-Fluorene	2.5
20.41	Hexadecane	2.3
21.91	9,10-Dihydrophenanthrene	0.8
25.23	Phenanthrene	7.1
32.29	Fluoranthene	1.8
33.41	Pyrene	<u>1.4</u>
		53% aromatics
		(30.6% of solvent F)

^aNot included on Figure 11.

^bComponents of Dowtherm.

Table 20

Phenolic Species in Solvent F

Compound	Scan no. on Figure 12
3-Methyl phenol	216
2,4-Dimethyl phenol	294
Ethyl phenol	321
3,4-Dimethyl phenol	348
Isopropyl phenol	392
Ethylmethyl phenol	396
C ₄ -Alkyl phenol	543
C ₅ -Alkyl phenol	657
C ₆ -Alkyl phenol	758

Table 21

Nitrogen Bases Identified by GC/MS in Solvent F^{a,b}

Scan no.	Library search result ^{c,d}	Compound	Comments
197	F = 967	2-Methylphenol	
209	F = 990	A methylaniline	
220		3- and 4-methylphenols	
251	F = 961	2,3-Dihydro-1H-indole	
280		Methyl-2,3-dihydro-1H-indole ^e	
302	F = 910	An ethylmethylpyridine	
312	F = 900	A trimethylpyridine	
326	F = 983	Naphthalene	
328	715/960	A dimethylphenol	Plus a methyl-2,3-dihydro-1H-indole
337		A dimethylphenol	
359	F = 967	A dimethylphenol	Plus a C ₃ -alkylbenzene
368	F = 986	1,2,3,4-Tetrahydromethylnaphthalene	Plus a C ₄ -alkylbenzene
379	872/993	5,6,7,8-Tetrahydroquinoline	
392	939/999	Quinoline	
405	F = 947	A methylpropylpyridine	
412	F = 940	An ethylmethylphenol	Or isopropylphenol plus a pyrazine or C ₄ -alkylpyridine?
418	887/999	Isoquinoline	
429	F = 913	1,2,3,4-Tetrahydromethylnaphthalene	
443	F = 900	2-Ethyl-4-methylphenol	Plus a C ₄ -alkylpyrazine? (Ion at 108 and the peak is too broad)
462	873/977	2-Methylnaphthalene	Plus a tetrahydromethylquinoline plus a tetrahydronaphthalenamine
472	906/952	1H-Indole	Plus a tetrahydromethylquinoline or isoquinoline. See text
483	892/997	2-Methylquinoline?	Possibly another isomer
492	880/985	A methylquinoline	Or isoquinoline
505	860/970	See 492	Presence of significant ion at M1 (142) along with relative volatility seem to eliminate naphthalenamines as a possibility. See text. Plus 2-(2-propenyl)phenol (721/883)
510		Unknown	Except for cluster for ions at 133 (28%), 132 (34), 131 (11), 130 (26), it matches isoquinoline, which is at scan 418
520	796/996	1-Methylisoquinoline	
528		See comment	MW = 161; tetrahydro-C ₂ -alkylquinolines or isoquinolines or 2,3-dihydro-1H-C ₃ -alkylindoles are possibilities; see text
535		See 492	Plus a dimethylbenzaldehyde (F = 990), MW = 134
543		See 492	Plus MW = 147
552		Unknown	MW = 150; a phenol or pyrazine mixture likely
559		See 492	Plus MW = 147
566	F = 990	See 492	

Table 21 (continued)

Scan no.	Library search result ^a	Compound	Comments
569	F = 870	A dimethylquinoline	Or isoquinoline or methylnaphthalenamine. MW = 157
572	915/978	1,1'-Biphenyl	MW = 154
589	825/980	A methyl-1H-indole	Methylindolizines are very similar; MW = 131
592	F = 910	An ethylquinoline	Or isoquinoline; MW = 157
595	850/960	A methylindolizine	See 589, plus MW = 161
599	F = 920	A dimethylnaphthalene	MW = 156; plus MW = 148
604	930/989	Diphenyl ether	MW = 170; plus MW = 157. Such as methylnaphthalenamine or a C ₂ -alkylquinoline or isoquinoline
617	F = 865	A dimethylnaphthalene	Plus MW = 164
624	860/975	A dimethylquinoline	Or isoquinoline; significant ion at M - 1; plus MW = 161
641		See 624	
650		See 624	Plus an ethylmethylquinoline (?), MW = 171
658		See 624	
667		An ethenylisoquinoline?	MW = 155; C ₅ -alkylbenzene; plus MW = 157
671		Unknown	MW = 171 and 175
685		See 624	
691	932/988	1,2-Dihydroacenaphthylene	(Acenaphthene)
697		A dihydro-C ₃ -alkylnaphthalene	
701		A C ₃ -alkylquinoline?	MW = 171; 170 (33%)
706	F = 890	See 624	Plus others, including a dimethyl-1H-indole, MW = 145, F = 902
722		An isopropyl-naphthalene	
730	F = 992	Dibenzofuran	MW = 168; plus MW = 171
740		A C ₃ -alkylquinoline	Plus MW = 169; plus an alkane
745		An ethylmethylquinoline	Or similar
752		C ₃ -Alkylnaphthalene	Plus others
754	F = 879	A naphthalenamine	
773	F = 905	A propylisoquinoline?	Or 2,3,4,9-tetrahydro-1H-carbazole (F = 907); plus MW = 182
782	793/931	4-Propylquinoline	Or similar; the MS spectra of propylquinolines and isoquinolines seem to differ vastly with position of the alkyl group. Plus 2,3,4-trimethylquinoline (837/939) or similar
793	873/975	2,3,4-Trimethylquinoline	Or similar; this is the only trimethylquinoline isomer in the NBS library
800	F = 883	7-Methyl-8-quinolinol	Plus MW = 184?
807	863/946	9H-Fluorene	Plus 2-isopropylquinoline (768/891) or similar
820	F = 920	A methylbiphenyl?	Plus MW = 185 (a C ₄ -alkylquinoline?)
829	F = 956	2-Methyl-1,1'-biphenyl?	
835	F = 909	9-Methyl-9H-fluorene	And a C ₄ -alkylnaphthalene and a methylbiphenyl plus?
854	F = 951	4-Methyldibenzofuran	MW = 182; plus MW = 185
857		A methylnaphthalenamine?	There are no compounds in this class in the computer library; plus MW = 185
868	902/966	4-Methyldibenzofuran	See scan 854. One is presumably an isomer. Plus MW = 185

Table 21 (continued)

Scan no.	Library search result ^a	Compound	Comments
874		Unknown	Matches 9H-carbazole (838/981) but Lee et al. (1979) confirm the peak at scan 1090 as being the correct retention time for the carbazole. It does seem to be MW = 167 plus MW = 185 (a methylpropylquinoline?)
878		A methyl dibenzofuran	Or (1,1'-biphenyl)-4-carboxaldehyde
886	849/971	(1,1'-Biphenyl)-2-amine	MW = 169
889		C ₄ -Alkylquinoline	MW = 185
894	F = 951	2-Ethyl-1,1'-biphenyl	Plus a methylnaphthalenamine
901		See 857	MW = 157; the boiling points of these compounds should be about 50°C higher than C ₂ -alkylquinolines (also MW = 157); see text
906		A butylquinoline?	MW = 185, large loss of -C ₃ H ₇ but it does not match 2-, 3-, 6-, or 7-butylquinoline or 1- or 3-butylisoquinoline
921		C ₅ -Alkylquinoline	MW = 199
930	908/982	9,10-Dihydrophenanthrene	MW = 180
940		C ₄ -Olefinic quinoline?	MW = 183; plus a methyl-9H-fluorene (F = 900); see also scan 835
945	F = 985	A methyl-9H-fluorene	MW = 180; see also scans 835 and 940; plus MW = 182, perhaps a dimethylbiphenyl
951	F = 889	9-Methyl-9H-carbazole	(Or 9H-fluorene-2-amine); MW = 181. The retention time relative to 9H-carbazole (scan 1090) and the presence of a group of carbazoles support the methylcarbazole here
972		n-Heptadecane	Plus? MW = 195 and 187?
991	F = 825	Dibenzothiophene	MW = 184; plus MW = 182
997	F = 920	A dimethylbiphenyl	Plus?
1021	F = 977	Phenanthrene	
1031	921/977	Acridine	Or phenanthridine (more likely) or a benzoquinoline; MW = 179
1044		See 1031	
1067	904/991	Benzo[h]quinoline	See 1031; according to Lee et al. (1979), the order of elution of these isomers is: benzo[h]quinoline, acridine, phenanthridine, benzo[f]quinoline. Other isomers are also possible
1077		Unknown	MW = 197; mixture likely
1079		An alkane	
1090	790/992	9H-carbazole	MW = 167; plus MW = 197 (olefinic C ₅ -quinoline?)
1102	F = 980	A methylbenzoquinoline	MW = 193
1116		See 1102	
1145		See 1102	Plus MW = 197 and 211
1155		See 1102	
1158	826/868	4H-Cyclopenta[def]phenanthrene	MW = 190; plus a methylbenzoquinoline

Table 21 (continued)

Scan no.	Library search result ^a	Compound	Comments
1163	F = 928	A methylphenanthrene	MW = 192; the 9-methyl isomer is the first to elute after the cyclopentaphenanthrene according to Lee et al. (1979)
1168	903/955	2-Methyl-9H-carbazole	MW = 181; plus MW = 193 and, possibly, 192; see 1102
1174		See 1102	
1191		See 1102	
1196		See 1102	
1198		A methyl-9H-carbazole	
1201		A hexahdropyrene	MW = 208 (or hexahydrofluoranthene)
1205		A C ₂ -alkylbenzoquinoline?	MW = 211
1215		A tetrahydrobenzophenanthridine	MW = 207; plus a methyl-9H-carbazole (F = 941)
1221		A dihydrofluoranthene	(Or dihydropyrene)
1224		A tetrahydrobenzophenanthridine	
1232		See 1224	
1238		See 1224	
1248		See 1224	
1265		See 1224	
1289	F = 932	4,5,-Dihdropyrene	
1296	958/991	Fluoranthene	
1325		A hexahdropyrene?	MW = 208
1333		Indeno[1,2,3-ij]isoquinoline?	(Azafluoranthene); MW = 203
1341	965/994	Pyrene	MW = 204
1352	904/970	1-Phenylnaphthalene	Plus MW = 221 and MW = 218
1379		Benzo[1mn]phenanthridine?	(An azapyrene); MW = 203
1383		See 1379	Plus?
1410	F = 953	1-Methylpyrene	Plus MW = 221 and 203
1416		4H-Benzo[def]carbazole	MW = 191; it is not believed to be 9H-fluorene-9-carbonitrile despite a close match (F = 913)
1432	825/915	A methylpyrene	MW = 216; or a 11H-benzofluorene
1444		A methylindene[1,2,3-ij]isoquinoline	MW = 217; or similar. See scan 1333 or an azabenzofluorene; see scan 1650
1452	855/941	See 1432	
1459		See 1444	
1463		Unknown	MW = 218
1472		See 1432	
1478		See 1432	
1491		Unknown	MW = 219; strong M - 1, M - 2, M - 3
1502		A C ₂ -alkylindeno[1,2,3-ij]isoquinoline	MW = 231; or similar; see scan 1444
1554		See 1502	
1565		See 1502	
1574		Unknown	MW = 234
1594		A benzacridine	MW = 229
1633		See 1594	
1640	897/958	Chrysene	

Table 21 (continued)

Scan no.	Library search result ^a	Compound	Comments
1650		Benzo[a]carbazole	MW = 217
1691	F = 900	A methylbenzacridine?	Or similar; MW = 243, plus MW = 232 (and 217?)
1703	F = 937	See 1691	Plus MW = 217
1739		See 1691	
1787 to 1834		Series of components	MW = 257
1844			MW = 253
1871	835/955	A benzo[fluoranthene	MW = 252
1922	710/840	A benzopyrene	MW = 252
1932	825/955	A benzopyrene	
1949	F = 910	Perylene	MW = 252
2025		Unknown	MW = 267
2167		Indeno[1,2,3-cd]pyrene	MW = 276
2226		Benzo[ghi]perylene	MW = 276
2262		Dibenzo[def,mno]chrysene	MW = 276

^aFor classes of compounds such as benzo[fluoranthenes, benzopyrenes, and perylene, all of which have the same molecular weight and mass spectral pattern, the relative retention order of Lee et al. (1979) was used. The location of many of the heterocyclic compounds such as benzacridines and indenoisquinolines is also based on data in this article.

^bIn general, the high purity/fit values obtained for unambiguous compounds such as typical polynuclear aromatic hydrocarbons show that the nitrogen-containing compounds chosen by the computer are probably incorrect isomers. The mass spectra of some of the nitrogen heterocyclic compounds vary greatly in some classes among isomers.

^cSee Table 16, footnote a, for discussion of library search results.

^dThere is an extremely large number of small components not documented in this table and minor components under larger components, some of which are documented. In the case where only fit values are given, it is because purity values drop when mixed spectra are present. If ion mapping and custom subtraction are used to isolate a component spectrum, high purity and fit values can be obtained in many of these cases.

Table 22
High-Resolution Mass Spectral Analyses Completed on Sample F and Fractions

Sample	Resolution	Electron energy	Data reduction				Total
			Hydro	Oxygen	Sulfur	Nitro	
Total	10,000	70 eV	X	X	X	X	X
Total bases			X	X	X		
Saturates			X	X	X		
Aromatics			X	X	X		
Phenols			X	X	X		
Nitrogen bases			X	X	X	X	
Total	10,000	10.5 eV	X	X	X	X	X
Total bases			X	X	X	X	X
Saturates			X	X	X		
Aromatics			X	X	X		
Phenols			X	X	X		
Nitrogen bases			X	X	X	X	
Total	20,000	10.5 eV	X	X	X	X	X
Total bases			X	X	X	X	X
Saturates			X	X	X		
Aromatics			X	X	X		
Phenols			X	X	X		
Nitrogen bases			X	X	X	X	
Total	40,000	10.5 eV	X	X	X	X	
Total bases			X	X	X	X	
Saturates			X	X	X	X	
Aromatics			X	X	X	X	
Phenols			X	X	X	X	
Nitrogen bases			X	X	X	X	

Table 23

Search Categories and their Z-Number and Elemental Ranges

Category ^a	Z-number	Hydrogen ^b	Carbon	Nitrogen	Oxygen	Sulfur
Hydro	0-40	0 - 2n	5-28	0	0	0
Oxygen	2-46	0 - 2n - 2	5-28	0	1	0
	6-40	0 - 2n - 6	5-28	0	2	0
	6-32	0 - 2n - 6	5-28	0	3	0
	10-18	0 - 2n - 10	5-28	0	4	0
Nitro	3-49	0 - 2n - 3	5-28	1	0	0
	7-41	0 - 2n - 7	5-28	1	1	0
Sulfur	2-44	0 - 2n - 2	5-28	0	0	1
	10-30	0 - 2n - 10	5-28	0	0	2
	10-30	0 - 2n - 10	5-28	0	1	1

^aThere is also a "total" search category which is a sum of hydro, oxygen, and sulfur. However, because it does not include nitro, it is not really a total.

^bn = number of carbon atoms. For some of the larger molecules, where n is large, $2n - Z > 0$, although not by much. For example: nitro; 1 nitrogen/1 oxygen; C_{28} , $Z = 41$, $H = 2n - Z = 56 - 41 = 15$. 15 would be the minimum number of hydrogen atoms in a $C_{28}H_{15}O_1N_1$ species in this nitro table.

Table 24

Elemental^a Analysis of Solvent F and Fractions

Sample	wt %				
	Carbon	Hydrogen	Nitrogen ^b	Oxygen	Sulfur ^c
Total	87.69	8.04	0.92	2.46	0.89
Base-free	87.28	8.09	0.64	2.47	1.52
Phenolics	82.04	8.24	2.22	7.11	0.39
Saturates	85.43	14.44	0.04	0.08	<0.01
Aromatics	90.46	7.91	0.09	1.04	~0.05
Nitrogen bases	83.31	6.91	5.32	4.12	0.34

^aNormalized to 100.00.

^bIt is interesting to note that, apparently, two-thirds of the nitrogen remains after nitrogen-base removal. Compare total to base-free sample for nitrogen.

^cSulfur analysis appears to vary more than others. Comparison between APCI data and Huffman Laboratory data shows discrepancies of up to 100%. The above data are from Huffman. There was insufficient sample for sulfur analysis on the saturates and aromatics. The values in this table are approximates from analysis of similar samples.

Table 25
Aromatic Fraction of Solvent F Analyzed By
High-Resolution Mass Spectrometry

Resolution	Ionization energy (eV)	Search file	Total ion counts ^a	Percentage of ion total ^b	Major components ^c	Counts			
10,000	70	Hydro	7.35-8.0M	8.1	C ₁₄ H ₁₀	71K			
					C ₁₆ H ₁₀	81K			
		Oxygen		2.4	C ₁₀ H ₂ O ₂	65K			
		Sulfur		0.98	C ₁₂ H ₈ S	9.4K			
10,000	10.5	Hydro	8.75-8.38M	28	C ₁₄ H ₁₀	180K			
					C ₁₂ H ₁₂	173K			
					C ₁₆ H ₁₀	48K			
					C ₁₂ H ₆ O	18K			
		Oxygen		3.0	C ₁₃ H ₁₀ O	13K			
					C ₁₃ H ₂₀ O ₃	14K			
					C ₁₂ H ₈ S	14K			
					C ₁₃ H ₁₀ S	5.4K			
		Sulfur		1.7	C ₁₀ H ₁₀ S	5.1K			
					C ₁₄ H ₁₀	154K			
					C ₁₂ H ₁₂	143K			
					C ₁₄ H ₁₄	104K			
20,000	10.5	Hydro	4.87-5.05M	45	C ₁₅ H ₁₂	69K			
					C ₁₆ H ₁₀	58K			
					C ₁₂ H ₁₀ O	99K			
					C ₁₂ H ₈ O	59K			
		Oxygen		8.8	C ₁₃ H ₁₀ O	32K			
					C ₁₄ H ₁₂ O	25K			
					C ₁₂ H ₈ S	12K			
					C ₁₀ H ₁₀ S	5.5K			
		Sulfur		2.5	C ₁₃ H ₁₀ S	5.5K			
					C ₁₁ H ₁₂ S	3.6K			
					C ₁₂ H ₁₂	9.6K			
					C ₁₂ H ₁₀	6.1K			
		40,000		10.5	Hydro	767-792K	19	C ₁₀ H ₈	3.1K
								C ₁₂ H ₁₆	2.8K
								C ₁₂ H ₁₀ O	9.3K
								C ₁₂ H ₈ O	4.6K
Oxygen			6.9		C ₁₀ H ₁₀ S		489		
					C ₂₄ H ₃₂ S ₂		300		
					C ₁₂ H ₈ S		129		
					C ₂₀ H ₂₆ S		128		
Sulfur	1.2								

^aM = millions; K = thousands.

^bThis is actually a percentage of the total of assigned masses and unassigned masses. Assigned masses are in the Z-tables. Unassigned masses do not fit in these mass windows. A third category not included here is the "exception" masses, which include calibration masses and known system background ions. It was noted that the total ion counts for a run varied, depending on the Z-number output class used for the search (hydro, oxygen, etc.). Also, the sum of assigned and unassigned counts varied similarly. There were other related counting differences. The Midwest Center for Mass Spectrometry has no answers presently for these discrepancies. The discrepancies account for the range shown for total ion counts.

^cNote that some formulations do not correspond to a real, expected structure, for instance, C₁₀H₂O₂ in the 10,000 resolution, 70-eV oxygen data.

Table 26

Weight Percents of Functional Groups

	Retention time windows (min)									
	5	10	15	20	25	30	35	40	45	50
Saturates										
Wt %	0.2	2.7	15.9	19.4	19.3	14.0	9.7	7.5	6.0	5.2
Adjusted wt %	0	0.1	0.64	0.78	0.77	0.56	0.38	0.3	0.2	0.2
Aromatics										
Wt %	0.23	2.3	25.6	16.8	17.4	18.8	10.1	5.0	2.3	1.5
Adjusted wt %	0	1.4	15.6	10.2	10.6	11.5	6.2	3.0	1.4	0.9
Phenols										
Wt %	1.1	10.4	22.9	16.5	10.6	11.1	8.7	7.1	6.7	4.9
Adjusted wt %	0.35	3.3	7.3	5.3	3.4	3.6	2.8	2.3	2.1	1.6
N bases										
Wt %	0.2	6.8	12.8	10.0	8.9	15.8	13.3	11.4	10.4	9.6
Adjusted wt %	0	0.2	0.38	0.3	0.27	0.47	0.4	0.34	0.31	0.29
Total for all functional groups	0.4	5.0	23.9	16.6	15.1	16.2	9.8	6.0	4.0	3.0
Accumulated total	0.4	5.4	29.3	45.9	61.0	77.2	87.0	93.0	97.0	100
Calculated boiling point (°F)	393	454	541	574	634	695	755	815	875	936

Table 27

Chemical Composition of Condensate (IBP to ~450°F) Determined by GC/MS

Scan ^a	Library search result ^b	Compound ^c	Comments
26			Small alkane
30			Small alkane
43	917/995	Benzene	
49	910/965	A dimethylcyclopentane	
53	965/990	Heptane	
62	938/994	Methylcyclohexane	
79			Unsat. alkyl
89	879/994	Toluene	Largest component
94	839/933	Dimethylcyclohexane	
105	934/994	Ethylmethylcyclopentane	
109	864/951	A dimethylcyclohexane	
117	904/985	Octane	
123			C ₈ cyclic alkyl, MW = 112 (isopropylcyclopentane) (801/956)
135	917/985	An ethylmethylcyclopentane	
141	858/976	A dimethylcyclonhexane (1,2-cis)	
149		Propylcyclopentane?	1137, 2,6-dimethylheptane, 902/963, MW = 128
158			C ₉ -Alkane?
163			C ₈ -Ketone, C ₉ -cycloalkane
172			81 real C ₉ -C ₁₁ -cycloalkane
180			C ₉ -C ₁₁ -Cycloalkane
193	934/999	Ethylbenzene	
196			C ₈ -C ₁₀ -bicyclo or diene
206	822/998	A dimethylbenzene	
211			C ₃ -C ₁₀ branched alkane
216		Propylcyclohexane	
219	907/969	A dimethylbenzene	But 1-ethenyl-3-methylenecyclopentene (912/980)
227	920/998	Nonane	
236	822/972	1-Propenylcyclohexane	Probably not exactly correct
248	902/997	Propylcyclohexane	
254	840/942	Nonanol	May not be exactly correct, a branched C ₉ 812/995, butylcyclopentane also, MW = 126
259	908/994	2,6-Dimethyloctane	MW = 142
265	902/985	3-Ethyl-2-methylheptane	MW = 142
274			F = 975 for octa-H-indenes and 935 for 1,9-nonanediol P + 700
278	936/998	Propylbenzene	
283			Alkane
290	888/996	An ethylmethylbenzene	
299		A trimethylbenzene	Plus an alkane
304	883/940	2-(Methylbutyl)cyclopentane	Or similar
309	943/971	3-Methylnonane	
315	920/997	An ethylmethylbenzene	
320	844/925	Octahydro-1H-indene (cis or trans)	319 = C ₁₀ -cycloalkane, such as isopropylmethylcyclohexane

Table 27 (Continued)

Scan ^a	Library search result ^b	Compound ^c	Comments
336	888/998	A trimethylbenzene	
341	F = 956	Phenol	
345			C ₁₀ -Alkene, MW = 140, 97/81/69/55
356	956/999	Decane	MW = 142
363			Aromatic trace C ₈ -alkylbenzene
378	819/996	A trimethylbenzene	
383	781/978	A methylisopropylbenzene	
390	969/987	2,6-Dimethylnonane	
396	922/985	2-Propenylbenzene	Or a methylstyrene, etc., MW = 118
403	846/993	Pentylcyclopentane	
414	939/993	3,7-Dimethylnonane	
420	757/971	1-Methyl-4-(1-methylethenyl)-trans-cyclohexane	477 counts
427	885/995	A methylpropylbenzene	
433		2-Methylpropylbenzene	
438	858/994	A dimethylethylbenzene	
448		A C ₈ -alkylbenzene	Methylpropylphenol, etc., F = 973 plus 122 + 07/108
455	868/997	2-Methyldecane	
467	F = 908	An ethyldimethylbenzene	Plus a 2, 3-dihydromethylindene or a methylpropenylbenzene
476	875/974	2,3-Dihydromethylindene	
485	768/964	2-Methylphenol	
498	840/967	An undecene	
512	937/999	Undecane	
529	F = 954	A tetramethylbenzene	? large 133/148 and 152 at 530 (F = 949 for 3,5,5-trimethylbicyclo[4.1.0]heptan-2-one)
537	739/945	A methylundecane	Or a dimethyldecane, etc.
554	881/993	2,3-Dihydromethylindene	
561	F = 950		C ₁₁ -Alkene or substituted cyclic alkane
569	881/972	2,3-Dihydromethylindene	Or a methylpropenylbenzene
574	F = 947	A C ₈ -alkylbenzene	Plus ? large 118 and 107
585	862/964	Tetralin	(1,2,3,4-Tetrahydronaphthalene)
590	F = 899	A dimethylphenol	Plus a trimethylphenol?
593	F = 973	4-Isopropylheptane	Plus 148/1197
601	F = 917	4-Methylundecane	Plus ? 105
608	745/972		C ₁₀ -C ₁₂ -alkane branched
618	952/998	Naphthalene	
623	804/934	An ethylphenol	
629	842/977	2,3-Dihydrodimethyl-1H-indene	
642	876/996	2,3-Dihydrodimethyl-1H-indene	
661	946/999	Dodecane	
666	902/997	1,2,3,4-Tetrahydro-2-methylnaphthalene	
681	933/991	2,6-Dimethylundecane	
696		Unknown	MW = 162
716	843/976	2,3-Dihydrodimethyl-1H-indene	
726	844/986	An ethylmethylphenol	

Table 27 (Continued)

Scan ^a	Library search result ^b	Compound ^c	Comments
739	881/995	1,2,3,4-Tetrahydro-5- or -6-methylnaphthalene	
756		A propylphenol	Mixture
761	F = 988	An ethylmethylphenol	Mixture
769		An alkane	Plus an ethylmethylphenol
783	861/993	2-Methylnaphthalene	
800	908/971	1-Methylnaphthalene	
804		Tridecane	
813	825/978	1,2,3,4-Tetrahydrodimethylnaphthalene	
826	F = 897	2,3-Dihydro-1,1,5-trimethyl-1H-indene	Mixture
844	772/928	6-Ethyl-1,2,3,4-tetrahydronaphthalene	Perhaps it is an isomer of this compound
850		See 844	Plus a component with predominant ions at 82/83
856			
866	802/990	An ethyl-1,2,3,4-tetrahydronaphthalene	
875			Mixture
884	F = 931	1,2,2A,3,4,5-Hexahydroacenaphthylene	Mixture
896	892/991	1,1'-Biphenyl	
906		An alkane	
911	F = 985	2-Ethynaphthalene	Plus a tetrahydrodimethylnaphthalene
924	820/926	A dimethylnaphthalene	
933	919/984	Diphenyl ether	
939	874/968	Tetradecane	
943	944/995	A dimethylnaphthalene	
947	F = 978	A dimethylnaphthalene	Mixture
954		A tetrahydrotrimethylnaphthalene?	Mixture; trace
965	718/992	A tetrahydrodimethylnaphthalene	
977		Alkane	Mixture
988	803/974	2-Isopropyl-naphthalene	
998		Alkane	Mixture
1003	F = 850	A dihydrotrimethylnaphthalene	Mixture
1016	F = 987	1,2-Dihydroacenaphthylene	Plus an alkane
1023	F = 888	An alkane	Plus a propylnaphthalene
1028		A propylnaphthalene	Plus a methylbiphenyl
1036	F = 972	A methylbiphenyl	
1047	771/959	An isopropyl-naphthalene	
1056	897/996	Dibenzofuran	
1062		Pentadecane	
1071	F = 929	A trimethylnaphthalene	
1076		An isopropyl-naphthalene	Possibly a trimethylnaphthalene
1084	747/937	A dihydrotrimethylnaphthalene	
1090	F = 900	An n-butyl- or isobutylnaphthalene	
1098	853/972	A trimethylnaphthalene	Perhaps 2,3,6- or 1,6,7-
1113			Mixture: 170/155; 188; 145; 82/83

Table 27 (Continued)

Scan ^a	Library search result ^b	Compound ^c	Comments
1122	F = 948	A methylisopropyl naphthalene	Plus an alkane, F = 989
1132	875/966	9H-Fluorene	
1135		An alkane	
1146	847/937	1-(2-Propenyl)naphthalene	
1154		A methylbiphenyl	Mixture
1159		A methylpropyl naphthalene	
1162	762/928	A methylbiphenyl	
1168		An alkane	
1179	769/946	Hexadecane	
1193	848/961	4-Methyldibenzofuran	
1208	F = 870	A dimethyl- or ethylbiphenyl	Or 1,1,-diphenylethane
1219	850/980	A dimethyl- or ethylbiphenyl	
1233	F = 920	An alkane	Plus 82/83 ions, which have appeared a few times, but remain unexplained
1250	F = 970	An alkane	
1255		Dihydrophenanthrene?	Ion ratios are incorrect, but the elution time is correct; mixture
1291	888/990	Heptadecane	
1297	F = 950	An alkane	
1317	F = 850	Dibenzothiophene	Mixture
1346	941/995	Phenanthrene	
1398		Octadecane	
1501		Nonadecane	
1600		Eiocosane	

^a Because of the different columns used, different carrier gas flow rates, and different column temperature program, the retention times (scan numbers) of specific components in this analysis will not directly match the data for the other samples in this report.

^b See Table 16, footnote a, for discussion of library search results.

^c Note that many peaks still contain more than one component. The one present in the greatest amount is typically listed in the compound column.

Table 28

Compounds Identified in the Saturate/Aromatic Fraction of the
350-450°F Distillate Cut, Determined by GC/MS

Scan ^a	Library search result ^b	Compound ^c	Comments
15		Dichloromethane	
21		Benzene	
35		Toluene	Added solvent
120		Mesitylene	1,3,5-Trimethylbenzene, added internal standard
278	885/990	2,3-Dihydro-methyl-1H-indene	
290	836/987	See 278	A methylpropenylbenzene is also possible
302	897/992	1,2,3,4-Tetrahydronaphthalene	(tetralin)
327	959/999	Naphthalene	
336	F = 976	2,3-Dihydrodimethyl-1H-indene	Plus something else, ion at 134
342	783/835	A tetrahydromethylnaphthalene?	Major ions at 117/131/146 do not match ratios of standards
348	908/980	2,3-Dihydrodimethyl-1H-indene	
362		Alkane	
367	899/997	1,2,3,4-Tetrahydro-2-methylnaphthalene	
378	896/993	1,2,3,4-Tetrahydro-1-methylnaphthalene	
384	808/929	A butenyldimethylbenzene?	
392		Possibly another isomer of 367	
399	758/983	o-Isopropyl- α -methylstyrene	A tetrahydrodimethylnaphthalene is also possible
410	847/977	2,3-Dihydro-1,3-dimethyl-1H-indene	Or another isomer
429	877/995	1,2,3,4-Tetrahydro-5-methylnaphthalene	Possibly the 6-methyl isomer
445		A tetrahydro-C ₂ -alkylnaphthalene?	Ions at 160/145 (100)/131/117
450		See 445	Ions at 160/145/131 (100)/117
461	849/980	2-Methylnaphthalene	Plus a tetrahydromethylnaphthalene
469	789/943	1-(2-Butenyl)-2,3-dimethylbenzene	This compound, with ions at 160/145 (100), may provide clues to those at scans 445 and 450
480	899/976	1-Methylnaphthalene	
489		An alkane	
495	744/941	1,2,3,4-Tetrahydro-2,6-dimethylnaphthalene	Major ion at 117 does not fit
511		An alkane	Mixture, PAH, 6 components
533		Heptylcyclohexane?	Ions at 182 (4%), 145 (6), 119 (4), 83 (100), 82 (76), 67 (15), 55 (57)
539	775/947	Decylcyclopentane	Does not seem exactly right but should have much in common with the actual component
570		An alkane	Plus 1,1'-biphenyl
586		An alkane	
616		An alkane	

^aBecause of the differences in analysis conditions, the retention times (scan numbers) of specific components in this analysis will not directly match the data in Tables 27 and 35. Comparisons with Table 32 can be made.

^bSee Table 16, footnote a, for discussion of library search results.

^cNote that many peaks still contain more than one component. The one present in the greatest amount is typically listed in the compound column.

Table 29

Molecular Composition of Phenols Identified in the 350-450°F Distillate Cut

Compound	Boiling point (°C; 760 mm)	Comments
Phenol	182	MW = 94, C_6H_6O
Methylphenols		MW = 108, C_7H_8O
2-Hydroxymethylbenzene	191-192	(Also called cresols)
3-Hydroxymethylbenzene	203	{ Not separable on column Presently in use
4-Hydroxymethylbenzene	202	
C_2 -Alkylphenols		MW = 122, $C_8H_{10}O$
Dimethylphenols		
2,3-Dimethylphenol	218	
2,4-Dimethylphenol	211-212	
2,5-Dimethylphenol	242, CRC	212, Aldrich
3,4-Dimethylphenol	225	
2,6-Dimethylphenol	212	
3,5-Dimethylphenol	219	Sublimes
Ethylphenols		
2-Ethylphenol	206	
3-Ethylphenol	214	
4-Ethylphenol	219	
C_3 -Alkylphenols		MW = 136, $C_9H_{12}O$
Trimethylphenols		
2,4,5-Trimethylphenol	234-235	
2,4,6-Trimethylphenol	220-221	
2,3,5-Trimethylphenol	230-231	
		No data for ethylmethylphenols were found
Propylphenols		
2-Isopropylphenol	212-213; 220	Aldrich; CRC ^a
3-Isopropylphenol	228; 234-235	Aldrich; CRC
4-Isopropylphenol	212; 221	Aldrich; CRC
2-Propylphenol	224-226; 220	Aldrich; CRC
3-Propylphenol	232, 228	Aldrich; CRC
4-Propylphenol	230-233	
C_4 -Alkylphenols		MW = 150, $C_{10}H_{14}O$
Tetramethylphenols		
2,3,4,6-Tetramethylphenol	230-252	{ This huge range is probably indicative of an impure standard
2,3,5,6-Tetramethylphenol	249-250	

Table 29 (Continued)

Compound	Boiling point (°C; 760 mm)	Comments
Methylisopropylphenols		
2-Isopropyl-5-methylphenol	233	
2-Methyl-5-isopropylphenol	238	
Diethylphenols		
1,2-Diethylphenol	183.5	
1,3-Diethylphenol	181-182	
1,4-Diethylphenol	182-183	
Butylphenols		
2-sec-Butylphenol	226-228	
2-tert-Butylphenol	224	
4-Isobutylphenol	235-239	
4-sec-Butylphenol	135-136 (25 mm)	(222°C at 760 mm, according to my nomograph)
4-tert-Butylphenol	236-238	

^a Aldrich and CRC (the Chemical Rubber Co. Handbook of Chemistry and Physics) are, respectively, the sources of the data when two values are given. Some other values were the same in both sources. Other components were only found in one source.

Table 30

Compounds Identified in the Phenolic Fraction
of the 350-450°F Distillate Cut, Determined by GC/MS

Compound	Library search ^a	Scan no.	Comments
Phenol and 2,5-cyclohexadiene-1,4-dione		123	No resolution; F = 945 for phenol and F = 907 for spectrum, remainder with the -dione after the phenol spectrum was subtracted. The quantities of the components are similar.
2-Methylphenol and 2-methyl-2,5-cyclohexadiene-1,4-dione		189	No resolution; F = 996 with 2-methylphenol, which is known to elute before the other cresols. F = 777 for spectrum, remainder with the -dione after the phenol spectrum was subtracted. The evidence of the other -dione at scan 123 adds more confidence to this match than the 777 Fit value would alone. The phenol is the major component.
3-Methylbenzonitrile	896/940	198	
A methylbenzenamine and N-phenylformamide		202	No resolution; F = 839 for the formamide. After its subtraction, the match with the amine = (881/967). The amine is apparently the major component.
3- and 4-methylphenols	875/990	213	These cresols are not resolved on this column.
A dimethylphenol	880/980	239	
An ethylphenol + ?	F = 980	282	Ions at m/z = 118 (16%), 120 (17), and 134 (5) for unknown component mapped.
A dimethylphenol	860/990	295	
3-Ethyl-5-methylpyridine	811/948	307	
A dimethylphenol	900/980	325	Naphthalene hidden as minor component at scan 319 (F = 896) 0.5 sec/scan run found naphthalene (936/960).
3-Ethylmethylphenol	773/899	333	Or another isomer or a trimethylphenol.
A dimethylphenol	885/990	350	
A trimethylphenol	780/980	355	Ion at m/z = 136 does not belong. It is 32% relative.
An isopropylphenol	835/975	360	Another similar component elutes at scan 357.
2-Propylphenol	827/994	384	Ions at m/z = 131 and 132 of 8.7 and 5.6% relative respectively, do not belong. A trimethylphenol (815/875) on tail at scan 387 in 0.5 sec/scan run.
An ethylmethyl- or isopropylphenol	760/980	392	Ions at m/z = 131, 132, 133, 134 of 6.0, 5.4, 5.3, and 10.5% relative, respectively, do not belong.
See 392	830/985	396	Same unmatched ions as in 392, although only about one-third as intense. In both cases, the ions were mapped to check authenticity. 3-Methyl-5-propylpyridine (803/832), small component on tail at scan 399, found in 0.5 sec/scan run.
2-Ethyl-5-methylphenol	840/980	405	Trace component on tail may be a C ₄ -alkylphenol.
An ethylmethyl- or isopropylphenol	860/980	410	
A C ₄ -alkylphenol	F = 815	420	Apparently, there are 3 trace methylbenzo(b)thiophene species in this region also, characterized by large ions at m/z = 147 and 148.

Table 30 (Continued)

Compound	Library search ^a	Scan no.	Comments
2-Ethyl-4-methylphenol	799/915	434	Ratios of major ions do not match library spectrum. 0.5 sec/scan run separated a second component, eluting before this compound. Mapping of ions and custom subtraction then produced a match of 933/992 with 2-ethyl-4-methylphenol. However, there is an unmatched ion at $m/z = 150$, about 6% relative, which maps with the scan 434 component. Keying on this ion, a match was found with 4-(1-methylpropyl)phenol ($F = 948$). When this spectrum was subtracted, the remaining spectrum matched 1-ethoxy-2-methylbenzene (705/913). See text.
A trimethylphenol	820/980	438	
A trimethylphenol	880/985	444	A C_4 -alkylphenol may be present just preceding this species.
Unknown		448	$m/z = 150$ (50%); 148 (28); 135 (100); 115 (17); 105 (15); 91 (25); 79 (10). Probably a mixture of C_4 -alkylphenol and a $MW = 148$ aromatic.
2-(1-Methylpropyl)phenol	$F = 940$	455	A methylnaphthalene also present at a similar level ($F = 944$).
4,6-Dihydro-3,4-dimethylpyrazolo[5,1,c]-as-triazine	748/894	462	Despite this match, it is probably just another C_4 -alkylphenol. The sharing of ions at $m/z = 150$ and 135 makes these species confusable.
2-Methyl-5-isopropylphenol	751/959	467	
A C_4 -alkylphenol	815/930	476	
A C_4 -alkylphenol	$F = 815$	484	
ar,ar,α-Trimethylbenzenemethanol	779/905	496	
1,1'-Biphenyl	$F = 873$	562	bp = 256°C
N-(2-Methylphenyl)formamide	786/993	570	bp = 288°C. The retention time is somewhat low for this boiling point.
1,1'-Oxybisbenzene	928/978	595	(Diphenyl ether) bp = 258-259°C

^aSee Table 16, footnote a, for discussion of library search quality of match values.

Table 31

Compounds Identified in the Nitrogen-Base Fraction
of the 350-450°F Distillate Cut, Determined by GC/MS

Scan no.	Library search result ^a	Compound	Comments
128	869/945	Benzenamine	(Aniline). Ion at 107 (6%) also present.
145	945/960	A dimethylpyridine	
151	800/800	A trimethylpyridine	
169	890/905	A trimethylpyridine	Or an ethylmethylpyridine
174	885/910	An ethylmethylpyridine	
193	947/960	A trimethylpyridine	Trimethylpyridines have much smaller M - 15 ions than ethylmethylpyridines
204	940/960	A trimethylpyridine	
210	910/990	A methylaniline	
217	941/983	A methylaniline	
221	910/985	A methylphenol	(A cresol). Plus about 10% ethylpyridine.
228		A C ₃ -alkylaniline?	135 (100%), 134 (50), 91 (5), 77 (13).
235	912/933	3-Ethyl-2,6-dimethylpyridine	Or similar.
251	F = 959	2,3-Dihydro-1H-indole	Plus a C ₄ -alkylpyridine or C ₃ -alkylaniline: 135 (23%), 134 (42).
264	813/819	3-Methyl-5-propylpyridine	Or similar. Also, N-(2-methylphenyl)formamide (801/810).
271	812/819	4-Ethyl-2,6-dimethylpyridine	
281		A methyl-2,3-dihydroindole	133 (54%), 132 (67), 130 (12), 118 (100), 117 (35).
303	864/986	N-Ethylbenzenamine	
315		A trimethylpyridine	Possibly a mixture with an ethylmethylpyridine (838/957).
321		A dimethylaniline	
324		A dimethyl- or ethylaniline	
327		A C ₃ -alkylpyrazine?	122 (76%), 212 (18), 120 (12), 107 (100). Some C ₂ -alkylphenols produce similar spectra. Naphthalene is also present (about 25%).
335		See 327	
351		A C ₃ -alkylpyridine?	Also ions at 146 and 148.
354		See 327	122 (35%), 121 (100), 120 (46), 107 (38), 106 (64) plus a dimethyl-2,3-dihydro-1H-indole: 147 (7%), 146 (8), 182 (12).
358		Unknown. MW = 119?	119 (17%), 118 (36), 117 (100), 116 (6.6), 90 (36), 89 (28), 63 (11), 59 (18).
393	805/970	Quinoline	
399		A C ₄ -alkylpyrazine?	The NBS library does not contain very many pyrazine structures. 136 (16%), 135 (33), 134 (9), 121 (100), 120 (46).
405	863/952	3-Methyl-5-propylpyridine	
414	867/961	N-Ethyl-2-methylaniline	Plus 3-ethyl-5-methylphenol (872/936).
422	745/842	N-Ethyl-2-methylbenzenamine	Or similar.

Table 31 (Continued)

Scan no.	Library search result ^a	Compound	Comments
429	F = 965	1,2,3,4-Tetrahydro-5(or 6)-methylnaphthalene	Plus something producing large ion at 120.
438		Unknown	136 (64%), 121 (65), 108 (31), 107 (100), 106 (12), 91 (9.4), 77 (26). A methylpropylpyrazine? See 414.
461	961/975	2-Methylnaphthalene	
471	931/990	1H-Indole	
481		1-Methylnaphthalene	
510		Unknown	133 (10%), 132 (18), 131 (10), 130 (28), 129 (100), 128 (11), 102 (13), 77 (4), 5 (11). Ions from 129 to 133 mapped and found to be real.

^aSee Table 16, footnote a, for discussion of library search results.

Table 32

Compounds Identified in the Saturate/Aromatic Fraction
of the 450-550°F Distillate Cut, Determined by GC/MS

Scan ^a	Library search result ^b	Compound ^c	Comments
17	952/974	Dichloromethane	
37	934/995	Toluene	Added solvent
120	918/986	Mesitylene	1,3,5-Trimethylbenzene, added internal solvent
325	965/999	Naphthalene	
366	805/987	1,2,3,4-Tetrahydro-2-methylnaphthalene	
427	800/979	1,2,3,4-Tetrahydro-5(or 6)-methylnaphthalene	
460	911/980	2-Methylnaphthalene	
479		1-Methylnaphthalene	
495	760/950	A tetrahydro-2,6(or 2,6)-dimethylnaphthalene	Or similar
509	715/864	Tetrahydro-2-methylnaphthalene	Mixture
546	800/975	Tetrahydro-6-ethylnaphthalene	Mixture?
563	839/978	1,2,2a,3,4,5-Hexahydroacenaphthylene	
570	936/992	1,1'-Biphenyl	
576	F = 890	Tetrahydrotrimethylnaphthalene	
585	841/972	1-Ethylnaphthalene	Or 2-ethyl or certain dimethyl isomers
597	910/975	A dimethylnaphthalene	
603	833/992	1,1'-Oxybisbenzene	(Diphenyl ether)
615		A dimethylnaphthalene	Plus an alkane, similar amounts
618		A dimethylnaphthalene	
637	795/996	A dimethylnaphthalene	Plus something else
655		See scan 637	
662	847/958	2-Isopropylnaphthalene	
689	840/875	1,2-Dihydroacenaphthylene	(Acenaphthene) spectrum does not really match as well as it should
701		An n-propylnaphthalene	Plus a methylbiphenyl
710	850/985	A methylbiphenyl	
720	790/940	An isopropylnaphthalene	
728	904/967	Dibenzofuran	
738		Pentadecane	
750		A C ₃ -alkylnaphthalene	Plus heavier impurities
756	800/960	1-methyl-2-(phenylmethyl)benzene	Or similar, possibly C ₂ -alkylbiphenyl (755/965)
764	F = 910	A n-butylnaphthalene	Plus MW = 188?
769	856/941	2-Methyl-1-propylnaphthalene	

Table 32 (continued)

Scan ^a	Library search result ^b	Compound ^c	Comments
788	F = 841	C ₄ -alkyl-2-indanone	MW = 188, see 764
794	F = 913	A Butylnaphthalene	Mixture
804	794/929	9H-Fluorene	
814		An alkane	
822		An alkane	Plus a C ₄ -alkylnaphthalene and something like 9H-fluorene
831	845/908	2-Butylnaphthalene	
832		sec-Butylnaphthalene	
846		An alkane	Mixture
856		Hexadecane	Hexadecane
912		An alkane	
928		An alkane	
936		An alkane	
970		Heptadecane	
976		An alkane	

^aBecause of differences in analysis conditions, the retention times (scan numbers) of specific components in this analysis will not directly match the data in Tables 27 and 35. Comparisons with Table 28 can be made.

^bSee Table 16, footnote a, for discussion of library search results.

^cNote that many peaks still contain more than one component. The one present in the greatest amount is typically listed in the compound column. Small peaks containing multiple components were ignored in many cases for this listing.

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Table 33

Identification and Quantitation of Compounds
 Found in the Phenol Fraction of the
 450-550°F Distillate Cut, Determined by GC/MS

Peak no.	Compound	Quantity (% of no. 25)
1	(a) Methylethylphenol	
	(b) Tetrahydroquinoline (?) $C_9H_{11}N$	
	(c) Quinoline	231.40
2	Methylethylphenol	23.02
3	(a) Isoquinoline, 108	
	(b) p-N-Propylphenol	470.37
4	Trimethylphenol	
5	Methyl-n-propyl or n-butylphenol	
6	Methylethylphenol	44.59
7	Indole	49.24
8	5,6,7,8-Tetrahydro-1-naphthalenamine (?), C_4 -Phenol	
9	Methylquinoline, sec-butylphenol	
10	Indanol, C_4 -phenol, isoindole (?)	210.37
11	sec-Butylphenol	7.36
12	Methylquinoline, sec-butylphenol	69.11
13	sec-Butylphenol	
14	Indanol	194.91
15	Methylquinoline, 122	315.72
16	Methylquinoline	59.30
17	Methylindanol, C_4 -phenol, 108	182.63
18	Methylquinolines	30.25
19	Methylindole	123.68
20	Methylindanol	113.02
21	Phenyl ether	67.34
22	C_5 -Phenol	
23	Methylindanol	95.56
24	Dimethylquinoline	89.70
25	Methylindanol	100.00
26	C_5 -Phenol	86.77
27	Methylindanol	109.30
28	2,2-Indanol, C_5 -phenol, 122	97.36
29	Dimethylindole	76.04
30	C_2 -Indanol	64.88
31	C_5 -Phenol, 108	
32	C_2 -Indanol	
33	Dimethylquinoline	
34	C_2 -Indanol	
35	C_5 -Phenol, dimethylindole	52.21
36	C_2 -Indanol	
37	Phenylphenol	98.88
38	C_2 -Indanols	129.09
39	$C_{11}H_{16}N_2$	68.55

Table 34

Compounds Identified in the Nitrogen-Base Fraction
of the 450-550°F Distillate Cut, Determined by GC/MS

Scan no.	Library search result ^a	Compound ^{b,c}	Comments
146	922/923	A dimethylpyridine	
193	940/950	A trimethylpyridine	
203	915/933	A trimethylpyridine	
210	885/990	A methylaniline	(Methylbenzenamine). Not N-substituted.
216	970/985	A methylaniline	
221	900/940	A trimethylpyridine	This is the first component which seems to differ from the 350-450°F nitrogen-base samples in their region of overlap. See Table 31.
227	861/870	4-Ethyl-2,6-dimethylpyridine	
234	903/912	3-Ethyl-2,6-dimethylpyridine	
250	F = 965	2,3-Dihydro-1H-indole	Plus a C ₄ -alkylpyridine or C ₃ -alkylaniline: 135 (12%), 135 (25). Note this is about half the level of impurity seen in Table 31.
281		A methyl-2,3-dihydro-1H-indole	133 (55%), 132 (71), 130 (17), 118 (100), 117 (35). Note the high reproducibility between this background subtracted spectrum and the one in Table 31.
285		A C ₄ -alkylpyridine?	
297		A C ₄ -alkylpyridine or a C ₃ -alkylaniline	Mixture. Ions at 135, 134, 120, 119, 118, and 107 (100%). Plus something with higher MW.
303	F = 958	3-Ethyl-4-methylpyridine	Or similar plus MW = 135 component.
313		An ethylmethylpyridine and a trimethylpyridine	Large ions at both M - 1 and M - 15 indicate a probable mixture. Perhaps there is a single isomer of one or the other which produces a mixed appearance spectrum.
321		See 313	121 (100%), 120 (75), 105 (57).
323		A dimethylaniline	Or see 313. Plus MW = 148 or 149.
326	F = 922	1,2,3,4-Tetrahydroquinoline	A methyl-2,3-dihydro-1H-indole cannot be excluded. Naphthalene is also present (about 25%). Ion at 121 (65%) does not fit any of these spectra.
338		C ₃ -alkylpyrazine?	
353		A C ₃ -alkylpyrazine?	Plus a C ₂ -alkyl-2,3-dihydro-1H-indole.
358		Unknown. MW = 119	Not 2,3-dihydro-1H-indole, nor is a vinylaniline or propenylpyridine likely. A dihydro-1H-indole other than the 2,3 isomer also does not look like it would match the spectrum very well. Scan 358, Table 31, shows the predominant ions.
379	900/997	5,6,7,8-Tetrahydroquinoline	The spectrum is distinct from the one for the 1,2,3,4-tetrahydro isomer.
396	942/999	Quinoline	Boiling point = 238°C.
406	868/980	3-Methyl-5-propylpyridine	
420	957/1000	Isoquinoline	Boiling point = 242°C.
437	F = 864	4-Ethyl-2,6-dimethylpyridine	Plus 2-methyl-1H-indole plus something else, possibly ions at 106 (60%), 107 (40%).

Table 34 (Continued)

Scan no.	Library search result ^a	Compound ^{b,c}	Comments
448	F = 919	An ethylmethylphenol	Plus a C ₂ -alkyl-2,3-dihydro-1H-indole?
463	F = 973	2-Methylnaphthalene	Plus a C ₂ -alkyl-2,3-dihydro-1H-indole or a 1,2,3,4-tetrahydromethylquinoline (F = 900)
477	920/988	1H-Indole	
488	895/996	3-Methylquinoline	
494	905/994	5-Methylquinoline	
512	771/936	1,2,3,4-Tetrahydroquinoline	This match is not as strong as it should be and few hydro-PAH compounds come out after the "parent" PAH. There is a lot of similarity to the species at scan 510, Table 31; however, the ion ratios are very different: 133 (97%), 132 (100), 131 (14), 130 (26), 129 (49), 128 (10), 118 (20), 117 (25), 103 (11), 102 (13), 91 (11), 77 (21), 66 (12), 65 (23), 51 (21). This may indicate a mixture or be a consequence of the ion statistics for the trace level in the 350-450°F nitrogen-base sample.
524	836/994	1-Methylisoquinoline	Plus a C ₃ -alkylaniline or other MW = 135 compound.
529		A methylpropylphenol	
534		A C ₃ -alkyl-2,3-dihydroindole?	MW = 161? Mixture (C ₄ -alkylphenol, too?).
540	F = 973	6-Methylquinoline	Spectrum closely matches that for 5- and 8-methyl isomers. See scan 494 plus 2,3-dihydro-1H-inden-1-ol (F = 984).
547	922/992	3-Methylquinoline	Possibly the isoquinoline or a different positional isomer
556		A sec-butylphenol?	Plus MW = 160
564		A methyl-1H-indole	Or a methylindolizine plus a C ₁ -alkylquinoline.
573	F = 986	1,1'-Biphenyl	Plus a methylquinoline or isoquinoline (or a methylindolizine?) plus a dimethylquinoline, etc.
588	835/984	2-Ethyl-naphthalene	Or a 1-ethylnaphthalene
593	868/968	2-Methyl-1H-indole	
599	F = 962	5-Methyl-1H-indole	A methylindolizine is also possible (F = 982) plus a methyl-2,3-dihydro-1H-indole plus higher molecular weight components.
606	896/996	Diphenyl ether	(1,1'-oxybisbenzene).
619	828/955	A dimethylnaphthalene	Plus something else, base ion at 135.
630	800/970	A dimethylquinoline	
642		A dimethylquinoline	Mixture. Probably at least 3 components. One other is probably an n-butyl-naphthalene.
652		Unknown	Mixture possible.
657	818/973	2,4-Dimethylquinoline	Other isomers possible.
670	783/916	Pentamethylbenzene	Plus a dimethyl-2,3-dihydro-1H-indole.
678	F = 925	2,5-Dimethyl-1H-indole	Other isomers possible. Mixture. One other likely component is a dimethyl-2,3-dihydro-1H-indole. Heavier species are also apparently present.
684		See 678	It may be possible that the C ₂ -alkyl-2,3-dihydro-1H-indole loses hydrogen to produce a spectrum similar to a C ₂ -alkyl-1H-indole. In such a case, the apparent mixture does not exist. The NBS library has only one C ₂ -alkyl-2,3-dihydro-1H-indole and no other dihydro-1H-indoles.

Table 34 (Continued)

Scan no.	Library search result ^a	Compound ^{b,c}	Comments
693	850/990	1,2-Dihydroacenaphthylene	Plus an ethylmethyldihydronaphthalene?
704		C ₃ -Alkylquinoline (or iso-)	Plus MW = 168?
711	F = 930	A dimethyl-1H-indole	Plus some C ₂ -alkylquinoline or isoquinoline.
724	885/964	An isopropyl-naphthalene	
732	852/993	Dibenzofuran	
741		A C ₃ -alkylquinoline?	Very large M, M - 1, M - 2, large amount of fragmentation. Alkane also apparently present.
750		A C ₃ -alkylquinoline	
775		Mixture	One of the minor components appears to be a trimethylnaphthalene.
791		Unknown	Trace. Could be mixture. Ions at 188, 170, 159, 158, 155, 145, 144, 131.
808	880/946	9H-Fluorene	
821	750/924	4-Methyl-1,1'-biphenyl	Plus an ethylmethyl-1H-indole.
834	772/875	A n-butyl-naphthalene	
859		N-Hexadecane	
868	F = 891	4-Methyldibenzofuran	Plus N-phenylbenzenamine (F = 910).
914		An alkane	
931		An alkane	
972		N-Heptadecane	
978		An alkane	
1020	885/912	Phenanthrene	Other good matches include anthracene and 1,1'-(1,2-ethynediyl)bisbenzene (877/904) and 2,3-diphenyl-2-cyclopropen-1-one (863/889).
1286		Fluoranthene	The trace level of these components is cause to suspect that their presence at all is an artifact. See text.
1333	905/906	Pyrene	
1373		An alkane	

^aSee Table 16, footnote a, for discussion of library search results.

^bAlthough many peaks appear to be composed of multiple components, overall the situation is less complex than in the saturate/polynuclear aromatic hydrocarbon fractions.

^cIn many cases, isoquinolines have the same mass spectral pattern as quinolines. At times, this choice was explicitly given. At other times, a specific compound seems to be a surer choice and it was noted, instead. In general, the NBS library does not contain very many nitrogen heterocyclic compounds with two or more rings. Typically, various isomers would have to be investigated individually to examine retention times and mass spectral patterns to assign specific components to more peaks.

^dThe NBS library contains few pyrazine-type spectra.

Table 35

Compounds Identified in the Saturate/Aromatic Fraction
of the 550-650°F Distillate Cut, Determined by GC/MS

Scan ^a	Library search result ^b	Compound ^c	Comments
629	844/991	Dibenzofuran	
710	F = 974	9H-Fluorene	Plus 9H-fluoren-9-one at scan 707 (839/983)
720	F = 888	1-(2-Propenyl)naphthalene	Or a methylbiphenyl plus a methylfluorene
729	F = 864	A methylbiphenyl	Plus a possible hydroxymethyldihydrofluorene
736	F = 850	2-Butylnaphthalene	A mixture of 3-4 components, one other possibly a methylfluorene
754	F = 953	4-Methyldibenzofuran	Plus a sec-butylnaphthalene
762			Ions at 178, minor and 167, major
769	842/963	A methyldibenzofuran	Or 9H-xanthene? Plus MW = 196
777	906/954	A methyldibenzofuran	
782		A methylisopropyl- or tert-butylnaphthalene	A mixture of at least 3 components Ions at 182, 178, 167, and 165
786	714/874	A dimethyl-biphenyl	
793	810/988	2-Ethyl-1,1'-biphenyl	Plus a 1-methylbutyl or methylbutylnaphthalene, MW = 198, loss of C ₃ H ₇ produced the base ion Plus another component
798		3-Pentylnaphthylene	
806	F = 948	1,2-Dimethyl-4-phenylmethylbenzene	
815			Mixture of 3 components, molecular weights of 208, 196, and 194
828	932/985	9,10-Dihydrophenanthrene	Ratio of M:M - 1:M - 2 is not as close as it should be, perhaps a different dihydrophenanthrene is actually present
836	835/993	A methyl-9H-fluorene	At least two other components present, one apparently MW = 208
845		Perhaps a fluorenol, but could be a methyldihydro-9H-fluorene	Major component MW = 182, also, a component with MW = 198, some hydro-PAH species elute after the present PAH
856		Perhaps a fluorenol, see 845	Plus a methylbutylnaphthalene
864	F = 943	A dimethylbiphenyl	Plus higher molecular weight species
873		Heptadecane	Plus a dimethylbiphenyl
879			Perhaps 2-hydroxy species of MW = 196 and 198
891			3 components, MW = 182, 184, and 196
897			2-3 components present, MW = 208, contains butyl group, MW = 196 and MW = 182
929	914/993	Phenanthrene	
932		Antracene	
939		Alkane	Plus MW = 192, possibly a methylphenanthrene
947			Mixture = alkane plus MW = 196, PAH
954		Unknown	MW = 210 (other major ions at 196, 195, 181, base ion)
961		See 954	
965	F = 884	2,3-Dimethyl-9H-fluorene	Plus another component, MW = 208
973		Unknown	MW = 210 (other major ions at 195, 194, 179, base ion), see 954
979		Octadecane	Plus MW = 210 PAH, see 954
988		Alkane	Plus at least two PAH species, ions at 210, 193, and 181
1002	F = 941	1,2,3-Trimethyl-4-propenyl-(E)-naphthalene	MW = 210, base ion at 195, other ions at 179 and 165, see 973
1009	F = 823	2-Phenylnaphthalene	Plus MW = 210 and, possibly, 196

Table 35 (Continued)

Scan ^a	Library search result ^b	Compound ^c	Comments
1014	F = 912	A methyl dibenzothiophene	Plus MW = 210
1023		Unknown	2-Methoxy-9H-fluorene may be one of the components
1035	891/975	A methylphenanthrene	
1040	882/977	A methylphenanthrene	
1051	F = 828	4-H-Cyclopenta[def]phenanthrene	Or MW = 204, also MW = 210 and 230 components
1057	793/952	A methylphenanthrene	Plus MW = 224 trace, ion at 204
1062	F = 879	A methylphenanthrene	Plus MW = 224 trace, ions at 210 and 204
1080	860/979	Nonadecane	Molecular ions for the longer alkanes are 1% relative abundance in current work, although in some earlier work they were about 10%. MS cleanliness and tuning may affect this, although calibration tuning has been kept fairly constant.
1082- 1160			There is one trace alkane about every 8 scans (12 sec), trace PAHs can also be found by ion mapping, ions at 208/180, 224/209/195
1113	845/961	A phenyl naphthalene	
1118	F = 879	2-(Phenylmethyl)naphthalene	Another trace one at 1128
1134	733/927	1-Heptadecanol	Large ions at 82/83
1139		Alkane	Plus 4-phenylbicyclohexyl (F = 967) and 236 and 206 species
1176		Eicosane	Because of weak molecular ions and the similarity of the spectra of all higher molecular weight alkanes, the correct one is often not found from the MS library. GC retention times provide evidence for correct assignment of the alkane once the spectrum is confirmed in the general classification.
1268	872/967	Heneicosane	

^aBecause of the differences in analysis conditions, the retention times (scan numbers) of specific components in this analysis will not directly match the data for the other samples in this report.

^bSee Table 16, footnote a, for discussion of library search results.

^cNote that many peaks still contain more than one component. The one present in the greatest amount is typically listed in the compound column.

Figure 1
Weight Percent Yields of Distillation Fractions (°F)

Figure 2
Elemental Distribution
Coal Liquid vs. Petroleum Distillates

Figure 3
Solvent F Elemental Distribution
Distillation Fractions

Figure 4
Fractions Determined by
GC Simulated Distillation

Figure 5
Functional Group Separation Distillation Fractions

Figure 6
GC Chromatogram of Solvent F

Figure 7
GC-MS Total Ion Chromatogram of Total Distillate (350-850°F)

Figure 8
GC Chromatogram of Saturates

Figure 9
GC Chromatogram of Aromatics

Figure 10
GC-MS Total Ion Chromatogram of Polynuclear Aromatic Hydrocarbons

Figure 11
GC Chromatogram of Aromatics Greater than 0.5%

Figure 12
Total Ion Chromatogram of Phenolics

Figure 13
Total Ion Chromatogram of Nitrogen Bases

Figure 14
GC Chromatogram of Phenols

Figure 15
GC Chromatogram of Nitrogen Bases

Figure 16
Functional Group Distribution

Figure 18
Naphtha
Light Ends Composition
IBP – 350°F

Figure 19
GC/MS Total Ion Chromatogram of Neutral Hydrocarbon
Fraction of 350–450°F Distillate of Solvent F

Figure 20
GC/MS Total Ion Chromatogram of Phenolic
Fraction of 350–450°F Distillate of Solvent F

Figure 21
GC/MS Total Ion Chromatogram of Nitrogen-Base
Fraction of 350–450°F Distillate of Solvent F

Figure 22
GC/MS Total Ion Chromatogram of Saturate/Aromatic
Fraction of 450–550°F Distillate of Solvent F

Figure 23
GC/MS Total Ion Chromatogram of Phenolic Fraction
of 450–550°F Distillate of Solvent F

Figure 25
GC/MS Total Ion Chromatogram of Saturate/Aromatic
Fraction of 550-650°F Distillate of Solvent F

Figure 26
 ^1H and ^{13}C NMR Spectra of IBP-450°F Distillate of Solvent F

Figure 27
 ^1H and ^{13}C NMR Spectra of 450-550°F Distillate of Solvent F

Figure 28
 ^1H and ^{13}C NMR Spectra of 550-650°F Distillate of Solvent F

Figure 29

^1H and ^{13}C NMR Spectra of 650° F- End Point Distillate of Solvent F

Figure 30
 ^1H and ^{13}C NMR Spectra of Recombined Distillate
of Solvent F, IBP-End Point

Figure 32
Ring Distribution Distillation Fractions

Figure 33
Estimated Product Slate Parent Aromatics
(Million Pounds/Year)

COAL PROCESS DEVELOPMENT UNIT (CPDU)

DATA ANALYSIS

S. V. Joshi*

Scale-up and design of the SRC-I Demonstration Plant are dependent on data generated from runs at the Wilsonville SRC-I Pilot Plant in Alabama and from runs through the coal process development unit (CPDU) at APCI. However, data from various sources are useful only if they can be correlated and shown to be reproducible.

Some of the most important data are the yields of various fractions of total liquid products. Much of the available CPDU data has been analyzed, and some preliminary comparisons were made with Wilsonville data. The results of the investigation are presented in this report, which is divided into five main sections.

- In the first section on error analysis, the precision of APCI's analytical work-up techniques and CPDU sampling procedures is investigated to establish the quality of the data. CPDU data reproducibility is also discussed.
- The second section addresses the limitations of APCI's mathematical model, developed in 1979 from a parametric study in the CPDU and used to predict pilot plant performance. CPDU data on Kentucky #9/14 coal were reexamined, and the model's predictions are compared with actual CPDU yields.
- The third section compares CPDU product yields obtained by three work-up methods. Determining the effects the methods have is important for data correlation.
- The fourth section compares data from seven CPDU runs of coal and solvents without additives, to obtain information on the effects of reaction temperature and solvent on the yields. By first establishing base-line data on coal and solvents alone, the effects of other factors can then be examined more effectively.
- The final section compares Wilsonville and CPDU yields. The quality of the data is examined, differences between the two operations are quantified, pilot plant data are compared with APCI's kinetic model predictions, and the CPDU and pilot plant yields of Kentucky #9 coals from two different mines are compared.

The findings are encouraging and useful for application to further coal liquefaction research. Conclusions can be summarized as follows:

- Solvent separation and distillation seem to be equally precise methods, and CPDU sampling errors are relatively trivial. Criteria for identifying inconsistent analyses and to compute least significant differences between yields* of two product streams can be quantified. Ash balances of $100 \pm 10\%$ do not have to be forced when calculating MAF yields. Finally, CPDU data seem to be reproducible, but more data are needed.

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- Laboratory data correlated reasonably well with APCI's kinetic model, but more data are needed to improve it.
- Yields of oils or distillates, benzene solubles, asphaltenes, preasphaltenes, and pyridine-insoluble residues differ considerably depending on the analytical method used. Solvent separation and/or distillation (with and without a heated column) have been tested. Data correlation requires a more detailed examination of these methods.
- Data from various CPDU runs can be correlated. During direct liquefaction of Kentucky #9 coal, moisture- and ash-free (MAF) conversion is about 90% and is independent of solvent composition and reaction temperature, but hydrocarbon gas, heteroatom gas, preasphaltene, and oil/distillate yields are affected by increasing temperature. Wilsonville recycle solvent appears to be more effective than other solvents in conversion to benzene-soluble oils and asphaltenes, but total hydrogen consumption seems to be independent of process solvent.
- Comparison of Wilsonville and CPDU data indicates that any discrepancies may be related to inconsistent analytical methods and to differences between the performance of the continuous process equipment downstream of the dissolver and its simulation in the laboratory at Wilsonville.

ERROR ANALYSIS OF CPDU DATA: SAMPLING AND ANALYSIS OF LIQUID PRODUCT

Research on direct liquefaction of coal invariably involves characterizing the products coming from a process unit. A variety of characterization methods, differing in both principle and technique, have been suggested and discussed in the literature. The choice of a method depends upon a number of criteria; precision is one of the most important, particularly for data analysis. At APCI, the condensed product collected from the CPDU has been characterized by distillation, by solvent separation, or by a combination of the two (details can be found in Schweighardt, 1981). The discussion presented here deals with the precision of these analytical methods. Also, errors associated with sampling the liquid from the main receiver in the CPDU are discussed.

Demonstrating the reproducibility of any experimental technique is vital for subsequent analysis of the collected data. A significant portion of the present discussion is also directed toward this problem, for which sampling and characterizing the liquid product are as relevant as operating the CPDU.

Precision of Analytical Methods

The solvent separation method used at APCI separates the total liquid product sample into oils, asphaltenes, preasphaltenes, and residue. On the other hand, the distillation method separates the sample into distillate, SRC (pyridine-soluble nondistillate material), and residue. The SRC fraction can be further solvent-separated into oils, asphaltenes, and preasphaltenes. All the fractions are operationally defined; therefore, the details of the techniques are of paramount significance. The following discussion deals with the precision with which any of the above fractions can be determined, given a total product liquid sample.

Ideally, to compute the errors associated with laboratory analysis, data should be available on total liquid samples that were analyzed several times by one method. Usually,

though, samples have been analyzed only once because of the cost of work-up. There are, however, several samples that were analyzed two or more times, generating data that are amenable to pooled-variance statistical analysis. Previous efforts at statistical analysis (Kingsley and Schweighardt, 1980a,b; Skinner et al., 1981; Skinner and Givens, 1981b) were hampered by either the relatively small number of degrees of freedom or the non-homogeneity of the data analyzed.

Solvent Separation. Solvent-separation data on oil, asphaltene, preasphaltene, SRC (asphaltenes plus preasphaltenes), and residue fractions were compiled (Tables 1-5, respectively). The estimated combined variance due to solvent separation of one CPDU sample was computed by first applying the F-test at a 95% confidence level to each data set, to check the homogeneity of the sum of square errors (SSE). Statistically nonhomogeneous samples were identified (these are asterisked in the tables). Then the SSEs for all the homogeneous data were pooled and divided by the pooled degrees of freedom.

Distillation. Data determined by the distillation method are presented in Tables 6-8 for distillate, SRC, and residue fractions, respectively. The same statistical analysis performed on the solvent-separation data was applied. The results are presented in the tables after each data set. Notice that the estimated variances are based on only 2 degrees of freedom each; therefore, the significance of these estimates is severely reduced.

Errors Associated with Sampling the Liquid Product Stream through the Main Receiver in the CPDU

The liquid product stream generated in the CPDU is sampled from the main receiver, and the samples are then characterized in the laboratory. The combined error associated with both steps can be determined by analyzing data on different total liquid samples collected from the same product stream. The relative importance of the error associated with sampling can then be judged by comparing the combined error with the precision of the analytical method used.

The best way to compute the error is to sample one product stream several times and then to characterize the samples by one analytical method. Such data were unavailable, so data on several product streams were evaluated. Each stream had been sampled two or more times, and each sample had been characterized by the same analytical technique. The data in Tables 9-13 are from solvent-separation analyses, and those in Tables 14-16 are from distillation work-up (nonhomogeneous samples are asterisked). All samples were collected from the main receiver 4-6 hr apart, after the CPDU was lined out.

The estimated combined variances due to CPDU product sampling and laboratory characterization were computed by (1) identifying statistically nonhomogeneous data using the *F*-test, (2) pooling the SSEs for the homogeneous data, and (3) dividing the SSEs by the pooled degrees of freedom. Table 17 compares the estimates of the combined variances with the estimated variances for laboratory analysis alone (for both solvent separation and distillation). The degrees of freedom on which each estimate is based are in parentheses.

Discussion

Variance due to the analytical method alone and the combined variance due to sampling of the main receiver and to the analytical method are statistically identical at a 95% con-

fidence level for all fractions. It follows that the variance can be better estimated by pooling the two results. The square root of the estimated variance (or the standard deviation) and the associated degrees of freedom for each fraction characterized by either solvent separation or distillation (Table 18) were computed. Notice that the values reported in Table 18 are based on *total* product liquid analysis. Standard deviations associated with moisture- and ash-free (MAF) yields of various fractions are 3 to 4 times the values listed in Table 18, depending upon the coal concentration in the slurry and the ash and moisture content of the coal.

The data in Table 18 can be used to identify inconsistent samples or analyses. Statistically, if a sample is analyzed twice or if the same product stream is sampled and analyzed twice, the maximum permissible differences between the two total product liquid analyses (solvent separation and distillation) can be calculated by the *F*-test. Results are presented in Table 19. It should be emphasized that the distillation results are slightly inflated because of the small data base.

The standard deviations listed in Table 18 and the Student's *t*-test were used to determine the least significant difference between the analysis of two product streams at a 95% confidence level (Table 20). The least significant difference is reduced by about 30% if the two product streams in question are analyzed twice rather than only once. Again, it should be mentioned that the values in Table 20 are for analysis of the total product liquid; corresponding values for MAF yields are about 3 to 4 times higher depending upon the coal concentration in the slurry and the ash and moisture contents of the coal.

Ideally, overall balances and all elemental balances should match, and calculation of various fraction yields should not involve any corrections to the raw data. The ash balance is a convenient way to measure the overall reliability of the raw data; it is important to set realistic limits on the ash balance so that any misleading data which do not fall within the limits may be screened out. In general, corrections for an error of 10% in ash balance result in corrections of about 2, 0.5, 0.5, and 0.8% in the MAF yields of oils/distillates, asphaltenes, preasphaltenes, and residues, respectively (Skinner and Givens, 1981b). Based on the results presented here, these errors seem acceptable compared to errors introduced in the MAF yields due to sampling and laboratory characterization. As there is no ideal method for forcing the ash balance, it seems reasonable to accept a 10-15% error in ash balances and to reject the samples where the ash balance is not within 10-15%. In such cases, the yield calculations need not be based on forced ash balance and the question of how to force the ash balance becomes redundant.

CPDU Data Reproducibility

Data analyses and correlations are severely hampered if the experimental technique is not reproducible. Because of the complex nature of the raw materials, the demonstration of reproducibility in coal liquefaction research requires control over various aspects that have an effect on CPDU operation:

- **Coal Variability:** Not only does coal from different mines vary, but coal from the same mine differs depending upon the exact place and time of mining. Also, the coal from two drums differs and, within a drum, coal properties may vary, even though all of the coal may be the same type. Control over this variability can be achieved only through mixing of large batches of coal.

- **Solvent Variability:** Solvent properties depend on the raw materials used and the conditions under which the solvent is produced. Because most solvents are coal-derived and processing conditions vary over a wide range, almost no two solvents are exactly alike. Control can be achieved only by mixing together large batches of solvent.
- **Product Characterization Method:** As mentioned earlier in this section, coal liquid product characterization is largely operational. There are a number of methods, all of which yield different results. The precision of each method also differs. Results can be quantitatively compared only if data are derived from a single method of product characterization and the precision of the method is known.
- **CPDU Modifications:** Modifying process equipment is an ongoing process, and the effects of equipment modifications on liquid product characteristics are largely unknown.
- **Control over Operating Variables:** Control over operating variables is, in principle, easy to achieve. However, the number of variables is large, including slurry concentration, slurry flow rate, gas feed rate, stirrer speed, and total pressures and temperatures in all the process equipment, including the reactor. Some variables, such as hydrogen partial pressure, are affected not only by operating variables, which can be directly controlled, but also by feed solvent and coal characteristics.

On the basis of these variables, CPDU data reproducibility was examined by comparing sets of data for samples from different runs (cases I-V).

Case I (Table 21). Each data set in case I (columns two and three in Table 21) is the average of two analyses of the liquid product stream. Space velocities and hydrogen flow rates in run HCL-32 differ slightly from those in run HCL-33. Kentucky #13 coal was used, but elemental analyses of the coal differed slightly for each run. For example, carbon and hydrogen contents of the run HCL-33 coal were respectively 1.9 and 0.4 wt % absolute higher than those for the run HCL-32 coal, and HCL-33 ash content was 2.5 wt % absolute lower. Total product liquids were analyzed by solvent separation in both runs, and the ash balances are both acceptable. Kentucky #13 was the last coal used in run HCL-32, and some solids accumulation was observed in the continuous stirred tank reactor at the end of the run.

Oil, asphaltene, and preasphaltene MAF yields for both runs agree statistically within the limits based on the precision of solvent separation.

Case II (Table 22). Hydrotreated creosote oil solvents used in runs BCL-22 and -24 differed somewhat, but the ash balances are fairly similar. The differences in MAF yields are statistically insignificant at a 95% confidence level.

Cases III and IV (Tables 23 and 24). The solvents used in runs XCL-10 and XCL-11 differed, but the differences in yields produced under otherwise identical conditions are statistically insignificant.

Case V (Table 25). The feed materials and processing conditions were fairly similar for both samples. The difference between the two MAF yield structures is statistically insignificant.

Replicability. On the basis of the evidence available, the CPDU data appear to be reproducible from run to run. However, feed coal and solvents must be better quality-controlled and multiple analyses must be performed before reproducibility can be estimated definitively.

Conclusions

- Precision associated with the two methods of liquid product characterization, solvent separation and distillation, was quantified. Solvent separation and distillation seem to be equally precise methods.
- Errors associated with liquid product sampling through the main receiver in the CPDU were shown to be relatively unimportant.
- Criteria for identifying nonhomogeneous samples were quantified.
- Least significant differences between the characterizations of two total liquid product streams were computed statistically.
- Calculation of the MAF yields need not involve forced ash balance if the ash balance is $100 \pm 10\%$.
- The CPDU data seem to be reproducible from run to run, but more data are needed to answer the question definitively.

ANALYSIS OF KINETIC MODEL PREDICTIONS

In 1979, APCI completed a study in the CPDU on the effects of parameters such as reaction temperature, pressure, superficial slurry liquid hourly space velocity (LHSV), and nominal residence time on coal liquefaction performance (Skinner, 1979). In the study temperatures ranged from 780 to 885°F, and the nominal slurry residence time ranged from 12 to 60 min. Kentucky #9/14 coal was used in a synthetic solvent (a 75:25 mixture of hydrotreated creosote oil and creosote oil); some data were obtained with only creosote oil or only hydrotreated creosote oil. Feed coal concentration varied between 39 and 42 wt %, and the hydrogen feed rate varied between 250 and 1,000 standard liters per hour (slph); pressure was usually a constant 2,000 pounds per square inch gage (psig). Products were analyzed by a combination of filtration and distillation (distillation II).

The data were used to estimate kinetic rate constants in a sequential model (Figure 1), and the model was subsequently used to predict Wilsonville Pilot Plant performance. Martin (1979) discovered that lower severity operation (higher SRC yield, lower process solvent yield) was predicted than was observed at Wilsonville.

The preceding section discusses the magnitude of experimental errors in the CPDU, and later sections show how observed yields may depend on the method of total product liquid analysis. Consequently, it is important to reexamine the data on Kentucky #9/14 coal and to determine the model's limitations by comparing observed and predicted results.

Comparison of Model Predictions with Laboratory Data

Comparison is limited to MAF yields of product liquid fractions, i.e., total distillate, asphaltenes, and preasphaltenes. Data from CPDU runs 10-16 were analyzed; the ash balance error for these runs is within $\pm 10\%$. Data at 885°F were disregarded because this temperature is outside the range to be used commercially. Also, at such high temperatures the CPDU is difficult to control and operate because retrograde reactions result in coking.

Figures 2 and 3 show the observed vs. predicted preasphaltene and distillate yields, respectively. Rate constants were calculated using most of the data in these figures and

some data with unsatisfactory ash balances. The figures clearly show that the kinetic model correlates the yields of liquid fractions fairly well, considering that the observed yields have a standard deviation of 4-5 wt % MAF coal. The kinetic model also predicted reasonably accurately the effect of nominal residence time on preasphaltene yield at 850°F (Figure 4). (Note that only a fraction of the data shown in Figure 4 were used to calculate rate constants; thus, correlation of the remaining data is a check on the predictions.)

Model Limitations

The mathematical model in Figure 1 is probably the simplest, but it is far from unique. A number of models have been published; many, if not all, of the proposed models would be able to predict the data equally well.

It is generally accepted that SRC-I coal liquefaction involves hydrogenation, hydrocracking, and hydrogenolysis reactions. Most of the reactions are thermal, although the mineral in coal may be catalytic. The reaction rate constants may depend on the partial pressure of hydrogen.

It is also generally accepted that the upgrading of coal products (preasphaltenes to asphaltenes to distillates) involves processes that eliminate functional groups and decrease molecular weights. Eliminating functional groups is faster than cracking the carbon skeleton; thus, the reactivity of any liquid fraction may be a decreasing function of nominal residence time.

Therefore, to improve the fit between the kinetic model and experimental data, both hydrogen partial pressure and residence time were examined. A Natural Gas Processor's Association (NGPA) program was used to calculate hydrogen partial pressure, but the predictions of the program are accurate only to $\pm 30\%$. Also, experimental variation in the partial pressure of hydrogen was small. The analysis showed that rate constants do indeed increase with increasing partial pressure and decrease with increasing residence time. Variation was statistically significant, but numerical agreement between the modified (complex) model and the data did not improve substantially over the agreement shown in Figures 2-4.

Other unanswered issues regarding the kinetic model include whether or not reverse/retrograde reactions are important, whether or not reactive pathways such as coal $\rightarrow$ asphaltenes, coal $\rightarrow$ oil, and preasphaltenes $\rightarrow$ oil are important, and whether or not the role of the process solvent should be modeled as a chemical reaction with coal or coal-derived species. Models addressing these problems are available in the literature, but data correlation may not be any better than that shown in Figures 2-4.

Conclusions

Laboratory data have been shown to correlate reasonably well with the developed kinetic model. The limitations of the model are many, and any improvements in the existing model are conceivable only if more data become available. Nonetheless, the model can be used to estimate the effects of various parameters on SRC-I process performance.

TOTAL PRODUCT LIQUID ANALYSIS: COMPARISON OF YIELDS OBTAINED BY DIFFERENT METHODS

As mentioned previously, APCI uses a variety of methods to characterize condensed products collected from the CPDU, including filtration and distillation (distillation II), solvent

separation, and a combination of distillation and solvent separation (distillation I) (Schweighardt, 1981). Usually, product samples are analyzed by only one method because of the cost of work-up. However, the ability to correlate results from different methods is essential in comparing data from various sources or even from various CPDU runs.

This section attempts to correlate results from solvent separation and distillation I. Distillation I results depend on whether or not the distillation column is heated. There are no available APCI data on distillation II that can be used for direct comparison, but published results were used to correlate this method with the other two.

Comparison of Distillation I Distillate Yield with Solvent-Separation Oil Yield

Both Distillation Pot and Column Heated (Forced Flash). Table 26 shows the relevant data derived using both methods (see also Figure 5). Two or more sample numbers indicate that two or more samples were collected from the CPDU under identical conditions but a few hours apart. Many yields are averages of two or three individual determinations. Losses observed during characterization are added to the oil yield (solvent separation) or to the distillate yield (distillation I). Ash balances were satisfactory for each method, so the data were uncorrected.

The data in Figure 5 indicate that the distillate yield approximately equals the yield of solvent-separated oils, although, on the average, the oil yield tends to be slightly greater than the distillate yield. The mean difference between the two is 0.9 wt % absolute, which is statistically significant at a 99% confidence level if estimates of variance for the two determinations are used (see previous section on error analysis).

Solvents used in coal-liquefaction runs are usually all oils or all distillates. Therefore, the 0.9 wt % absolute difference translates into a difference of about 3-4% absolute between MAF yields of oils and distillates, with the former being higher.

Distillation Pot Heated, Column Not Heated. Table 27 compares the yield of distillates by distillation I when the column is not heated with the yield of solvent-separated oils. The distillate yield is substantially lower than that of oils, with the mean difference being 5.1 wt % absolute. Again, this difference is statistically significant at a 99% confidence level, translating into a difference of about 15-20% absolute between the MAF yields of oils and distillates, with the former being higher (Skinner and Givens, 1981b). Interestingly, Cronauer and Ruberto (1979) have also found differences of a similar magnitude.

It can be concluded that the MAF yield of solvent-separated oils generally exceeds the yield of distillates determined by distillation I; the difference is large when the column is not heated and small but significant when the column is heated. The reader is cautioned that this conclusion is valid only for APCI techniques; the yield of solvent-separated oils alone may vary depending upon the solvents used and the method and order of separation (Mima et al., 1976).

Comparison of Benzene-Soluble Yields Determined by Solvent Separation or by Distillation I

Benzene solubles include oils plus asphaltenes from solvent separation, or distillates plus benzene-soluble distillation bottoms from distillation I. The data in Table 28 show that the weight percent yield of benzene solubles determined by solvent separation is much

greater than that determined by distillation I; the mean difference is 3.8 wt % absolute. (No distinction is made about heating the distillation column.) The difference is statistically significant at a 99% confidence level, and at least one other study (Cronauer and Ruberto, 1979) supports this conclusion.

The differences between the yields of solvent-separated oils and distillates and the data in Table 28 lead to the following deductions:

- the MAF yield of asphaltenes determined by solvent separation is much greater than that of nondistillable benzene solubles determined by distillation I with a heated column;
- the MAF yield of asphaltenes from solvent separation is only marginally less than that determined by distillation I without the heated column.

Comparison of Pyridine-Insoluble Residue Yields Determined by Solvent Separation or Distillation

Cronauer and Ruberto (1979) also reported that the yield of pyridine-insoluble residues, determined by distillation may exceed that obtained by solvent separation of the undistilled sample, if the liquid is distilled at a high enough temperature ($>600^{\circ}\text{F}$). At Air Products, distillations are normally done below 600°F , and the residue is obtained by extracting the bottoms with pyridine.

The yield of residues is slightly more using solvent separation than that using distillation I (Table 29). The mean difference is 0.9 wt % absolute, which is statistically significant at a 99% confidence level.

Comparison of Preasphaltene Yields Obtained by the Two Methods

Based on the yield differences observed between benzene solubles and pyridine-insoluble residues obtained by the two methods, the preasphaltene yield from distillation I should be higher than that determined by solvent separation. Table 30 confirms this. The mean difference between the two preasphaltene yields is 4.7 wt % absolute (statistically significant at a 99% confidence level). The difference calculated on the basis of MAF coal may mean a difference of 14-19 wt % between the MAF yields of preasphaltenes obtained by two analytical methods.

Distillation II (Filtration/Distillation)

Considerable data at Air Products have been obtained using distillation II (for details see Kingsley et al., 1981). In fact, as mentioned previously, modelling related to the SRC process (Skinner, 1979; Martin, 1979) relied solely on the data obtained using Kentucky #9/14 coal, a synthetic solvent, and this method of product work-up. Unfortunately, the past data cannot be fully exploited: the method has been discontinued, and there are insufficient data to compare distillation II yields with solvent-separation or distillation I yields.

However, Kingsley's report (1981) gives the following information:

1. Addition of 550-850°F distillates followed by hot filtration (distillation II) yields less of the 550-850°F cut than does distillation I.
2. Without hot filtration the difference observed in point 1 is even greater.

Distillation II involves distillation of two product liquid samples. Comparison of the distillates yield from the first sample with that obtained from the second (after addition of the diluent, hot filtration, and distillation) supports the first point just mentioned. Figure 6 compares distillate yields obtained by distillation II and distillation I (column not heated) compiled from various laboratory notebooks, related to three CPDU runs. All the evidence seems to suggest that the yield of distillates by distillation II may be about 2-3 wt % less than that by distillation I without the heated column.

Because the distillations at Air Products are carried out at temperatures less than 600°F, and because there is only a marginal difference between the yield of pyridine insolubles by solvent separation and that by distillation I, we may safely assume that the yield of pyridine-insoluble residue by distillation II resembles yields obtained by the other methods.

Distillation II uses toluene instead of benzene to separate the SRC into (oils + asphaltenes) and preasphaltenes, but generally the difference between toluene and benzene solubilities may be assumed to be negligibly small. Furthermore, filtration and residue removal before subjecting the sample to high temperatures should help to reduce thermal degradation. The second point of Kingsley et al. (1981) certainly supports this view. It is suggested, therefore, that the preasphaltene yield obtained by distillation II should fall between yields obtained by solvent separation and distillation I. When viewed together, the data from CPDU runs XCL-21 and -27 (Skinner and Givens, 1981a,b) suggest that the preasphaltene yields obtained by distillation II resemble those obtained by solvent separation.

Conclusions

Product characterizations affect total liquid product analysis as follows:

- The yield of solvent-separated oils *substantially* exceeds that of distillates from distillation I *without* a heated column.
- The yield of solvent-separated oils only *marginally* exceeds that of distillates from distillation I *with* a heated column.
- The yield of distillate by distillation II may be about 2-3 wt % lower than that from distillation I without a heated column.
- The benzene-soluble yields determined by solvent separation are substantially greater than those determined by distillation I.
- By deduction, the asphaltene yields determined by solvent separation are substantially greater than those determined by distillation I *with* a heated column.
- By deduction, the asphaltene yields determined by solvent separation are only marginally less than those determined by distillation I *without* a heated column.
- The pyridine-insoluble yields determined by solvent separation are only slightly greater than those determined by distillation I.
- The yield of pyridine-insoluble residue determined by distillation II is assumed to resemble the yields obtained by solvent separation and distillation I.

- The preasphaltene yields determined by solvent separation are substantially less than those determined by distillation I.
- Preasphaltene yields obtained by distillation II, which should fall between those determined by solvent separation and distillation I, are similar to solvent-separation yields.

Extrapolation of these CPDU results to results anticipated for a commercial unit is difficult. Batch distillations require about 6-8 hr, while commercial distillations in continuous units have much shorter residence times. Laboratory distillations make the net product slate look less attractive. This is not surprising because products of direct coal liquefaction are known to be thermally sensitive.¹

COMPARISON OF COAL/SOLVENT DATA FROM VARIOUS CPDU RUNS AND FOR A KENTUCKY #9 COAL

Earlier discussions in this report dealt with APCI's kinetic model (Skinner, 1979; Martin, 1979). The total liquid product work-up data obtained by distillation II were reasonably well explained by this mathematical model, although its predictions for Wilsonville Pilot Plant yields were poor. Since 1979 a particular Kentucky #9 coal has been processed frequently in the CPDU, but a formal parametric study has not been undertaken. Numerous solvents and work-up methods have been used in seven runs testing this coal (Table 31). Characteristics of various samples of coal from these runs varied minimally (Table 32).

In the first sections of this report it was established that the CPDU data are reproducible and that different analytical methods give varying product yields. In light of this information, it is important to compare the CPDU data to obtain useful information on the effects of reaction temperature and process solvent on direct liquefaction of Kentucky #9 coal. Once the base-line data on coal and solvents without any additives are well-established, the effects of dissolver solids, SRC recycle, and nonferrous mineral matter can be examined more effectively.

The only data points considered have ash-balance errors within $\pm 10\%$. The yields for CPDU runs 21, 23, and 27 were calculated based on forced-ash balance, whereas those for runs 22, 24, 28, and 29 are based on forced organic matter balance. Both material-balance techniques yield essentially identical results if the ash balance is satisfactory. Most of the data are for 30 wt % coal slurries and a nominal slurry residence time of 40 min. Two of the points in run 21, however, are for 40 wt % coal slurry, and 38 wt % was used in run 29. It is assumed that this variation in coal concentration affects the process performance insignificantly, mainly because of a lack of data indicating otherwise. All data from CPDU runs 21 and 23 and one point from run 27 were obtained at a 30-min residence time; these data were corrected to 40-min times using the mathematical model (Skinner, 1979; Martin, 1979). In the runs hydrogen gas flow rates to the reactor ranged from 300 to 600 slph, but this variation is also assumed to be negligible. Based on the error analyses presented earlier, MAF coal conversion is expected to have a standard deviation of 1-1.5%,

¹It is worth noting that yields obtained at Wilsonville Pilot Plant by laboratory distillation (V110 method) are generally indicative of less severe operation than yields obtained in process equipment downstream of the dissolver (process method) (see O'Leary et al., 1981).

and oil, asphaltene, and preasphaltene yields should have standard deviations of about 5% MAF coal.

Conversion

For this analysis, percent MAF coal conversion is defined as 100 minus percent insoluble organic matter (IOM). IOM is pyridine-insoluble residue minus ash. Whenever necessary, MAF conversions for 30-min residence were corrected to 40-min times by using equation 1:

$$(\text{conv})_{40} = \frac{94 \frac{40}{30}}{\frac{94}{(\text{conv})_{30}} + \frac{40}{30} - 1} \quad (1)$$

The formula assumes that only 94% of the macerals in this Kentucky #9 coal are reactive and that the conversion of reactive macerals to pyridine-soluble products is first order. Figure 7 shows the conversion data obtained in runs 21-29 for a nominal residence time of 40 min. All the solvents seem to be equally effective in converting coal to pyridine solubles, and the MAF coal conversion appears to be almost independent of reaction temperature. Conversion may increase by at most 1% if the temperature level is raised from 780 to 865°F; on the average, 90% of this Kentucky #9 coal can be converted to pyridine solubles in the temperature range investigated. The scatter observed is within experimental error.

C₁- to C₄-Hydrocarbon Gas Yield

Hydrocarbon (HC) gas yield varies as a function of temperature in CPDU runs 21-29 (Figure 8). Wherever necessary, observed gas yields for 30-min residence were converted to yields for 40-min residence using equation 2, which assumes that gas production is zero order (Skinner, 1979; Martin, 1979):

$$(\text{gas yield})_{40} = \frac{40}{30} (\text{gas yield})_{30} \quad (2)$$

Increasing the temperature from 780 to 865°F increases the HC gas yield sixfold. The data in Figure 8 and Table 31 seem to indicate that the gas yield rises with increasing solvent hydrogen content. This is hardly surprising, because most of the hydrocarbon gases are produced from cracking of both solvent and coal products. For this Kentucky #9 coal, the curve in Figure 8 correlates HC gas yield at a nominal residence time of 40 min and for a solvent containing 8 wt % hydrogen.

Heteroatom Gas Yield

CO, CO₂, H₂S, and NH₃ (if any) are considered to be heteroatom gases. Their combined MAF yield is plotted as a function of temperature in Figure 9. Equation 2 was used for

residence-time correction when necessary, although its validity for heteroatom gas yield is questionable. Yields seem to increase slightly with increasing temperature and do not seem to depend on hydrogen content of the process solvent.

Water Yield

The data in Figure 10 show the observed MAF yield of water as a function of temperature. Residence times were not corrected. No trends can be discerned from the data; therefore, we conclude that the MAF yield of water can be assumed constant and roughly equal to 2.5 wt % for Kentucky #9 coal in the temperature range studied.

Preasphaltene Yield

The yield of preasphaltenes is plotted as a function of temperature for a nominal residence time of 40 min in Figure 11. The data for 30-min residence time were recalculated according to equation 3:

$$(\text{preasp})_{40} = \frac{\text{total liq}}{\left[\frac{\text{tot liq}}{(\text{preasp})_{30}} - 1 \right] \left(\frac{40}{30} \right) + 1} \quad (3)$$

where tot liq is the total liquid yield (preasphaltenes + asphaltenes + oils) observed at 30-min residence time. Equation 3 assumes that preasphaltene conversion to benzene solubles is first order and that total liquid yield changes insignificantly when the nominal residence time increases from 30 to 40 min. Preasphaltene yield clearly decreases with temperature, but, statistically, the scatter in Figure 11 cannot be explained by experimental error alone.

Therefore, let us first limit ourselves to the data obtained in runs 21, 27, and 29 which used Wilsonville recycle solvents. Note that the methods of liquid product characterization used in these runs are different (Table 37). The preasphaltene yields from runs 21 and 27 are similar. This is not surprising because preasphaltene yields determined by solvent separation and distillation II are believed to be similar, as pointed out earlier in this report. On the other hand, yields from run 29 are about 15% higher. Distillation I is used for total liquid analysis in run 29, and is expected to yield higher values for preasphaltene yield by approximately the same amount as observed here (see section on total product liquid analysis). The lower line in Figure 11 correlates the data from runs 21, 27, and 29 and represents the preasphaltene yield for the Kentucky #9 coal in Wilsonville recycle solvent, determined by solvent separation. A separate line is drawn through the data obtained in runs 22, 23, 24, and 28, all of which used solvent separation. All the solvents [hydrotreated creosote oil (HTCO), creosote oil (CO), and Ft. Lewis SRC-II heavy distillate (SRC-II HD)] appear to have an equal effect on liquefaction, producing similar preasphaltene yields. The two lines in Figure 11 also show that, for Kentucky #9 coal, Wilsonville recycle solvent reduces the preasphaltene yield by about 10% (absolute, MAF coal) compared to the other three solvents.

Asphaltene Yield

For material-balance calculations, all MAF yields except asphaltene yields were examined and compared as independent quantities. The MAF yields of asphaltenes were specified and correlated after the conversion, hydrogen consumption, and MAF yields of all other fractions were specified and correlated.

Oil/Distillate Yield

The yield of oils or distillates was calculated by equation 4:

$$\frac{(\text{oils/distillates})_{\text{products}} - (\text{oils/distillates})_{\text{feed}}}{(\text{MAF coal})_{\text{feed}}} \quad (4)$$

$(\text{Oils/distillates})_{\text{feed}}$ were determined by analyzing the starting solvents, which for CPDU runs are almost all oils/distillates (see Table 33 for analyses of solvents used in runs 21-29). The solvents used in runs 23 and 28, low in oil content, would lead to inflated oil yields according to equation 4; to correct this, these solvents were arbitrarily assumed to contain 96% pentane-soluble oils. The pentane-insoluble materials in the solvents are probably low molecular weight rather than full-range asphaltenes. Hence, the assumed 96% oil content of the two solvents seems reasonable.

Also, all the oil/distillate yields observed for a nominal residence time of 30 min were corrected to a 40-min residence time by increasing by 4-5% absolute (Skinner, 1979; Martin, 1979).

The corrected data are plotted in Figure 12 (MAF oil/distillate yield vs. temperature). Yield clearly increases with rising temperature, but the scatter cannot be explained in terms of experimental error alone. As with the preasphaltene yield, we first examined data from runs 21, 27, and 29, all of which used Wilsonville recycle solvent. The yield from run 27 appears somewhat higher compared to that from runs 21 and 29. Note that total liquid product work-up was by solvent separation in run 27 and distillation I in run 29. The results from run 21 are regarded as distillation I data.² Agreement between the results of runs 21, 27, and 29 seems satisfactory; distillation I work-up is expected to give marginally lower distillate yields compared to those for solvent-separated oils. The upper line in Figure 12 correlates these data, and represents the yield of solvent-separated oils vs. temperature for Kentucky #9 coal in Wilsonville recycle solvent.

A separate line is drawn through the data obtained in runs 22, 23, 24, and 28, all of which used solvent separation for product analysis. Use of H₂CO, CO, or SRC-II HD appears to affect oil yield insignificantly, but in comparison, the MAF oil yields obtained with Wilsonville recycle solvent are about 15% higher.

²In run 21, total product liquid was analyzed by distillation II. The distillation bottoms were analyzed in series for heptane, toluene, and pyridine solubility. For this report, we used the heptane-soluble yield from run 21 as the oil yield. All the distillate is assumed to be heptane soluble. Although I have correlated the yield of distillates from distillation II to that from distillation I or to the yield of oils from solvent separation, the correlation between the yield of heptane solubles by distillation II and the yield of pentane-soluble oils by solvent separation was not established. I propose that the yield of heptane solubles determined by distillation II be regarded as equal to the yield of distillates by distillation I, with the heated column.

Total Hydrogen Consumption

The total hydrogen consumption observed in runs 21-29 (Figure 13) includes the gaseous hydrogen consumed and the hydrogen lost by the solvent. Consumption was calculated by elemental rather than gas balance. The data obtained at 30-min residence time were not corrected. The plot in Figure 13 shows that total hydrogen consumption increases rapidly with increasing temperature. The curve represents a correlation of the data.

Total hydrogen consumption, which appears to be accurate within ± 0.4 wt % absolute, is surprisingly independent of process-solvent hydrogen content, even for such radically different process solvents as creosote oil and Wilsonville recycle solvent. As a corollary to this, the total hydrogen consumed in once-through runs is probably the same as the total hydrogen consumed in recycle runs. Other data from the CPDU on Kentucky #9/14 coal support this view (Skinner and Givens, 1980a,b).

Conclusions

The most important conclusion is that the data gathered in various CPDU runs can be cross-correlated. The following conclusions are specific for direct liquefaction of Kentucky #9 coal at 780-865°F:

- MAF conversion is about 90% and is independent of solvent composition and reaction temperature.
- Hydrocarbon gas yields increase rapidly with temperature, whereas heteroatom gas yields increase slightly with temperature.
- Water yields may be almost temperature independent.
- Preasphaltene yields decrease with increasing temperature. Under identical reaction conditions, Wilsonville recycle solvents appear to convert preasphaltenes to benzene solubles more effectively than the other solvents.
- The oil/distillate yields increase with increasing temperature. Again, Wilsonville recycle solvents appear to be more effective.
- Total hydrogen consumption (determined from the CPDU data) appears to be independent of the process solvents. Generally, the total hydrogen consumed in once-through operation may be indistinguishable from total consumption observed during recycle with an equilibrium solvent.

COMPARISON OF WILSONVILLE AND CPDU YIELDS

Comparison of Wilsonville Pilot Plant data with CPDU data is extremely valuable for scale-up and design of the SRC-I Demonstration Plant. This section summarizes previous comparisons and discusses new data that define the problems involved in comparison.

CPDU vs. Wilsonville Operation

First, the quality of both data sets must be established. Recent work by Joshi (1981) and by O'Leary et al. (1981) documents data collection and yield calculation techniques

for the CPDU and Wilsonville, respectively, which should be helpful in assessing errors and demonstrating overall reproducibility of each data set. As pointed out in the error analysis section of this report, ash balances are important in judging the validity of yields, and duplicate measurements help to eliminate inconsistent data.

In principle, if all the differences between two units are recognized and quantified, then the yields they generate should be similar. The following sections address most of the important differences between CPDU and Wilsonville operations. Note that some differences can be more easily quantified than others.

Coal. Coal is not an ideal chemical feedstock. As mentioned earlier, coals from different mines vary and coals from the same mine differ depending on the place and method of mining. Kentucky #9 coal used in both units may be very different. Thus, before the data are compared, the coal feedstocks must be characterized as being reasonably identical, unless correlations predicting the effect of characteristics on process performance are available.

Reactor Size and Operating Variables. The CPDU reactor is a continuously stirred, 1-L autoclave, whereas the Wilsonville dissolver is an 18.2-ft³ bubble column with a length/diameter ratio of 24. Also, the Wilsonville dissolver is coupled with a preheater section, which has an effective total volume of 3.2 ft³. Fortunately, ICRC (1979) determined that the effect of slurry preheater variables on Wilsonville process performance was negligibly small, and Ying et al. (1980) reported that the dissolver was almost completely backmixed (the number of equivalent continuously stirred tank reactors being marginally greater than 1). Moreover, the reactor and dissolvers are not limited by the rate of gas/liquid mass transfer of hydrogen.

Preferably, the data to be compared should be obtained under identical conditions (residence times, temperatures, and pressures), but equations or models can be used to compare data obtained under different conditions.

Solvent. Solvent properties depend on raw materials and production conditions. Because most solvents are coal-derived and the processing conditions vary over a wide range, no two solvents are exactly alike. In addition, the role of solvent in direct coal liquefaction is not clearly understood. The CPDU operation is for the most part once-through; the solvent is not recovered from the product or recycled. On the other hand, the Wilsonville solvent is continuously recovered from the product and recycled to the dissolver. We do not know how and to what extent the yields obtained with an equilibrium solvent differ from those obtained with a similar, nonequilibrium solvent.

Solids Accumulation. The concentration of solids in the CPDU reactor equals that in the exit stream leaving the reactor, whereas solids have been observed to accumulate at Wilsonville.³ Under typical operating conditions, the only solids that accumulate are 80 mesh and larger (ICRC, 1979). Whether such accumulated solids actively catalyze coal dissolution reactions, particularly when 95% of the coal itself is -200 mesh, is unknown. Evidence from Wilsonville is inconclusive, and the CPDU experiments addressing the issue have used filter cake or Kerr-McGee ash concentrate instead of blown-down dissolver solids (Skinner and Givens, 1981a,b; Skinner et al., 1981). A recent study indicates that the catalytic effect of dissolver solids is very small at best (Vargese et al., 1981).

Data Collection and Material-Balance Methods. The only downstream separation equipment in the CPDU is the gas/liquid separator. The condensed product is not distilled

³A solids withdrawal system was installed in February 1978 to alleviate the problem and has been operating with reasonable success over the last 2 years.

in a continuous still but instead is sampled and analyzed in the laboratory. At Wilsonville, in contrast, a continuous distillation column recovers the solvent, and the distillation bottoms are sampled and analyzed in the laboratory. Efforts to correlate the yields obtained by analyzing the feed to the distillation column in the laboratory with yields obtained in the continuous process equipment have not been very successful. Among other things (O'Leary et al., 1981), we do not know whether distillate yields obtained in the laboratory batch distillations truly represent the short residence time in a continuous distillation column.

Also, analytical methods used to characterize the products from the two units are different. As discussed previously, the apparent yield structures depend significantly on the method used. The results of Wilsonville analytical methods have not been directly compared with those of CPDU analytical methods, although some work is in progress.

Comparison of Model Predictions with Wilsonville Pilot Plant Data

The second section of this report discussed APCI's mathematical model (Skinner, 1979), devised to predict the performance of coal liquefaction units. It was concluded that laboratory data correlate reasonably well with the model, but more data are needed.

This kinetic model has also been used to predict the performance of Wilsonville and Ft. Lewis Pilot Plants (Martin, 1979). In both cases, the model predicted yields that correspond to lower severity operation than actually observed.

Predictions of SRC yields at Wilsonville were too high and those for distillate production were too low (Table 34). Because both residence-time effects and mixing had been accounted for, the discrepancies were attributed to the differences between Wilsonville recycle solvent and the synthetic solvent used in the CPDU, to solids accumulation observed in the Wilsonville dissolver, and to differences in fluid dynamics that result in different hydrogen mass transfer rates in the two reactors (Thorogood and Yeh, 1979). (Correlations in the existing literature and work at APCI show that neither of the reactors is hydrogen-starved.)

However, the effect of different analytical methods was completely overlooked. The data used to calculate the kinetic model were derived from product analyses that used distillation II (filtration and distillation). The previous section on total liquid product analysis concluded that distillate yields determined by distillation II are considerably lower than either the yield of distillates obtained by distillation I or the yield of oils obtained by solvent separation. In fact, these differences are of the same magnitude as the discrepancies between observed and predicted yields listed in Table 34. Thus, if the yields obtained by solvent separation better represent process performance at Wilsonville, then the discrepancies in Table 34 may be attributable to APCI's methods of total liquid product analysis.

To understand the quantitative effect of process solvent on liquefaction yields of Kentucky #9/14 coal and the catalytic effect of accumulated solids, more information is needed.

Comparison of Wilsonville and CPDU Yields

In light of the preceding discussion and because solvent separation typically is used in CPDU operations, yields of two Kentucky #9 coals obtained in the CPDU using solvent separation were compared with those obtained at Wilsonville. Calculation of the yields is detailed elsewhere (Joshi, 1981; O'Leary et al., 1981).

Pyro Kentucky #9 Coal (Lewis et al., 1979a,b). The Pyro coals processed in Wilsonville runs 157-162 and in CPDU runs 21, 23, 27, and 29 were essentially similar (Table

35). The recycle solvents in Wilsonville contained 8.6-8.9 wt % hydrogen, whereas CPDU solvents were 8.1-8.8 wt %. Material balances were obtained in Wilsonville runs 159-162, and run 159 operated at a slightly higher space velocity than the other three. Solids were not withdrawn from the dissolver in runs 159 and 160, but they were withdrawn in runs 161 and 162. The total pressure in the dissolver in runs 159, 160, and 161 was 1,700 psig, whereas it was 2,100 psig in run 162.

Table 36 compares CPDU and Wilsonville yields. CPDU yields were acquired directly from data that were shown to be internally consistent earlier in this report (see section on coal/solvent data). Wilsonville yields appear to be internally consistent, although, surprisingly, yields from runs without solids withdrawal (159 and 160) are about the same as those from runs with solids withdrawal (161 and 162). Wilsonville yields were calculated by the process method (O'Leary et al., 1981) and are elementally balanced. Raw ash balances are good, except that for run 159. The CPDU data are for a 40-min residence time, whereas the Wilsonville data reflect a 35- to 45-min residence. Correcting the Wilsonville data to the 40-min time using Martin's model (1979) would change gas yields by 10% (relative) and organic liquid/SRC yields by about 2.5 wt % MAF coal (absolute).

Fies Kentucky #9 Coal. The Fies coals processed in CPDU runs 32 and 39 under demonstration plant conditions and at Wilsonville in runs 218-220 (Gaspar and O'Leary, 1981) were essentially identical, except for their total sulfur and pyritic sulfur contents (Table 37). During the Wilsonville runs solids were withdrawn from the dissolver, and some light solvent-refined coal (LSRC) was recycled with the process solvent. LSRC addition is generally believed to increase organic liquid yields.

Wilsonville and CPDU data for Fies Kentucky #9 coal appear to be internally consistent and fairly similar (Table 38). The Wilsonville ash balances are unsatisfactory, however.

Discussion. The variances in MAF conversion observed between the two units for both Pyro and Fies coals are attributable to different analytical methods. Hydrogen consumption in the CPDU appears low compared to that at Wilsonville for both coals; however, when it is recalculated based on gas balance rather than elemental balance (Joshi, 1981), the difference is greatly reduced. Hydrocarbon and heteroatom gas yields from both units for both coals are reasonably similar. [Note that the organic liquid yield is probably the least accurate of all the numbers determined at Wilsonville (O'Leary et al., 1981)]. Surprisingly, organic liquid and SRC yields are similar. The differences in yields in both Tables 36 and 38 may be related to the difference between the performance of the continuous process equipment and its simulation in the laboratory.

Conclusions

Data on direct liquefaction of Kentucky #9/14 coal from Wilsonville runs and from the CPDU using distillation II for product work-up were dissimilar. However, data on Kentucky #9 Pyro and Fies coals in different runs in Wilsonville and through the CPDU using solvent separation for work-up were very similar. This indicates that the discrepancies between Wilsonville and CPDU data may be related to inconsistent analytical methods and to differences between the performance of the continuous process equipment downstream of the dissolver and its simulation in the laboratory. Previously, these discrepancies were attributed to solids accumulation in the Wilsonville dissolver and to the use of different solvents.

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Table 1

Multiple Determinations of Oil Yields by
Solvent Separation of One CPDU Sample^a

Sample no.	Wt % oils	df	SSE
21-132	62.6, 64.9, 63.9, 62.8, 62.4	4	4.5
23-95	58.4, 58.5	1	0.0
23-102	57.5, 59.7	1	2.4
23-108	65.9, 64.7	1	0.7
23-120	54.6, 64.4	1	48.0*
23-163	68.2, 69.5, 67.0, 69.7	3	4.8
23-164	63.0, 62.1	1	0.4
23-169	70.7, 72.0, 73.4	2	3.7
23-189	63.7, 67.8	1	8.4*
23-204	65.3, 67.4	1	2.2
23-210	68.7, 71.2	1	3.1
27-81	73.5, 73.6	1	0.0
27-96	77.5, 75.3	1	2.4
27-149	63.9, 62.2	1	1.5
27-159	69.1, 66.6	1	3.1
27-129	61.8, 66.4	1	10.6*
27-192	59.6, 63.8	1	8.8*
31-206	67.3, 69.9	1	3.4

$$\text{mean } s^2 = \frac{\sum \text{SSE}}{\sum \text{df}} = 1.6$$

$$\text{total df} = \sum \text{df} = 20$$

^aAbbreviations used are: df, degrees of freedom; SSE, sum of squared errors; s^2 , sample variance.

Table 2

Multiple Determinations of Asphaltenes
by Solvent Separation of One CPDU Sample

Sample no.	Wt % asphaltenes	df	SSE
21-132	8.0, 8.9, 8.4, 10.3, 8.1	4	3.5
23-102	11.4, 12.0	1	0.2
23-108	7.4, 7.1	1	0.1
23-120	7.1, 8.4	1	0.8
23-169	11.6, 10.0, 10.3	2	1.5
23-189	9.2, 11.2	1	2.0
23-210	9.0, 9.3	1	0.1
23-163	11.7, 11.1, 13.8, 10.4	3	5.5
27-81	8.6, 9.9	1	0.9
27-96	7.8, 7.8	1	0.0
27-129	11.4, 8.5	1	4.2
27-149	10.0, 9.0	1	0.5
27-159	7.6, 8.8	1	0.7
27-192	15.2, 13.6	1	1.3
31-206	12.6, 10.2	1	2.9

mean $s^2 = 1.16$

total df = 21

Table 3
Multiple Determinations of Preasphaltenes
by Solvent Separation of One CPDU Sample

Sample no.	Wt % preasphaltenes	df	SSE
21-132	11.2, 8.3, 9.5, 8.9, 10.8	4	6.1
23-102	14.2, 12.0	1	2.4
23-108	10.9, 9.5	1	1.0
23-120	8.1, 18.2	1	51.0*
23-163	13.6, 10.3, 12.1, 11.1	3	6.1
23-169	10.3, 10.8, 8.3	2	3.5
23-189	16.6, 13.9	1	3.7
23-210	8.9, 10.4	1	1.1
27-81	10.8, 10.1	1	0.3
27-96	7.5, 8.2	1	0.3
27-129	7.1, 8.6	1	1.1
27-149	8.1, 8.9	1	0.3
27-159	5.9, 7.3	1	1.0
27-192	12.8, 10.6	1	2.4
31-206	7.4, 7.4	1	0.0

mean $s^2 = 1.47$

total df = 20

Table 4

Multiple Determinations of SRC by
Solvent Separation of One CPDU Sample

Sample no.	Wt % SRC	df	SSE
21-132	19.2, 17.2, 17.9, 19.2, 18.9	4	3.2
23-102	26.6, 24.0	1	3.4
23-108	18.3, 16.6	1	1.5
23-120	15.2, 26.6	1	65.0*
23-169	21.9, 20.8, 18.6	2	5.7
23-189	25.8, 25.1	1	0.8
23-210	17.9, 19.7	1	1.6
23-163	25.3, 21.4, 25.9, 21.5	3	17.4*
27-81	19.4, 20.0	1	0.2
27-96	15.3, 16.0	1	0.3
27-129	18.5, 17.1	1	1.0
27-149	18.1, 17.0	1	0.0
27-159	13.5, 16.1	1	3.4
27-192	28.0, 24.2	1	7.2*
31-206	20.0, 17.6	1	2.9
$\text{mean } s^2 = 1.46$ $\text{total df} = 16$			

Table 5

Multiple Determinations of Residue by
Solvent Separation of One CPDU Sample

Sample no.	Wt % residue	df	SSE
21-132	18.8, 17.9, 18.2, 18.0, 18.7	4	0.38
23-102	17.0, 16.4	1	0.18
23-108	17.0, 17.5	1	0.13
23-120	20.2, 19.1	1	0.61
23-158	16.7, 14.4	1	2.65*
23-163	7.8, 8.5, 7.2, 8.1	3	0.90
23-169	7.6, 7.4, 7.9	2	0.13
23-189	9.0, 8.6	1	0.08
23-204	12.1, 12.1	1	0.0
23-210	11.8, 10.7	1	0.61
27-81	7.0, 6.5	1	0.13
27-96	7.2, 8.7	1	1.13*
27-129	18.1, 18.0	1	0.01
27-149	18.0, 18.4	1	0.08
27-159	17.4, 17.3	1	0.01
27-192	12.4, 12.0	1	0.08
31-206	12.6, 12.6	1	0.0
mean s^2 = 0.16			
total df = 21			

Table 6

Multiple Determinations of Distillate
by Distillation of One CPDU Sample

Sample no.	Wt % distillate	df	SSE
23-169	65.2, 65.5, 64.8	2	0.25
$\text{mean } s^2 = 0.13$ $\text{total df} = 2$			

Table 7

Multiple Determinations of SRC
by Distillation of One CPDU Sample

Sample no.	Wt % distillate	df	SSE
23-169	26.5, 27.8, 28.6	2	2.24
$\text{mean } s^2 = 1.12$ $\text{total df} = 2$			

Table 8

Multiple Determinations of Residue
by Distillation of One CPDU Sample

Sample no.	Wt % residue	df	SSE
23-169	8.3, 6.7, 6.6	2	1.82
$\text{mean } s^2 = 0.91$ $\text{total df} = 2$			

Table 9

Analysis of Two or More CPDU Samples from
One Product Stream: Oils by Solvent Separation

Sample no.	Wt % oils	df	SSE
32-15,37	68.3, 69.8	1	1.6
32-87,101	64.2, 63.6	1	0.2
32-125,139	70.9, 68.6	1	2.7
32-163,170	65.6, 64.8	1	0.3
33-21,28	66.5, 67.5	1	0.5
33-51,65	70.0, 67.7	1	2.7
33-94R,101	71.1, 74.5	1	5.8
33-137,151	69.6, 67.8	1	1.6
33-173,180,187	70.4, 68.5, 70.4	2	2.4
27-50,56	74.0, 74.7	1	0.3
27-122,129	64.3, 61.8, and 66.4	1	10.6*
27-188,192	63.5, 57.6, and 63.8	1	12.0*
31-109,113	71.9, 71.4	1	0.1

mean. s^2 = 1.52

total df = 12

Table 10

Analysis of Two or More CPDU Samples from
One Product Stream: Asphaltenes by Solvent Separation

Sample no.	Wt % asphaltenes	df	SSE
32-15,37	10.9, 9.4	1	1.0
32-87,101	9.3, 10.9	1	1.3
32-125,139	10.0, 8.7	1	0.8
32-163,170	8.3, 9.8	1	1.2
33-21,28	9.8, 7.2	1	3.4
33-51,65	8.1, 9.7	1	1.2
33-94R,101	9.6, 8.9	1	0.3
33-137,151	8.4, 9.1	1	0.3
33-173,180,187	8.2, 10.1, 9.4	2	1.9
27-50,56	10.3, 8.4	1	1.8
27-122,129	11.1, 11.4, and 8.5	1	6.8
27-188,192	11.3, 15.2, and 13.6	1	20.5*
31-109,113	9.7, 11.0	1	0.7

mean $s^2 = 1.59$

total df = 13

Table 11

Analysis of Two or More CPDU Samples from
One Product Stream: Preasphaltenes by Solvent Separation

Sample no.	Wt % preasphaltenes	df	SSE
32-15,37	12.0, 12.5	1	0.1
32-87,101	15.6, 14.7	1	0.4
32-125,139	10.8, 13.8	1	4.6
32-163,170	13.5, 12.3	1	0.7
33-21,28	11.2, 12.3	1	0.7
33-51,65	11.8, 12.6	1	0.3
33-94R,101	12.0, 10.1	1	1.8
33-137,151	13.5, 14.7	1	0.7
33-173,180,187	12.6, 12.1, 10.9	2	1.5
27-50,56	9.1, 9.5	1	0.1
27-122,129	6.1, 7.1, and 8.6	1	7.2
27-188,192	12.7, 12.8, and 10.6	1	4.4
31-109,113	5.6, 5.0	1	0.2

mean $s^2 = 1.62$

total df = 14

Table 12

Analysis of Two or More CPDU Samples from
One Product Stream: SRC by Solvent Separation

Sample no.	Wt % SRC	df	SSE
32-15,37	22.8, 21.9	1	0.4
32-87,101	24.9, 25.6	1	0.3
32-125,139	20.8, 22.5	1	1.5
32-163,170	21.8, 22.1	1	0.1
33-21,28	21.0, 19.5	1	1.1
33-51,65	19.9, 22.3	1	2.8
33-94R,101	21.6, 19.0	1	3.4
33-137,151	21.9, 23.8	1	1.8
33-173,180,187	20.8, 22.2, 21.3	2	1.0
27-50,56	19.4, 17.9	1	1.1
27-122,129	17.2, 18.5, and 17.1	1	1.2
27-188,192	24.0, 28.0, and 24.2	1	9.4
31-109,113	15.3, 16.0	1	0.3

*

mean $s^2 = 1.15$

total df = 13

Table 13

Analysis of Two or More CPDU Samples from
One Product Stream: Residue by Solvent Separation

Sample no.	Wt % residue	df	SSE
32-15,37	8.9, 8.3	1	0.17
32-87,101	10.9, 10.9	1	0.0
32-125,139	8.3, 8.9	1	0.17
32-163,170	12.6, 13.1	1	0.12
33-21,28	12.6, 13.0	1	0.10
33-51,65	10.1, 10.0	1	0.0
33-94R,101	7.3, 6.5	1	0.32
33-137,151	8.7, 8.3	1	0.08
33-173,180,187	8.7, 9.4, 9.3	2	0.29
27-50,56	6.6, 7.4	1	0.32
27-122,129	18.5, 18.1, and 18.0	1	0.41
27-188,192	12.7, 12.4, and 12.0	1	0.58
31-107,113	12.9, 12.7	1	0.02

mean s^2 = 0.18

total df = 14

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Table 14

Analysis of Two or More CPDU Samples from
One Product Stream: Distillate

Sample no.	Wt % distillate	df	SSE
32-87,101	65.2, 65.6	1	0.08
33-94,108	71.5, 71.7	1	0.02
33-137,151	66.5, 65.8	1	0.25
33-173,180,187	69.7, 67.1, 68.7	2	3.44
27-50,56	69.3, 69.4	1	0.01
27-122,129	68.0, 69.2	1	0.72
27-188,192	57.5, 63.2	1	16.25*
27-277,284	57.9, 56.9	1	0.50
$\text{mean } s^2 = 0.63$ $\text{total df} = 8$			

Table 15

Analysis of Two CPDU Samples from
One Product Stream: SRC by Distillation

Sample no.	Wt % SRC	df	SSE
32-87,101	22.6, 23.6	1	0.50
33-94,108	22.3, 22.5	1	0.02
33-137,151	26.1, 28.4	1	2.65
33-173,187	23.0, 24.3	1	0.85
$\text{mean } s^2 = 1.0$ $\text{total df} = 4$			

Table 16

Analysis of Two CPDU Samples from
One Product Stream: Residue by Distillation

Sample no.	Wt % residue	df	SSE
32-87,101	12.2, 10.8	1	0.98
33-94,108	6.2, 5.8	1	0.08
33-137,151	7.4, 5.8	1	1.28
33-173,187	7.6, 7.0	1	0.18
mean $s^2 = 0.63$			
total df = 4			

Table 17

Estimated Variances Associated with Laboratory Analyses
Compared with Estimated Combined Variances Associated with
the CPDU Sampling and Laboratory Analyses^a

Fraction	s^2 lab	s^2 combined
Solvent separation		
Oil	1.60 (20)	1.52 (12)
Asphaltenes	1.16 (21)	1.59 (13)
Preasphaltenes	1.47 (20)	1.62 (14)
SRC	1.46 (16)	1.15 (13)
Residue	0.16 (21)	0.18 (14)
Distillation		
Distillate	0.12 (2)	0.63 (7)
SRC	1.12 (2)	1.0 (4)
Residue	0.91 (2)	0.63 (4)

^aThe degrees of freedom on which each estimate is based are in parentheses.

Table 18

Standard Deviations of Component Weight Fractions
Based on Total Product Liquid Analysis

Fraction	Std dev (wt %) (absolute)	df
Solvent separation		
Oil	1.25	32
Asphaltenes	1.15	34
Preasphaltenes	1.24	34
SRC	1.15	29
Residue	0.41	35
Distillation		
Distillate	0.78	9
SRC	1.02	6
Residue	0.85	6

Table 19

Statistically Permissible Maximum Differences between
Two Analyses of Total Product Liquid (95% Confidence Level)

Solvent separation		Distillation	
Fraction	Difference (wt %)	Fraction	Difference (wt %)
Oil	3.6	Distillate	2.5
Asphaltenes	3.3	SRC	3.5
Preasphaltenes	3.6	Residue	2.9
SRC	3.3		
Residue	1.2		

Table 20

Least Significant Difference (LSD) between the Analysis
of Two Total Product Liquid (TPL) Streams (95% Confidence Level)

Fraction	LSD (wt %), each TPL analyzed	
	Once	Twice
Solvent Separation		
Oil	3.6	2.5
Asphaltenes	3.3	2.3
Preasphaltenes	3.6	2.5
SRC	3.3	2.3
Residue	1.2	0.8
Distillation		
Distillate	2.5	1.8
SRC	3.5	2.5
Residue	2.9	2.1

Table 21

CPDU Data Reproducibility: Case I

Sample no.	32-163,170	33-21,28
Coal type	Ky #13	Ky #13
Solvent	Recovered WRS ^a	Recovered WRS
Coal concn (wt %)	40	40
LHSV ^b (hr ⁻¹)	1.51	1.41
Total pressure (psig)	2,000	2,000
Temp (°F)	836	838
H ₂ flow rate (wt % MAF coal)	8.1	8.8
Ash balance (%)	90	98
Conversion (% MAF coal)	82.0	82.5
Total H consumption (% MAF coal)	1.6	1.6
SRC sulfur (wt %)	0.75	0.65
% MAF yields		
C ₁ -C ₄	7.3	7.1
Other gases	2.4	2.7
H ₂ O	3.1	4.6
Oils	10.4	15.5
Asphaltenes	21.8	19.9
Preasphaltenes	37.1	32.7
Residue	19.9	19.8
Analytical method used	Solv. sep.	Solv. sep.

^aWRS, Wilsonville recycle solvent.^bLHSV, liquid hourly space velocity.

Table 22

CPDU Data Reproducibility: Case II

Sample no.	22-96	24-211
Coal type	Ky #9	Ky #9
Solvent	HTCO	HTCO
Coal concn (wt %)	30	30
LHSV (hr^{-1})	1.50	1.50
Total pressure (psig)	2,000	2,000
Temp ($^{\circ}\text{F}$)	850	850
H ₂ flow rate (wt % MAF coal)	6.3	7.5
Ash balance (%)	111	95
Conversion (% MAF coal)	92.9	89.5
Total H consumption (% MAF coal)	1.24	1.87
SRC sulfur (wt %)	0.97	1.04
% MAF yields		
C ₁ -C ₄	5.2	5.2
Other gases	2.3	3.0
H ₂ O	4.5	1.5
Oils	9.0	4.1
Asphaltenes	26.2	36.0
Preasphaltenes	44.9	39.8
Residue	8.0	11.7
Analytical method used	Solv. sep.	Solv. sep.

Table 23

CPDU Data Reproducibility: Case III

Sample no.	10-98	11-109
Coal type	Ky #9/14	Ky #9/14
Solvent	25% CO ^a + 75% HTCO	HTCO
Coal concn (wt %)	40	40
LHSV (hr ⁻¹)	3.0	3.0
Total pressure (psig)	2,000	2,000
Temp (°F)	850	850
H ₂ flow rate (slph)	550	550
Ash balance (%)	98	90
Conversion (% MAF coal)	91.3	92.3
Total H consumption (% MAF coal)	1.4	1.4
SRC sulfur (wt %)	0.99	1.0
% MAF yields		
C ₁ -C ₄		
Other gases total gases	5.9	4.6
H ₂ O	3.7	3.1
Oils	8.8	8.6
Asphaltenes		
Preasphaltenes SRC	72.9	76.0
Residue	8.7	7.7
Analytical method used	Dist. II	Dist. II

^aCO, creosote oil.

Table 24

CPDU Data Reproducibility: Case IV

Sample no.	12-72	13-35
Coal type	Ky #9/14	Ky #9/14
Solvent	25% CO + 75% H ₂ CO	H ₂ CO
Coal concn (wt %)	40	40
LHSV (hr ⁻¹)	1.3	1.3
Total pressure (psig)	2,000	2,000
Temp (°F)	850	850
H ₂ flow rate (slph)	550	550
Ash balance (%)	107	93
Conversion (% MAF coal)	94.0	92.2
Total H consumption (% MAF coal)	2.1	1.8
SRC sulfur (wt %)	0.72	0.70
% MAF yields		
C ₁ -C ₄		
Other gases	total gases	
H ₂ O		
Oils/distillate		
Asphaltenes		
Preasphaltenes	SRC	
Residue		
Analytical method used	Dist. II	Dist. II

Table 25

CPDU Data Reproducibility: Case V

Sample no.	10-92	14-78
Coal type	Ky #9/14	Ky #9/14
Solvent	25% CO + 75% HTCO	25% CO + 75% HTCO
Coal concn (wt %)	40	40
LHSV (hr ⁻¹)	2.0	2.0
Total pressure (psig)	2,000	2,000
Temp (°F)	850	850
H ₂ flow rate (slph)	550	550
Ash balance (%)	97	99
Conversion (% MAF coal)	91.8	92.7
Total H consumption (% MAF coal)	1.7	1.5
SRC sulfur (wt %)	0.84	1.03
% MAF yields		
C ₁ -C ₄		
Other gases total gases	7.7	6.4
H ₂ O	6.1	4.3
Oils/distillate	9.3	14.5
Asphaltenes		
Preasphaltenes SRC	68.7	67.5
Residue	8.2	7.3
Analytical method used	Dist. II	Dist. II

Table 26

Comparison of Distillate Yield (by Distillation I,
Column Heated) with Oil Yield (by Solvent Separation)

Sample	Oil yield (wt %)	Distillate yield (wt %)
23-169	72.00 ^a	72.2
32-15,37	68.1 ^b	69.1
32-87,101	63.9 ^b	65.4 ^b
32-125,139	70.0 ^b	69.4
33-21,28	66.5 ^b	66.9
33-94,101,108	72.3 ^b	71.6 ^b
33-137,151	68.9 ^b	66.2 ^b
33-173,180,187	69.2 ^a	68.5 ^a
36-15,30	72.6 ^b	69.5
36-56,63	71.9 ^b	71.2
36-85,92	67.1 ^b	63.6
36-110,117	68.4	65.0
36-136	67.8	64.1

^a Average of three determinations.

^b Average of two determinations.

Table 27

Comparison of Distillate Yield (by Distillation I,
Column Not Heated) with Oil Yield (by Solvent Separation)

Sample	Oil yield (wt %)	Distillate yield (wt %)
23-169	72.0 ^a	65.2 ^a
27-50	74.0	69.3
27-56	74.7	69.4
27-81	73.5	68.7
27-96	76.4	71.1
27-106	74.4	71.2
27-122	64.3	57.4
27-129	62.0	58.1
27-149	62.2	56.5
27-159	66.6	62.4
27-188	63.5	57.9
27-192	61.7	58.4
27-260	75.4	72.6

^aAverage of three determinations.

Table 28

Comparison of Benzene Solubility Determined by Solvent
Separation with That Determined by Distillation I

Sample	Distillation I	Solvent separation
	(distillates + oils + asphaltenes) (wt %)	(oils + asphaltenes) (wt %)
23-169	77.9 ^a	82.6 ^a
33-101,108	78.5	82.0 ^b
33-187	78.4	79.8
36-56	76.9	82.0
36-136	72.5	79.8

^a Average of three determinations.

^b Average of two determinations.

Table 29

Comparison of Pyridine-Insoluble Residue Yield
by Distillation I with That by Solvent Separation

Sample	Distillation (wt %)	Solvent separation (wt %)
23-169	7.5 ^a	7.4 ^a
32-15,37	8.2 ^b	9.0 ^b
32-87,101	11.5 ^b	11.0 ^b
32-125,139	7.6	8.6 ^b
33-21,28	11.4	12.9 ^b
33-94,101,108	6.0 ^b	7.0 ^b
33-137,151	7.4	8.5 ^b
33-173,180,187	7.3 ^b	9.2 ^a
36-15,30	5.1	6.2 ^a
36-56,63	6.8	7.5 ^a
36-85,92	7.9	9.2 ^a
36-110,117	6.6	7.6
36-136	6.0	7.9

^a Average of three determinations.

^b Average of two determinations.

Table 30

Comparison of Preasphaltene Yield by
Distillation I with That by Solvent Separation

Sample	Solvent separation (wt %)	Distillation I (wt %)
23-169	10.0 ^a	14.6 ^a
33-101,108	7.0 ^b	10.0
33-187	11.0	14.3
33-56	10.5	16.3
33-136	12.3	21.5

^a Average of three determinations.

^b Average of two determinations.

Table 31

CPDU Runs with Kentucky #9 Coal

Run no.	Solvent ^a	Wt % H in solvent	Analytical method
21	WRS	8.8	Distillation II
22	HTCO	7.7	Solvent sep.
	CO	5.9	
23	WRS	8.8	Solvent sep.
	CO	5.9	
24	HTCO	7.5	Solvent sep.
	CO	6.4	
27	WRS	8.1	Solvent sep.
28	SRC-II HD	7.4	Solvent sep.
29	WRS	8.5	Distillation I (column heated)

^a Abbreviations used are: WRS, Wilsonville recycle solvent; HTCO, hydro-treated creosote oil; CO, creosote oil; SRC-II HD, heavy distillate (550°F+) from SRC-II pilot plant at Ft. Lewis.

Table 32

Variation in the Characteristics of
Kentucky #9 Coal Used in Different CPDU Runs

	Range (wt %)
Carbon	69.3-70.3
Hydrogen	4.7-4.8
Nitrogen	0.9-1.5
Sulfur	3.0-3.3
Volatile matter	35.1-37.0
Ash	13.0-13.4
Moisture	1.8-1.9
Pyritic sulfur	1.6-1.8

Table 33

Analysis of Starting Solvents Used in
Runs 21-29

Run no.	Solvent	Wt %	
		Oils	Distillates
21	WRS	97.3	-
22	HTCO	96.3	-
23	CO	90.3	-
24	CO	98.4	-
	HTCO	98.8	-
27	WRS	97.5	-
28	SRC-II HD	90.8	-
29	WRS	-	98.7

^aAbbreviations used are: WRS, Wilsonville recycle solvent; HTCO, hydrotreated creosote oil; CO, creosote oil; SRC-II HD, heavy distillate (550°F+) from SRC-II pilot plant at Ft. Lewis.

Table 34

Prediction of Wilsonville Dissolver Performance Using the Kinetic Model

Run no.	Temp (°F)	Nominal residence time (min)		Net yield (lb of reactable coal)				
				SRC	Total distillates	C ₁ -C ₄ gases	Other gases	% S in SRC
64-1	834	53.5	Pred	0.657	0.175	0.067	0.101	0.54
			Expt1	0.601	0.214	0.108	0.114	0.46
66-2	850	37.6	Pred	0.778	0.095	0.036	0.091	0.61
			Expt1	0.730	0.102	0.082	0.109	0.52
76-1	824	22.1	Pred	0.915	0.007	0.018	0.059	1.05
			Expt1	0.766	0.157	0.035	0.064	0.78
80	853	27.3	Pred	0.859	0.037	0.023	0.080	0.73
			Expt1	0.632	0.255	0.057	0.056	0.69
81	852	20.4	Pred	0.911	0.011	0.016	0.061	1.02
			Expt1	0.680	0.225	0.046	0.075	0.72

Table 35

Variation in the Characteristics of
Pyro Kentucky #9 Coal

	Range (wt %)	
	CPDU	Wilsonville
Carbon	69.3-70.3	68.7-72.0
Hydrogen	4.7-4.8	4.5-5.1
Nitrogen	0.9-1.5	0.9-1.7
Sulfur	3.0-3.3	2.8-3.6
Ash	13.0-13.4	10.4-13.4
Pyritic sulfur	1.6-1.8	1.1-1.6

Table 36

Comparison of CPDU Data with Wilsonville Data: Pyro Kentucky #9 Coal,
Elementally Balanced Yields, Percent Moisture- and Ash-Free Coal, Process Method

	CPDU data with WRS ^a	Wilsonville run no.			
		159	160	161	162
Temp (°F)	825	825	825	825	825
Res. time (min)	40	35	45	45	45
Wt % H in solvent	8.1-8.8	8.6	8.9	8.9	8.8
Ash balance (%)	100	85.2	95.2	99.2	99.3
Conversion (%)	90	92.1	93.7	93.9	93.3
H ₂ consumed	1.4	1.8	2.6	2.3	2.6
HC gas	4.2	2.8	4.6	4.0	7.0
Heteroatom gas	2.7	2.3	4.3	2.0	3.0
Water	2.5	4.3	1.4	7.1	4.7
Organic liquid	15.0	21.3	24.9	16.4	20.9
SRC	67.6	65.6	64.3	65.9	60.6
Wt % S in SRC	1.0	0.85	0.84	0.89	0.94

^aWilsonville recycle solvent.

Table 37

Characteristics of Fies Kentucky #9 Coal

	Range (wt %)	
	CPDU	Wilsonville
Carbon	71.1-71.4	69.7-71.3
Hydrogen	5.0-5.1	4.7-5.1
Nitrogen	1.5-1.6	1.1-1.5
Sulfur	2.9-3.0	3.4-3.7
Ash	8.9	8.5-8.7
Pyritic sulfur	0.9-1.0	1.2-1.4

Table 38

Comparison of CPDU Data with Wilsonville Data: Fies Kentucky #9 Coal
Unadjusted Yields, Percent Moisture- and Ash-Free Coal, Process Method

Run no.	CPDU data	Wilsonville run no.		
		219	220AB	220DE
Temp. (°F)	840	840	840	840
Res. time (min)	40	39	38	38
Wt % H, solvent	8.1-8.5	9.0	9.0	8.6
LSRC:coal	0	0.08:1	0.12:1	0.12:1
Ash balance (%)	94	85	85	85
Conversion (%)	90.1	92.5	93.6	93.5
H ₂ consumed	1.6	2.5	2.5	2.3
HC gas	7.3	3.7	4.1	4.2
Heteroatom gas	2.6	4.1	3.2	3.9
Water	3.1	2.5	4.3	5.0
Organic liquid	24.2	28.2	32.9	29.6
SRC	53.5	58.6	53.6	54.3
Wt % S in SRC	0.93	0.93	0.96	0.98

Figure 1
Reaction Sequence and Component Balances

$$\frac{dC}{dt} = -k_1(C)$$

$$\frac{dP}{dt} = k_1(C) - k_2(P) - k_7(P)X_S - k_8(P)X_O W_C - k_9(P)$$

$$\frac{dA}{dt} = k_2(P) - k_3(A) - k_7(A)X_S - k_9(A)$$

$$\frac{dD}{dt} = k_3(A) - k_9(D)$$

$$\frac{dG_S}{dt} = k_7(P + A)X_S$$

$$\frac{dG_O}{dt} = k_8(P)X_O$$

$$\frac{dG_{C(1)-C(4)}}{dt} = k_9(P + A + D)$$

C = COAL
P = PREASPHALTENE
A = ASPHALTENE
D = DISTILLATE
G_S = SULFUR GASES

G_O = OXYGEN GASES
G_{C(1)-C(4)} = HYDROCARBON GASES
X_S = WEIGHT FRACTION RESIDUAL SULFUR
X_O = WEIGHT FRACTION RESIDUAL OXYGEN
W_C = OXYGEN GASES CARBON:OXYGEN RATIO

Figure 2
Preasphaltenes Yield (% MAF Coal)

Figure 3
Total Distillates Yield (% MAF Coal)

Figure 4
Preasphaltenes Yield, 850°F (% MAF Coal)

Figure 5
Solvent-Separated Oil Yield Vs. Distillation I
(Heated Column) Distillate Yield

Figure 6
Comparison of Distillate Yields:
Distillation II Vs. Distillation I
(Column Not Heated)

Figure 7
Conversion vs. Temperature

Figure 8
Hydrocarbon Gas Yield vs. Temperature

Figure 9
Heteroatom Gas Yield vs. Temperature

Figure 10
Yield of Water vs. Temperature

Figure 11
Preasphaltenes Yield vs. Temperature

Figure 12
Oils/Distillates Yield vs. Temperature

Figure 13
Total H Consumption vs. Temperature

EFFECT OF SOLVENT INITIAL BOILING POINT (IBP) ON DISSOLVER PERFORMANCE

D. Garg* and E. N. Givens*

To study the effect of solvent IBP on dissolver performance, a process solvent from the Ft. Lewis Pilot Plant (SRC-I mode) was distilled to recover three different IBP fractions. The fractions, namely 389, 445, and 538°F+ cuts, were reacted at 840 and 815°F with Lafayette Kentucky #9 coal under SRC-I Demonstration Plant design conditions.

Test results showed that coal conversion and SRC production increased slightly with increasing solvent IBP. No other major differences were apparent with changes in solvent IBP. However, a net loss in distillate oil production was noted with all three IBP cuts.

There appears to be an optimum reaction temperature for the conversion of Ky #9 coal in that conversion was greater at 815°F than at 840°F. Oil production decreased significantly with decreasing reaction temperature. In addition, hydrogen consumption decreased and SRC sulfur content increased with decreasing temperature.

Although these results indicate a temperature effect on coal conversion, the effect of solvent IBP alone does not appear to be significant. It should be noted that this conclusion is based on a single-pass run and does not necessarily reflect the impact of solvent IBP at steady-state conditions.

INTRODUCTION

The initial boiling point (IBP) of the process solvent can influence the performance of the dissolver and change the coal liquefaction product slate. The SRC-I Pilot Plant at Wilsonville typically uses a variety of solvents boiling above approximately 450°F. It is felt that solvents with high initial boiling points are of higher quality, and that the yield of more desirable products increases with solvent quality. An ongoing research program at Air Products is designed to study and systematically document the effect of solvent IBP on coal liquefaction.

EXPERIMENTAL PROGRAM

Three different IBP cuts were used in CPDU Run CCL-37 to study the effect of solvent IBP on liquefaction of Lafayette Kentucky #9 coal at 840 and 815°F. A list of sample numbers and process conditions (similar to those of the proposed SRC-I Demonstration Plant) is given in Table 1.

*Air Products and Chemicals, Inc.

Materials

Solvents. Process solvent received at Air Products from the Ft. Lewis Pilot Plant was generated when the unit was running in an SRC-I mode. For this study, approximately 75 and 50 wt % of the process solvent was recovered as 550 and 650°F fractions, respectively.

Three solvent fractions, i.e., the original process solvent and the two distilled fractions, were analyzed by simulated distillation. These analyses determined that the initial boiling points of the solvents were 389, 445, and 538°F, respectively. The simulated distillation of the three solvent fractions (Figure 1) showed that the amount of higher boiling point materials increased with an increase in IBP of the solvent.

The three solvent fractions were further analyzed by capillary gas chromatography (GC) to determine the boiling point distribution (Table 2), as well as to identify major compounds present in the samples (Table 3). Note that approximately half of the 538°F+ cut boils above 750°F. The 445°F+ cut contained a lower concentration of phenol compared with the 389°F+ solvent. The highest IBP solvent was found to contain minor amounts of the first eight compounds listed in Table 3, whereas the concentration of the last nine compounds listed was much higher than that in both the 389 and 445°F+ cuts.

Table 4 shows that hydrogen and oxygen contents decreased with increasing IBP, whereas the nitrogen and sulfur contents increased with IBP. The average molecular weight also increased with an increase in solvent IBP.

The distribution of aromatic (H_{AR}), benzylic (H_a), and other (H_o) protons given in Table 5 shows that the absolute concentrations of H_{AR} and H_o decreased with increasing solvent IBP. The lowest IBP solvent contained slightly higher concentrations of H_a and H_o than did the other two solvents, suggesting that the lowest IBP solvent has higher hydrogen donor capability (determined by concentrations of H_a and H_o) than the other two solvents, and thus should perform better in coal liquefaction reactions. However, the differences between absolute H_a and H_o values of the three different solvents are not significant enough to result in substantial differences in coal conversion.

The structural parameters given in Table 6 show that the aromaticity (f_a) was not greatly affected by solvent IBP. (The aromaticity values (f_a) calculated by using a modified Brown-Ladner equation and determined by ^{13}C NMR were in good agreement.) However, the degree of substitution (σ) increased with increasing solvent IBP.

The oxygen content of solvent (Table 7) decreased with increasing solvent IBP, as did the concentration of phenols. Nitrogen content and the concentration of pyridine-type compounds increased with increasing solvent IBP.

Coal. Washed Lafayette Ky #9 coal was ground to 95% minus-200-mesh particles, air-dried, and screened through a 150-mesh sieve before use. The detailed analysis of the screened sample is reported in Table 8.

Analytical Work-Up

The three process solvents were vacuum-distilled to recover the distillable and non-distillable fractions using a single-plate vacuum-flash-distillation unit equipped with a Vigreux column to achieve adequate reflux. The distribution of these fractions is summarized in Table 9. From the coal liquefaction product slurry, the distillation bottoms, consisting of solvent-refined coal (SRC), insoluble organic matter (IOM), and mineral matter, were mixed with pyridine, heated, and filtered to separate the pyridine solubles and insolubles. The

pyridine solubles were vacuum-distilled to boil off pyridine and recover solid SRC, which was solvent-separated to further divide it into asphaltene and preasphaltene fractions. The pyridine insolubles were washed with methylene chloride and dried in an inert atmosphere.

Distillation data for starting solvents given in Table 9 were used to calculate the net product distribution following liquefaction.

RESULTS AND DISCUSSION

Effect of Solvent IBP on Coal Liquefaction

At 840°F, coal conversion increased slightly with increasing solvent IBP from 389 to 445°F+. Production of hydrocarbon gases, $\text{CO} + \text{CO}_2$, $\text{H}_2\text{S} + \text{NH}_3$, and water was unaffected by a change in solvent IBP (Table 10). All three solvents yielded a net loss in distillate oil; the larger decrease with higher IBP solvent (samples 37-73 and 37-102) was due to the lower reaction temperature of 835°F compared with 840°F, and was accompanied by an increase in SRC yield. The SRC yields achieved with the two higher IBP solvents were usually larger than that of the unfractionated Ft. Lewis solvent (389°F+); this appears to be associated with the increased coal conversion generally observed with the higher IBP solvents, particularly at the 840°F reaction temperature. Hydrogen consumption approximated 1 wt % MAF (moisture/ash free) coal, and SRC sulfur content averaged 1.2%, but no definite trends in these values or in SRC composition (asphaltenes and preasphaltenes) with changes in solvent IBP were apparent (Table 10). As shown in Table 11, the distribution of elements in various SRC samples showed no relationship between carbon, hydrogen, and nitrogen contents and solvent IBP.

At 815°F, coal conversion remained unchanged with lower IBP solvents, but decreased slightly with highest IBP solvent (Table 12). Production of hydrocarbon gases, $\text{CO} + \text{CO}_2$, and $\text{H}_2\text{S} + \text{NH}_3$ increased with increasing solvent IBP. Water production was slightly lower with higher solvent IBP. Once again, all three solvents yielded a net loss in distillate oil; the largest decrease was noted with the highest IBP solvent (i.e., sample 37-119). The decrease in distillate oil production was accompanied by an increase in SRC yield. Greater hydrogen consumption and lower SRC sulfur contents were noted with higher solvent IBP (Table 12). The concentration of asphaltenes in SRC increased, while that of preasphaltenes decreased with increasing solvent IBP. As shown in Table 13, no definitive relationship between carbon, hydrogen, and nitrogen contents in SRC and solvent IBP was noted.

Effect of Reaction Temperature on Coal Liquefaction

With lower IBP solvents, conversion of coal was either unchanged or increased with decreasing reaction temperature (Table 12), suggesting that there is an optimum temperature for liquefaction of Lafayette Ky #9 coal. Production of hydrocarbon gases, $\text{CO} + \text{CO}_2$, and $\text{H}_2\text{S} + \text{NH}_3$ decreased with decreasing temperature.

Distillate oil production was very sensitive to reaction temperature, as reflected in the steadily greater decreases noted from 840 to 835 to 815°F (Tables 10 and 12). At 815°F, distillate oil production also showed a greater decrease with increasing solvent IBP. These results were corroborated by another study (Skinner and Givens, 1981), in which an oil

production of 13.7% of coal was achieved at 865°F. Conversely, SRC production increased with decreasing temperature.

Hydrogen consumption was generally lower at 815°F than at 840°F, and the reduction in hydrogen consumption with the lowest IBP cut was much greater than with the highest IBP cut. SRC sulfur content increased with decreasing temperature with lower IBP solvents, but no significant difference was noted with the highest IBP cut.

SRC samples contained more hydrogen at 815°F than at 840°F (Table 13). However, no significant differences in carbon and nitrogen contents were noted.

CONCLUSIONS

Although temperature appears to affect coal conversion, the effect of solvent IBP alone is not significant. However, it should be noted that this conclusion is based on a single-pass run, and does not necessarily reflect the impact of solvent IBP at steady-state conditions.

LITERATURE CITED

Skinner, R. W., and E. N. Givens. 1981. See following article in this Quarterly Technical Report on Effects of accumulated solids on dissolver performance (October to December 1980).

Table 1

Summary of Process Conditions for Liquefaction
of Lafayette Kentucky #9 Coal

Sample no.	Solvent (°F+)	Temperature (°F)	Pressure (psig)	Time (min)	Solvent/coal by weight	Hydrogen feed rate (M scf/T)
37-17	389	839	2,000	45.7	60/40	30.88
37-24	389	839	2,000	46.2	60/40	30.94
37-32	389	810	2,000	46.1	60/40	31.24
37-64	445	840	2,000	40.9	60/40	27.02
37-73	445	835	2,000	46.1	60/40	31.90
37-84	445	815	2,000	43.6	60/40	30.22
37-95	538	840	2,000	44.1	60/40	29.71
37-102	538	835	2,000	47.0	60/40	32.46
37-119	538	815	2,000	43.4	60/40	29.39

Table 2

Boiling Point Distribution for Three Different
IBP Solvents as Determined by Capillary GC

Solvent	Boiling point fraction (wt %)						
	IBP-450°F	450-500°F	500-550°F	550-600°F	600-650°F	650-700°F	700-750°F
389°F+	6.34	12.62	14.15	13.28	14.38	9.95	9.20
445°F+	0.77	4.57	8.53	12.66	17.48	16.00	9.52
538°F+	0	0	0.64	3.23	13.12	14.11	19.57

Table 3

Major Compounds Present in 389°F+ Solvent

1. Phenol	10. Fluorine
2. Tetralin	11. Phenanthrene
3. Naphthalene	12. Anthracene
4. 2-Methylnaphthalene	13. Carbazole
5. 1-Methylnaphthalene	14. Methylphenanthrene
6. Biphenyl	15. Fluoranthene
7. Dimethylnaphthalene	16. Pyrene
8. Acenaphthalene	17. Methylpyrene
9. Dibenzofuran	

Table 4

Elemental Analysis of the Different IBP Solvents

	389°F+ cut	445°F+ cut	538°F+ cut
Element (wt %)			
C	87.4	86.6	88.0
H	8.4	8.1	7.6
O	3.0	2.8	2.6
N	0.8	1.0	1.2
S	0.4	0.5	0.6
$\bar{n}Mw^a$	195	235	270

^aNumber-average molecular weight.

Table 5

Distribution of Protons in the Different IBP Solvents

	389°F+ cut		445°F Cut		538°F+ cut	
Total hydrogen (wt %)	8.4		8.1		7.6	
Distribution of protons (%)						
	<u>Abs</u> ^a	<u>Rel</u> ^b	<u>Abs</u>	<u>Rel</u>	<u>Abs</u>	<u>Rel</u>
H ^c _{AR}	2.9	35.0	2.8	34.8	2.3	30.5
H ^d _a	2.5	30.1	2.4	29.4	2.5	32.5
H ^e _o	3.0	34.9	2.9	35.8	2.8	37.0

^aAbs. = absolute.^bRel. = relative.^cAromatic.^dBenzylic.^eOther.

Table 6

Modified Brown-Ladner Structural Parameters
for Different IBP Solvents

Parameter	389°F+ cut	445°F+ cut	538°F+ cut
f_a	0.66	0.65	0.65
σ	0.32	0.33	0.39
H_{AR}/C_{AR}	0.80	0.81	0.72
f_a^a	0.67	0.67	0.65

^a f_a determined by ¹³C NMR.

Table 7

Distribution of Oxygen and Nitrogen Compounds
in the Different IBP Solvents

	389°F+ cut		445°F+ cut		538°F+ cut	
Oxygen distribution (wt %)						
Total	3.0		2.8		2.6	
	<u>Abs</u> ^a	<u>Rel</u> ^b	<u>Abs</u>	<u>Rel</u>	<u>Abs</u>	<u>Rel</u>
O as ether	1.45	48.3	1.59	56.8	1.43	55.0
O as OH	1.55	51.7	1.21	43.2	1.17	45.0
Nitrogen distribution (wt %)						
Total	0.8		1.0		1.2	
	<u>Abs</u>	<u>Rel</u>	<u>Abs</u>	<u>Rel</u>	<u>Abs</u>	<u>Rel</u>
N as quinoline	0.62	77.5	0.77	77.0	0.91	75.8
N as NH	0.18	22.5	0.23	23.0	0.29	24.2

^aAbs = absolute.

^bRel = relative.

Table 8

Analysis of Lafayette Kentucky #9 Coal

Components (wt %)	Batch 1	Batch 2	Mean
Moisture	1.45	1.21	1.33
Volatiles	38.85	39.11	38.98
Fixed carbon	49.49	49.91	49.70
Ash	10.50	9.84	10.17
C	72.35	72.20	72.28
H	5.03	5.06	5.05
N	1.57	1.66	1.62
S	2.56	2.47	2.52
O	8.37	8.15	8.26

Table 9

Distillation of Starting Solvents

	389°F+ cut	445°F+ cut	538°F+ cut
Distillable (wt %)	97.5	96.2	91.7
Nondistillable (wt %)	2.5	3.8	8.3

Table 10

Effect of Solvent IBP on Liquefaction of Kentucky #9 Coal

Sample no.	<u>37-17</u>	<u>37-24</u>	<u>37-64</u>	<u>37-73</u>	<u>37-95</u>	<u>37-102</u>
Solvent	389°F+		445°F+		538°F+	
Feed composition	60% solvent/40% coal					
Temperature (°F)	839	839	840	835	840	835
Pressure (psig)	2,000	2,000	2,000	2,000	2,000	2,000
Residence time (min)	45.7	46.2	40.9	46.1	44.1	47.0
H ₂ flow rate (M scf/T)	30.9	30.9	27.0	31.9	29.7	32.5
Product distribution						
(wt % MAF coal)						
HC	7.9	6.5	6.9	7.7	7.4	7.5
CO, CO ₂	1.0	1.0	1.0	1.0	0.9	0.9
H ₂ S, NH ₃	1.6	1.4	1.7	1.8	1.6	1.6
Distillate oil	(0.5) ^a	(0.2)	(1.8)	(6.0)	0.3	(4.7)
SRC	73.5	75.7	80.1	83.5	78.1	80.6
Asphaltene	34.8	30.2	28.1	30.2	37.5	39.5
Preasphaltene	38.7	45.5	52.0	53.3	40.6	41.1
Water	3.0	3.0	2.5	2.8	2.5	2.6
IOM	16.3	14.9	11.8	11.7	11.9	14.8
Conversion	83.7	85.1	88.2	88.3	88.1	85.2
H ₂ consumption						
(wt % MAF coal)						
From gas	0.68	0.41	0.34	0.72	0.47	0.56
From solvent	0.26	0.25	0.38	0.08	0.50	0.26
Total	0.94	0.66	0.72	0.80	0.97	0.82
SRC sulfur (%)	1.18	1.20	1.12	1.06	1.23	0.96

^a() = negative value.

Table 11

Distribution of Elements in the SRC
Samples Obtained at 840°F

Sample no.	<u>37-17</u>	<u>37-24</u>	<u>37-64</u>	<u>37-73</u>	<u>37-95</u>	<u>37-102</u>
Solvent	389°F+		445°F+		538°F+	
Temperature (°F)	839	839	840	835	840	835
SRC (wt %)						
C	88.2	87.8	86.6	87.7	88.2	88.0
H	5.3	5.2	5.2	5.3	5.3	5.3
N	2.1	2.1	2.2	2.1	2.2	2.1
S	1.2	1.2	1.1	1.1	1.2	1.0
O (by difference)	3.2	3.7	4.9	3.8	3.1	3.6

Table 12

Effect of Temperature on Liquefaction of Kentucky #9 Coal

Sample no.	<u>37-17</u>	<u>37-32</u>	<u>37-64</u>	<u>37-84</u>	<u>37-95</u>	<u>37-119</u>
Solvent	389°F+		445°F+		538°F+	
Feed composition	60% solvent/40% coal					
Temperature (°F)	839	815	840	810	840	815
Pressure (psig)	2,000	2,000	2,000	2,000	2,000	2,000
Residence time (min)	45.7	46.1	40.9	43.6	44.1	43.4
H ₂ flow rate (M scf/T)	30.9	31.2	27.0	30.2	29.7	29.4
Product distribution (wt % MAF coal)						
HC	7.9	3.4	6.9	5.6	7.4	5.0
CO, CO ₂	1.0	0.8	1.0	0.9	0.9	0.9
H ₂ S, NH ₃	1.6	1.2	1.7	1.6	1.6	1.4
Distillate oil	(0.5) ^a	(8.5)	(1.8)	(8.6)	0.3	(14.2)
SRC	73.5	92.6	80.1	91.1	78.1	94.6
Asphaltene	34.8	27.8	28.1	40.1	37.5	44.5
Preasphaltene	38.7	64.8	52.0	51.0	40.6	50.1
Water	3.0	3.0	2.5	2.0	2.5	2.6
IOM	16.3	9.8	11.8	9.8	11.9	13.4
Conversion	83.7	90.2	88.2	90.2	88.1	86.6
H ₂ consumption (wt % MAF coal)						
From gas	0.68	0.08	0.34	0.44	0.47	0.43
From solvent	0.26	0.09	0.38	0.13	0.50	0.05
Total	0.94	0.17	0.72	0.57	0.97	0.48
SRC sulfur (%)	1.18	1.36	1.12	1.23	1.23	1.18

^a() = negative value.

Table 13

Effect of Temperature on the Distribution of Elements in SRC Samples

Sample no.	<u>37-17</u>	<u>37-32</u>	<u>37-64</u>	<u>37-84</u>	<u>37-95</u>	<u>37-119</u>
Solvent	389°F+		445°F+		538°F+	
Temperature (°F)	839	815	840	815	840	815
SRC (wt %):						
C	88.2	85.2	86.6	87.3	88.2	87.3
H	5.3	5.4	5.2	5.5	5.3	5.5
N	2.1	2.2	2.2	2.1	2.2	2.1
S	1.2	1.4	1.1	1.2	1.2	1.2
O (by difference)	3.2	5.8	4.9	3.9	3.1	3.9

Figure 1
Simulated Distillation of Solvents Distilled
to Different Initial Boiling Points

EFFECTS OF ACCUMULATED SOLIDS ON DISSOLVER PERFORMANCE: INTRODUCTION

Scaling up to the commercial-size coal dissolver (6,000 tons per day) that will be installed in the SRC-I Demonstration Plant will be based on data from the smaller dissolvers in the Wilsonville and Ft. Lewis Pilot Plants. At Wilsonville, an accumulation of mineral-rich solids in the dissolver has been observed for several years, but it is uncertain that solids will similarly accumulate at the higher velocities of commercial dissolvers.

Commercial dissolver designs propose gas and slurry velocities about 10 times greater than those at Wilsonville, velocities that would impede the accumulation of solids. Moreover, any solids that did build up would consist of larger particles than those seen at Wilsonville, leading to less activity per weight due to less surface being exposed.

No clear, concise experimental data exist that establish the effects of the accumulated solids. If they have no effect, the commercial scale-up problem is straightforward. If, however, they do have a catalytic effect on coal conversion, augmenting the reaction, then some quantification of that effect will be needed in order to determine the dimensions and design of commercial dissolvers. International Coal Refining Co. (ICRC) suspects that, without possible catalytic effects due to the solids, the yields of lighter coal liquid products may decrease.

To solve this problem, Air Products and Chemicals, Inc. has been feeding solids into the continuous stirred tank reactor (CSTR) of the coal process development unit (CPDU) at its Corporate Laboratories. The solids are introduced in the presence of feed slurry (coal and solvent). Because Wilsonville was operating in a solids withdrawal mode and because both Wilsonville and APCI lacked the capability to wash and dry solids in a very dilute blowdown slurry, actual Wilsonville dissolver solids were unavailable. Therefore, Wilsonville filter cake and Kerr-McGee ash concentrate (K-MAC) were used to simulate them. Similar results were anticipated, because all should contain the same mineral forms (pyrrhotite rather than pyrite and partial clay dewatering). However, filter cake and, in particular, K-MAC contain more reactive carbon compounds (unconverted coal and SRC) than true dissolver solids. The conversion of these reactive materials must be accounted for when calculating net product yields and kinetic constants.

Difficulties associated with pumping and processing feed slurries containing more than 45 wt % solids have limited residue concentrations to a maximum 15 wt %, added to a 30 wt % coal slurry. Thus, where the solids in the Wilsonville dissolver are commonly found at the 20-30 lb/ft³ level or higher, in the CPDU the maximum concentration is about 10-15 lb/ft³. At Wilsonville, the velocities are low enough that solids readily accumulate. Obviously, to see effects at the lower levels will require greater experimental sensitivity.

The three articles that follow summarize the research performed from January to December 1980; the fourth article analyzes the data gathered. This work had been withheld from publication to avoid premature disclosure of inventions. U.S. Patent Applications have now been filed.

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EFFECTS OF ACCUMULATED SOLIDS ON DISSOLVER PERFORMANCE (JANUARY-MARCH 1980)

R. W. Skinner* and E. N. Givens*

We draw seven conclusions from the work to date:

- (1) Liquefaction residues can catalyze coal liquefaction fractions, particularly hydrogen consumption and preasphaltene conversion.
- (2) The preasphaltenes contained in the Kerr-McGee ash cannot be removed by heating to 300°F in Wilsonville solvent. They are converted (59%) to toluene-solubles during the liquefaction reaction at 850°F. Kerr-McGee ash displays less catalytic activity than filter cake, presumably because of its preasphaltene content. Therefore, Kerr-McGee ash may not be as good a substitute for dissolver solids as filter cake.
- (3) In the absence of added residue, solvent yield varies inversely with reaction temperature (for Pyro Kentucky #9).
- (4) An increased concentration of coal in the feed improves liquefaction performance.
- (5) The presence of coal seems to enhance solvent hydrogenation:
 - Wilsonville solvent alone loses hydrogen at typical coal liquefaction conditions, even at a lower reaction temperature and a higher hydrogen pressure than was originally used at Wilsonville when the solvent was produced.
 - The addition of mineral residue does not alter the solvent hydrogen loss.
 - The addition of coal plus mineral residue produces an increased solvent hydrogen content.
- (6) The reaction of solvent alone results in a small amount of cracking to hydrocarbon gas. The extent of cracking is a strong function of solvent hydrogen content. At 850°F Wilsonville solvent yields 1 wt % hydrocarbon gas, while creosote oil yields only 0.1 wt % gas.
- (7) An ancillary study of the effect of atmosphere (air vs. nitrogen) during grinding and drying shows that, apart from increasing the water yield, the mild surface oxidation caused by drying coal in air has a minimal impact upon liquefaction performance (Skinner, 1981).

*Air Products and Chemicals, Inc.

THE WILSONVILLE EXPERIENCE

At Wilsonville, solids have been added or withdrawn to control accumulation and/or catalysis of the liquefaction reaction. Although the mechanism of solids accumulation is not clearly understood, it seems to be associated with the growth and agglomeration of solid particles, as well as with low gas and slurry velocities.

Coal minerals, particularly iron pyrites, have been shown by other investigators to be catalytically active in coal liquefaction. However, the extent of catalysis by coal minerals as they occur in dissolver solids is less clear. In addition to the obvious chemical changes—such as pyrite reduction and the dewatering of clays—that occur in these minerals at liquefaction conditions, their surface area and catalytic activity could be altered by coking, agglomeration, sintering, carbonate deposition, and other physical changes.

The presence of dissolver solids at Wilsonville increases the reaction exotherm across the dissolver. Additionally, as dissolver solids accumulate during the processing of an iron-deficient Western coal, coal conversion increases significantly over a period of several days. However, further accumulation of dissolver solids has no measurable effect. Similarly, the gradual accumulation of solids during the processing of a Western Kentucky coal does not appear to significantly influence liquefaction behavior. This suggests that prolonged residence in the dissolver may deactivate the solids.

DESIGN OF THE EXPERIMENTAL PROGRAM

In several ways this CSTR study provides a worst-case measure of the performance of a commercial dissolver. First, the CSTR is fully back-mixed, causing the concentration of reacting species throughout the reactor to equal their effluent concentration. This will reduce the overall reaction rate for positive-order reactions. Second, this complete back-mixing eliminates the accumulation of potentially catalytic minerals.

Difficulties in pumping and processing feed slurries containing more than 45 wt % solids have limited the concentrations examined to 15 wt % residue added to 30 wt % coal slurry—less than the mineral loadings achieved at Wilsonville.

Because the effects of coal concentration in the feed upon liquefaction performance are not sufficiently understood to determine the reaction severity that is most appropriate for scale-up, the program includes an examination of these effects.

Since solvent boiling range is another variable that seems to influence dissolver performance, the program studies three solvents, cut from the same Wilsonville process solvent, and boiling in the ranges 400-850°F, 500-850°F, and 600-850°F.

Although most of the work in the program is being done with oncethrough, non-steady-state, process solvent, two solvent recycle experiments are included in the plan to confirm the validity of our conclusions when applied to the solvent recycle mode.

The first CPDU run under the program, designated Run XCL-21, was completed in August 1979. The unit was on stream for a total of 294 hours, during which product samples were collected at 31 different sets of reaction conditions. Complete product work-ups and analyses were performed on 16 of these product slurry samples; partial data are available on the other samples.

The reaction conditions for these data points are summarized in Table 1. Note that the catalytic effect of the mineral-rich reaction residues (filter cake and Kerr-McGee ash concentrate) is assessed by addition to solvent alone and by addition to coal slurries. The

purpose of adding the residues to solvent in the absence of coal was to quantify any mineral catalysis of solvent hydrogenation/dehydrogenation and to measure the extent to which the carbonaceous portion of the residues was converted to pyridine-solubles and/or toluene-solubles.

The second CPDU run, Run XCL-23, was completed during November 1971. A total of 42 product samples was collected during the 281 hours that the unit was on stream. The data collected for the reaction of solvent alone and/or solvent plus residue are discussed in this report; the reaction conditions for those data points are listed in Table 2. The remainder of Run XCL-23 is discussed in the following article.

Materials

Analytical data characterizing the three coal feedstocks are presented in Table 3A. The bulk of the work was done with Kentucky #9 coal from the Pyro Mining Company. Air-dried and inert-prepared Kentucky #6 coal, also from Pyro, were each used in two experiments that assessed the impact of surface oxidation of coal upon liquefaction performance.

The analyses of Kentucky #9 have been performed by three laboratories: Air Products and Chemicals, Inc. (APCI), the Pittsburgh Energy Technology Center of the Department of Energy (PETC), and Huffman Laboratories in Wheatridge, Colorado. Where these laboratories obtain different results on the same analysis, the value used for material-balance calculations is underlined.

The most serious disparity has been occurring in American Society for Testing and Materials (ASTM) dry ash determinations, crucial numbers in calculating coal conversion and the forced-ash balance product yields. The results from APCI are consistently much lower than those from the other laboratories. The ASTM D3174 ash determinations from Huffman, reported on a dry basis, have been used for all calculations; they are intermediate between the Air Products and PETC values and have been shown to be adequately reproducible on the Kentucky #9 coal. ASTM ash determinations on liquefaction residue samples agree well with values from Huffman.

The Kentucky #6 coal has about the same volatiles content as the Kentucky #9 coal. The major element analyses are also very similar. However, the Kentucky #6 coal contains significantly lower concentrations of ash and iron. This suggests that catalysis of the coal liquefaction reactions by indigenous minerals should be less pronounced in the case of the Kentucky #6 coal.

Four Wilsonville liquefaction residue samples were used as mineral-rich residue additives in these two runs: Kerr-McGee ash concentrate from Kentucky #6/11 coal, filter cake from Indiana V coal, filter cake from Emery coal, and filter cake from Kentucky #9 coal. Analytical data characterizing these samples are reported in Table 3B. The ash and iron contents of these residues differ substantially, varying from 29.6 wt % ash and only 1.1 wt % iron for the Emery filter cake to 65.3 wt % ash and 7.4 wt % iron for the Indiana V filter cake. The Emery filter cake is low in iron content and high in calcium because it was generated from a Western subbituminous coal.

Most of the experiments reported here were conducted using the Kerr-McGee ash and the Kentucky #6/11 filter cake. Compared to the Kerr-McGee ash, the filter cake residue contains substantially more ash (67.3 wt % vs. 37 wt %) and iron (7.35 wt % vs. 3.22 wt %). This difference is caused largely by the concentration of preasphaltenes (pyridine-soluble, toluene-insoluble) in the ash. Subtracting the percentage of toluene-solubles from

the pyridine-solubles leaves a preasphaltene concentration in the ash of 24.8 wt %. The filter cake, however, contains only 4.4 wt % preasphaltenes. These residues each contain 4-5 wt % of toluene-soluble asphaltenes and oils. Table 3B also gives a C, H, N, and sulfate-ash analysis of the pyridine-insoluble portion of the filter cake and Kerr-McGee ash.

Data describing the starting solvents are shown in Table 3°C. The solvents were fractionated in a laboratory vacuum flash distillation using a Vigreux column to provide moderate ureflux. The IBP-420°F light oil cut and the 420-550°F light solvent cut were recovered overhead at a distillation pressure of 100 torr. The 550-780°F heavy solvent is recovered overhead at a pressure of roughly 0.2 torr. The residual bottoms are defined as solvent-refined coal (SRC). The elemental analyses for these four standard fractions are also included in Table 3°C.

Figure 1 is a graph of the boiling point distribution of the Wilsonville recycle solvent, as measured by a gas chromatographic (GC) simulation of distillation (ASTM D2887). The data points from the laboratory Vigreux column distillation are also plotted. Note that the 420°F and 550°F cut points achieved by the laboratory distillate are in excellent agreement with the D2887 simulated distillation, but the nominal 780°F cut point in the laboratory distillation corresponds to only a 700°F cut point according to the D2887 procedure. The discrepancy seems to arise in translating the observed boiling point to a corrected atmospheric boiling point.

Figure 2 is the boiling point distribution curve for the hydrotreated creosote oil starting solvent as determined by a single-plate flash distillation.

Conditions

During CPDU Run XCL-21, product samples were collected at 31 different sets of reaction conditions, including changes in the feed slurry composition. These reaction conditions are described in Table 4 and identified by balance period number.

Liquid level control in the gas-liquid separator and the level readings in the main product receiver were somewhat erratic during much of the run. Since mid-run recalibrations indicated that the slurry feed rate readings were stable and accurate, product yield calculations assume that the slurry feed rate is correct; the main receiver product rate is adjusted to close the overall material balance.

Operation

All of the CPDU runs thus far have been conducted with once-through solvent; i.e., no effort has been made to achieve steady-state solvent composition through solvent recycle. This greatly increases the number of reaction conditions that can be examined during the course of a single CPDU run. Although none of the data points represent equilibrium, conclusions drawn from those data regarding the effect of residue addition are believed to be valid. Several closed-loop solvent recycle experiments will be conducted later to confirm this assumption.

The feed slurries were prepared at room temperature, typically in 100 to 150 kilogram (kg) batches, immediately prior to use, and stored in a charge tank equipped with a turbine agitator and a recycle pump to maintain a uniform suspension of the solids. Slurry handling has been planned to minimize consumption of recycle solvent.

The filter cake experiment began by slurrying 14 wt % filter cake in the solvent. After part of this slurry was processed, the unused portion was weighed and sufficient Kentucky #9 coal added to bring the slurry composition to 10 wt % filter cake and 30 wt % coal. Separate base-line experiments were conducted with only coal slurried in solvent, no filter cake added.

A similar procedure was followed in the experiments with Kerr-McGee ash. A slurry of 14 wt % Kerr-McGee ash in Wilsonville recycle solvent was prepared at ambient temperature and evaluated in the CPDU. This slurry was then cooked for 16 hours at 300°F in the charge tank in an attempt to dissolve the preasphaltenes from the Kerr-McGee ash that could obstruct access of reactant to the mineral surface. After cooling to ambient temperature, the cooked slurry was evaluated in the CPDU. Then the remaining slurry was weighed and sufficient coal was added to create a feed slurry of 30 wt % Kentucky #9 coal and 10 wt % cooked Kerr-McGee ash in Wilsonville solvent. A separate slurry was prepared to evaluate the effect of adding 10 wt % uncooked Kerr-McGee ash to a 30 wt % coal slurry.

The feed slurry was pumped to the CSTR from a feed tank maintained at ambient temperature. The feed tank, equipped with a recycle pump to mix the slurry, was refilled each hour from the charge tank. Whenever the feed slurry composition was changed, the feed tank was drained and then flushed several times with the new feed slurry. When reaction conditions were altered, at least 10 reactor volumes of slurry were processed through the reactor at the new conditions prior to beginning to collect any product samples for analysis.

A continuous type of reactor was selected for these experiments so that the vapor composition in the reactor, including the partial pressure of light solvent components, would match that of an SRC-I dissolver. The stirred autoclave design of the CSTR ensures that the coal minerals are well mixed and do not accumulate in the reactor. Cold-flow experiments, conducted in a Plexiglas model, have confirmed that the flat-bladed turbine agitator of the CSTR keeps the solids well distributed throughout the reactor volume, so that coal minerals will not accumulate.

Although the propensity of baffles to coking prohibits baffling the reactor, the thermowell effectively kills the vortex and the void fraction is only 0.13. Because all the sensible heat to bring the slurry to reaction temperature is provided by resistance heating of the reactor, the reactor wall is about 25°F hotter than the bulk slurry.

The product gas and slurry leaving the CSTR are quenched to 325°F to freeze the reactions, before flowing to a gas/liquid separator, at reactor pressure. The product slurry is throttled into the product receiver, at a rate that maintains a constant, small inventory in the separator.

Water, light hydrocarbons, and gases, which flash from the product slurry in the 30-psig receiver, are combined with the product gas stream from the separator. The combined gas stream is cooled to about 60°F to condense the water and light organics, prior to entering the gas chromatograph and dry test meter for product gas yields and volume measurement.

Product Work-up

Two product slurry samples [1 to 1.5 liters (L)] were collected at each set of reaction conditions. The first product sample was vacuum-distilled to recover the 550-780°F heavy solvent fraction, which was added to the second product sample to facilitate handling and filtration. The second sample was topped at 550°F to permit a vacuum filtration of the remaining heavy solvent and the SRC and residue fractions to be conducted at 400°F without excessive flashing of the filtrate.

The filter cake was collected on Whatman #5 paper, boiled in pyridine, washed with toluene, and dried under vacuum at 210°F, to yield the ash/unconverted coal residue fraction. The filtrate was distilled at 0.2-1.0 torr to separate the heavy solvent from the SRC bottoms fraction.

In calculating product yields, the SRC and heavy solvent yields were algebraically corrected to account for losses to the wet filter cake and on the glassware. The residue yield was adjusted to force the overall ash balance to close.

Since the vacuum distillations were essentially single-plate flashes, using a Vigreux column to achieve adequate reflux but no more than one or two plates, the distillate cuts overlapped each other in boiling range to a significant degree. In Figure 3 the boiling range distribution, as determined by GC-simulated distillation, is graphed for each of the standard distillation cuts. Note, for example, that the nominal 420-550°F boiling cut contains 15 wt % of material boiling below 420°F and about 11 wt % boiling above 550°F.

A more serious problem with the laboratory distillation was the difficulty in reaching the 780°F end point. An 850°F end point had been the target; however, in the laboratory batch distillation 780°F was the maximum end point that could be achieved and even this could not be done consistently. A 98 wt % recovery point is difficult to achieve with any precision since the product is beginning to crack significantly as the cut point is approached, such that the vacuum degrades and the cut point must be taken at variable total pressure. In fact, this cut point was made at distillation pressures between 0.2 and 1.2 torr (exceeding 0.35 torr on only two occasions).

The GC-simulated distillation procedure, ASTM D2887, was used to determine the boiling point distribution for the distillate liquid, so that the yield of a standard 450-700°F solvent fraction could be mathematically determined. The 700°F end point for this fraction was the highest end point that could be selected without significant loss to the bottoms of material boiling within the prescribed range for any of the product samples.

The SRC (vacuum bottoms) was fractionated into oils, asphaltenes, and preasphaltenes by a solvent extraction procedure which does not recover the fractions for analysis. A 1-gram (g) sample of the SRC was added to 200 mL of heptane and allowed to stand at 75°F, with intermittent sonication, for two hours in order to leach the heptane-soluble oils. The residue was recovered by filtration, washed with heptane, and dried. The weight loss was equated to oil content.

The concentration of toluene-soluble oils plus asphaltenes in an SRC sample was similarly determined. A 1-g sample of SRC was added to 200 mL of toluene and allowed to stand at 75°C for two hours prior to recovery of the toluene-insoluble residue by filtration.

RESULTS: REACTIONS OF SOLVENT WITHOUT COAL

Wilsonville recycle solvent and creosote oil, without added coal or mineral residue, were reacted in the CPDU at typical coal liquefaction reaction conditions. The purpose of these tests was to ascertain the extent to which these solvents would crack or hydrogenate/dehydrogenate in the presence of 2,000 psig hydrogen pressure, through strictly thermal reactions with no added coal or mineral residue to serve as catalyst or to exert a hydrogen demand on the solvent. Creosote was totally unreactive, but Wilsonville recycle solvent lost hydrogen and experienced moderate cracking to hydrocarbon gas.

These experiments were then repeated with the addition of various mineral-rich residues to determine whether the minerals would catalyze solvent hydrogenation and/or cracking.

The mineral residue had little effect. Creosote oil was hydrogenated to a small degree; the Wilsonville solvent lost hydrogen as it had in the earlier experiments without added residue. A substantial amount of the preasphaltenes and insoluble organic matter (IOM) in the residues was converted to pyridine and toluene solubles.

Solvent Hydrogenation

Solvent hydrogenation is believed by many investigators to be the key transfer step for incorporating gaseous hydrogen into the final product. The transfer of combined hydrogen from process solvent to coal and coal products is assumed to be rapid and readily attained. But the reaction of molecular hydrogen (H_2) with the solvent is a slower and more difficult step. The incentive for establishing whether or not the presence of reactor solids is crucial in the SRC-I reactor is the need to determine the specific effect these solids may have on the reaction of molecular hydrogen with the solvent.

The reaction conditions in these experiments were the same as for the coal processing portion of the run discussed below. The conditions under which the solvent was tested in the laboratory compare as follows with those at Wilsonville during generation of the solvent in Wilsonville Run 166:

	Temp (°F)	Pressure (psig)	Partial pressure hydrogen, inlet (psig)	Hydrogen rate (wt % feed)	Space velocity (hr)	Coal in feed (wt %)
XCL-21	815, 850, 885	2,000	2,000	2.2	2	0
Run 166	825	2,100	1,400	3.6	1.7	38.5

Wilsonville Solvent. Products produced in these experiments were filtered and the hydrogen contents of the filtrates determined. Hydrogen content of the filtered liquid product was less than that of the feed solvent in every case. In these experiments the hydrogen concentrations were measured for full-range solvent rather than the 420-780°F cut used in other comparisons of this study.

The different hydrogen contents for the starting solvent listed in Table 5 reflect the interaction between the solvent and residues as well as minor contamination of transfer lines. Starting solvent hydrogen content was determined by analyzing the filtrate obtained from the feed slurries prior to processing through the CPDU. By following this procedure, the error associated with removing hydrocarbon materials from the residues was largely eliminated. Also, by following this procedure, any contamination due to residual solvents in the transfer lines, specifically creosote, was accounted for, since samples of feed slurry were taken from the process unit immediately upstream of the feed pump. For example, the lower hydrogen concentration for the filter cake sample in Table 5 probably reflects creosote contamination of the transfer line.

The probability of leaching carbonaceous material from the residue or binding solvent molecules to the residue, especially the Kerr-McGee residue, is evident from an analysis of the Kerr-McGee ash and Wilsonville residues (Table 3B). Kerr-McGee ash material used

in this study contained 4.2 wt % toluene solubles and 29 wt % pyridine solubles. In fact, the purpose of cooking the ash in the solvent at 300°F for 16 hours prior to starting the experiment was to dissolve as much of this hydrocarbon material as possible in order to expose the ash surface. The room temperature interaction of Wilsonville solvent with Kerr-McGee results in a 20% increase in the toluene-insoluble carbonaceous matter in the ash.

The solvent alone lost hydrogenation in every case, the loss varying inversely with temperature. The addition of 14 wt % residue did not significantly change the results.

The changes in hydrogen content relative to the starting solvents fell between 0.1 and 0.4 wt % as shown in Figure 4, where solvent hydrogen loss is plotted vs. temperature. At 850°F the loss of the hydrogen from the starting solvent was slightly higher when filter cake was added to the feed. At 885°F the relative order in hydrogen change remained the same even though all the changes increased.

The changes in solvent hydrogen content were small, but they followed a consistent pattern and appear to be real. The loss of hydrogen at 815°F was surprising. This was a lower temperature and higher hydrogen partial pressure than the Wilsonville reaction conditions (Run 166) at which this solvent had been generated. Therefore, since the solvent must contain less than the chemical equilibrium hydrogen content at 815°F and 2,000 psig H_2 pressure, a net hydrogenation would be expected. A limited amount of solvent cracking to gas occurred. Since the product gas contained a high weight percent of hydrogen, gas formation tended to reduce the hydrogen content of the remaining liquid. For example, the cracking of a methyl group removed a substituent containing 25 wt % hydrogen.

The added liquefaction residues contained SRC and unconverted coal and, therefore, exerted a small hydrogen demand upon the solvent as these large organic molecules cracked and formed free radicals that had to be terminated by hydrogen. However, the hydrogen demand exerted by the carbonaceous portion of the residue was minuscule compared to the hydrogen demand exerted by the 38.5 wt % coal present during the Wilsonville run in which the starting solvent was generated.

Data presented below show that processing a 10 wt % cake/30 wt % coal slurry at identical reaction conditions (815°F) resulted in a net hydrogenation of the solvent.

Creosote Oil. Creosote oil was also hydrogenated in a wholly thermal reaction without added coal or filter cake. These experiments were conducted at a superficial liquid hourly space velocity of 2 hours⁻¹, with a hydrogen feed rate equal to 2.2 wt % of the feed. Reaction temperatures of 780, 815, 845, and 885°F were investigated at a system pressure of 2,000 psig; a reaction temperature of 850°F was tested at a reduced system pressure of 1,000 psig.

As seen in Table 6, creosote oil was virtually inert over this range of reaction conditions. The hydrogen content, sulfur content, and number-average molecular weight of the product liquid were all unchanged from the creosote oil feed parameters, within the analytical precision. The maximum gas yield, which occurred at 885°F, was equivalent to only 0.2 wt % of the creosote oil feed. Judging from the data in Table 6, the hydrogen elemental analysis has a very high precision and should detect any change in solvent hydrogen content of greater than 0.1 wt %.

The addition of 25 wt % of filter cake derived from Emery coal provided a minor catalytic enhancement of creosote oil hydrogenation. The maximum hydrogenation occurred at 850°F and 2,000-psig pressure and was only 0.35-0.56 wt %. Hydrogenation was very limited at the other reaction conditions, being generally less than a 0.2 wt % increase in the solvent's hydrogen content, as these observations show:

		Absolute wt % increase in solvent hydrogen content (Emery filter cake)			
		780°F	815°F	850°F	885°F
2,000 psig		0.06	0.22	0.35-0.65	0.13
1,000 psig		—	—	0.10	—

At 885°F the increase in solvent hydrogen content was only 0.13 wt %. This small degree of net hydrogenation may have been caused by the loss of hydrogen-rich alkyl side groups from the solvent molecules as a result of increased cracking at this high reaction temperature. The hydrogen content of the creosote oil is so low in comparison to Wilsonville solvent that any chemical equilibrium limitation of hydrogenation at 885°F is difficult to accept.

Since the Emery filter cake is low in ash content and is especially deficient in iron, this experiment was repeated using Kentucky #9 filter cake. At the identical process conditions studied above, the following increases in solvent hydrogen content were observed:

		Absolute wt % increase in solvent hydrogen content (Ky #9 filter cake)			
		780°F	815°F	850°F	885°F
2,000 psig		0.35	0.31	0.34	0.37
1,000 psig		—	—	0.33	—

These increases in solvent hydrogen content are small, considering the very low hydrogen content of the starting solvent, and are not a function of reaction temperature. Another study has shown increases in solvent hydrogen of twice this magnitude from the reaction of coal and creosote oil at identical reaction conditions. Therefore, filter cake is, at best, a poor catalyst for creosote oil hydrogenation.

Solvent Cracking

As evidenced by the product gas yields reported in Table 7, a small but significant amount of solvent cracking took place during the thermal reaction of Wilsonville process solvent in a hydrogen atmosphere without added coal or minerals. The gas yield is temperature-sensitive, ranging from 0.3 wt % of the solvent at a reaction temperature of 815°F to 2.4 wt % of the solvent at a reaction temperature of 885°F. All of the data were collected at a liquid hourly space velocity of 2 hours⁻¹ under 2,000-psig hydrogen pressure. Virtually no H₂S or NH₃ was detected in the product gas, which consisted primarily of hydrocarbons, with methane predominating.

The addition of 14 wt % residue, either Indiana V filter cake or Kerr-McGee ash, to the feed solvent resulted in slightly greater yields of product gas. The low gas yield achieved at 850°F with added uncooked Kerr-McGee ash does not fit the pattern of the other data points and may be incorrect.

The total extent of solvent cracking is shown in Figure 5, which is a boiling point distribution curve for the entire feed or product stream, including product gas but excluding solids. The top curve of Figure 5 is the boiling point distribution, in weight percent, of the

starting Wilsonville solvent. The lower curve is the boiling point distribution of the filtered product (gas included) for the case in which Wilsonville solvent plus 14 wt % added Indiana V filter cake was reacted at 885°F. This is the case in which the greatest amount of cracking took place. The lower curve shifts 5 wt % to the right compared to the virgin Wilsonville solvent. About half of the shift represents the product gas yield; most of the remainder arises from the small quantities of organic condensate and water which were produced.

Also plotted in Figure 5 are the boiling point distributions for the filtered product (including gas) from the reaction at 850°F of Wilsonville solvent with 14 wt % of cooked Kerr-McGee ash and Indiana V filter cake.

The product gas yields from the experiments with creosote oil solvent are reported in Table 8. Without added residue, creosote oil yields almost no product gas, the maximum being 0.2 wt % at 885°F. This compares to a gas yield of 2.4 wt % from Wilsonville solvent at 885°F. A difference in gas yield of this order of magnitude indicates that the rate of solvent cracking is a strong function of solvent composition. The proton nuclear magnetic resonance analysis of the hydrogen distribution for these solvents below suggests that the Wilsonville solvent should be more prone to thermal cracking:

	Absolute wt % of hydrogen as	
	<u>H_O (0-2 ppm)</u>	<u>H_α (2-3.5 ppm)</u>
Wilsonville solvent	4.4	2.7
Creosote oil	0.3	0.9

The concentration of H_O is a good indicator of the concentration of saturates and of alkyl side chains on the solvent molecules. The H_α concentration is a reasonably good measure of the concentration of hydroaromatic rings. The alkyl side chains are subject to thermal cracking that will produce hydrocarbon gas directly. Hydroaromatic rings can undergo ring-opening cracking reactions, creating side chains that may subsequently yield hydrocarbon gas. Creosote oil is deficient in side chains and hydroaromatic rings because it is produced under high-temperature coking conditions.

The addition of 25 wt % Kentucky #9 filter cake to the creosote oil feed significantly increased the gas yield. At 885°F the gas yield was increased to 1 wt % of the solvent. The addition of 25 wt % of Emery filter cake had an even larger impact upon the product gas yield, increasing it to 2.4 wt % at 885°F.

Thus, the composition of the added filter cake also seems to substantially affect the gas yield. Emery coal is a Western subbituminous coal which gives rise to a filter cake containing only 29.3 wt % dry ash, compared to 57.6 wt % dry ash in the Kentucky #9 filter cake. Since the Emery filter cake has a low ash content, the extra product gas obtained in the Emery filter cake experiment probably arose from gasification of the high concentration of organic constituents in the filter cake, rather than from increased mineral catalysis of solvent cracking. And the bulk of the 1 wt % product gas yield observed at 885°F upon the hydrogenation of creosote oil with added Kentucky #9 filter cake may also have originated from the filter cake rather than from the solvent.

Reaction of Residue in Solvent

The carbonaceous portion of the liquefaction residues used in these experiments consists of a mixture of coal macerals, primarily vitrinite and fusinite, vitroplast, preasphaltenes,

some asphaltenes and oils, and a small amount of coke. These entities would not be expected to pass through the CSTR as inerts in the reaction of solvent/residue slurries. A considerable fraction of the toluene-insoluble species is converted to toluene-soluble products.

Reaction of Kerr-McGee Ash Concentrate in Wilsonville Solvent. The Kerr-McGee ash used in these experiments contained 29 wt % of carbonaceous material that is soluble in pyridine; 25 of the 29 wt % is toluene-insoluble and is classed as preasphaltenes. The reason for precooking the Kerr-McGee ash in Wilsonville solvent for 16 hours at 300°F was to dissolve the preasphaltenes so that the mineral surface was exposed and able to function as a catalyst.

To determine whether or not this pretreatment step was successful, the solid residue was filtered from a precooked feed slurry sample and also from an uncooked feed slurry sample. The residue was washed with toluene to remove the solvent, dried, and analyzed. The analysis consisted of a qualitative petrographic examination as well as ASTM D3174 ash and carbon determinations.

The quantity of carbonaceous material that was dissolved by the solvent can be computed from the change in the carbon/ash ratio. The results of the petrographic analyses and this calculation are summarized in the first two rows of Table 9.

Slurrying the Kerr-McGee ash in Wilsonville solvent at ambient temperature actually increased the concentration of pyridine-soluble carbonaceous matter (preasphaltenes) by 20%. This may have been caused by a chemical or physical interaction between the solvent and the preasphaltenes which bound the solvent to the Kerr-McGee ash particles. The pretreated feed slurry showed only a 10% increase in the preasphaltene content of the recovered Kerr-McGee ash. This suggests that the pretreatment step removed only a small fraction of the preasphaltenes from the Kerr-McGee ash and that the Kerr-McGee ash particles still bound some solvent.

The petrographic analyses showed that the solids recovered from these two feed slurries were similar. In each case, vitroplast was the primary constituent and more than 50 vol % of this vitroplast had an abnormal cenosphere appearance, with mineral and coal maceral particles incorporated into (and completely covered by) the cenospheric vitroplast. The petrographer believed that the vitroplast in these cenospheres could be preasphaltenes rather than true vitroplast, which consists of thermally altered vitrinite macerals.

The second most common constituent of these residues was granular residue. This is a conglomeration of carbonaceous and mineral particles that are too fine to definitively classify. The third major constituent was unconverted vitrinite macerals. Since vitrinite is the most readily converted of the coal macerals, this material might be expected to be reactive during the coal liquefaction experiments and to be converted to pyridine-soluble products. Each of these residues contains less than 1 vol % of semi-coke. Semi-coke is believed to be inert in coal conversion processes.

The product slurries from the reaction of 14 wt % Kerr-McGee ash in Wilsonville solvent were also recovered for analysis via filtration and washing with toluene. The same analyses discussed above were performed on these recovered residue samples. Additionally, the recovered residues were boiled in pyridine to remove the preasphaltenes and the pyridine-insoluble fraction was then analyzed for carbon and ash. This permitted the fractional conversion of the pyridine-insoluble carbonaceous matter in the original Kerr-McGee ash to be calculated separately from the fractional conversion of the preasphaltenes.

The residues recovered from the 815°F product slurry evidenced a significant conversion of the carbonaceous portion of the Kerr-McGee ash. About half of the preasphaltenes

and 13 wt % of the pyridine-insoluble carbonaceous matter was converted during the reaction.

Petrographic analysis revealed that vitropast concentration was sufficiently reduced so that granular residue had replaced vitropast as the predominant species. However, 30-50% of the remaining vitropast was still of the cenosphere form. The semi-coke concentration had increased slightly.

At a reaction temperature of 850°F, 17% of the pyridine-insolubles and 59 wt % of the preasphaltenes were converted. The cenospheres had been largely eliminated, but semi-coke constituted over 5 vol % of the recovered residue.

At 885°F, 20% of the pyridine-insolubles and 81% of the preasphaltenes were converted. The petrographic report is the same as for the 850°F sample.

The data suggests the following conclusions:

1. The cenosphere vitropast is composed of preasphaltene.
2. The preasphaltenes are substantially converted to toluene-solubles at reaction temperatures of 815°F or above.
3. At temperatures above 850°F, a significant portion of the preasphaltenes is coked.

The third conclusion is based upon the petrographer's characterization of more than half of the coke present as mesophase coke formed from SRC.

Reaction of Filter Cake in Creosote Oil. As noted above, a feed slurry of 25 wt % Kentucky #9 filter cake in creosote oil solvent was hydrogenated in the CPDU at the same reaction conditions as those investigated for the Kerr-McGee ash in Wilsonville solvent. The product slurries from these experiments were filtered to retrieve the reacted filter cake. The recovered filter cake was boiled in toluene to remove any solvent or SRC asphaltenes clinging to the particles. The washed solids were then ashed and the extent to which the carbonaceous matter converted to toluene-soluble products was calculated. Following is the fractional conversion of toluene-insolubles (coke, unconverted coal, and preasphaltenes) as a function of reaction temperature:

Temperature (°F)	Ash in toluene-insolubles (wt %)	Conversion (wt %)
780	59.2	11
815	62.1	21
850	64.3	28
885	67.6	38
Feed	56.3	

All of the above data were collected at a reaction pressure of 2,000 psig. At 1,000 psig and a reaction temperature of 850°F, the calculated conversion was 27 wt %. The very slight dependence upon reaction pressure suggests that coking is not significant, at least at reaction temperatures below 850°F. Indeed, the measured conversion increased sharply with the reaction temperature, the conversion at 885°F being about 1/3 higher than the conversion at 850°F.

RESULTS: COAL LIQUEFACTION EXPERIMENTS

The product slurries from the coal liquefaction experiments, with or without added mineral residue, were separated into the following product fractions by means of the dis-

tillation-based fractionation procedure described in the experimental design section: IBP-420°F light oil (IBP, initial boiling point); 420-550°F light solvent; 550-780°F heavy solvent; 780°F+ solvent-refined coal (SRC); and pyridine-insoluble residue.

The SRC fractions were subjected to solubility analyses. Hot heptane and hot toluene divided the fraction into heptane-soluble SRC oils, heptane-insoluble but toluene-soluble asphaltenes, and the toluene-insoluble preasphaltenes. The SRC subfractions were not isolated from the separation solvents for elemental analysis.

Calculations of product, hydrocarbon gas, heteroatom gas, and water yields were based upon a forced-ash balance between the total feed and product streams, in which the weight of the residue fraction in the product stream is adjusted to force this balance. The relative weights of the other product slurry fractions with respect to each other are not affected since the absolute quantity of each is changed by the same correction factor. The absolute weights of product gases and water are not adjusted.

Reaction of Coal in Wilsonville Solvent

To provide a base line from which to assess the effect of added mineral residues, the reaction of Kentucky #9 (Pyro) coal in Wilsonville solvent was studied at coal concentrations of 20, 30, and 40 wt %. The reaction conditions coincided with those used for the mineral residue/solvent experiments, namely, 2,000-psig pressure; liquid hourly space velocity (LHSV) of 2 hours⁻¹; 815, 850°F; H₂ rate, 2.2 wt % of total feed. The results of this study are summarized in Tables 10 and 11.

At both reaction temperatures, increasing the coal concentration improved both the coal conversion and the total oil yield. The preasphaltene yield did not change significantly. This may be at variance with the belief that reaction severity can be correlated in terms of coal loadings, i.e., pounds of coal per cubic foot per hour, based upon dissolver volume. With this correlation, doubling the coal concentration from 20 to 40 wt % should adversely affect yields to the same extent as increasing LHSV by a factor of two.

Coal Conversion. At a reaction temperature of 815°F, the coal conversion increased from 86.5 to 89.7% when the coal concentration was increased from 20 to 40 wt % (see Figure 6). At a coal concentration of 30 wt %, an intermediate conversion level of 87.9% was achieved. At a reaction temperature of 850°F, the coal conversion was 88.7 and 88.3% for 20 and 30 wt % coal in the feed slurry, but increased to 89.7% for a 40 wt % coal slurry. Increasing the reaction temperature resulted in slightly higher coal conversions at each of these coal loadings.

Solvent Hydrogen Content. In all cases, the 420-780°F solvent fraction recovered from the product slurry contained less hydrogen than the corresponding boiling cut from the feed solvent. As seen in Figure 7 the hydrogen content of the recovered solvent did not vary consistently as a function of coal concentration. While the recovered solvent hydrogen content was roughly constant at 8.9-9 wt % at the 850°F reaction temperature, it decreased slightly from 9 to 8.7 wt % when the coal concentration was increased from 20 to 40 wt % at the 815°F reaction temperature.

Surprisingly, the reaction temperature had almost no impact upon the recovered solvent hydrogen content. Also, the reduction in hydrogen content of the recovered solvent was no greater than that reported earlier for the reaction of the solvent alone.

Hydrogen Consumption. The reason that increasing the coal concentration or the reaction temperature did not reduce the recovered solvent hydrogen content is that both

of these changes caused a substantial increase in the absolute weight of gaseous hydrogen that was consumed.

In Figure 8 the absolute volumetric reaction rate for gaseous hydrogen consumption, in grams/liter-hour, is plotted as a function of coal concentration, at each of the reaction temperatures. Although one or both of the data points at 20% coal concentration appear to be in error, the trends are clear. At 40% coal concentration, increasing the reaction temperature from 815 to 850°F causes a marked increase in gaseous H₂ consumption from 6.3 to 10.9 g/L-hr. A similar increase was noted at 30% coal concentration. However, at the 20 wt % coal concentration the calculated H₂ consumption was slightly higher at 815°F, which does not seem reasonable. Increasing the coal concentration from 30 to 40 wt % caused the H₂ consumption to increase by about one-third at each of these reaction temperatures.

The total hydrogen consumed by the coal, including the net hydrogen donated by the solvent, was not a significant function of coal concentration. However, the total hydrogen consumption did increase from 1.2 to 1.4 wt % (MAF coal basis) to 1.5 to 1.8 wt % as the reaction temperature was increased from 815 to 850°F.

Gas Yield. As shown in Figure 9, the yield of hydrocarbon gas is a very strong function of reaction temperature. The hydrocarbon gas yield reported for the 40 wt % coal slurry at 815°F appears to be too large. Ignoring this point, an increase in reaction temperature from 815 to 850°F is seen to result in more than a doubling of the hydrocarbon gas yield.

There is a general trend toward reduced hydrocarbon gas yield at increased coal concentration. This occurs because hydrocarbon gas can be produced by cracking of the solvent as well as from the coal. If the fraction of the solvent that is cracked is largely independent of coal concentration, then the yield of hydrocarbon gas from the solvent will look much greater at reduced coal concentrations, when reported on an MAF coal basis.

In the first section discussing results, the gas yield from cracking Wilsonville solvent by itself at these reaction conditions was reported to be 1 wt % of the solvent at 850°F and 0.3 wt % of the solvent at 815°F. The gas yields from solvent alone can be restated on a weight percent MAF coal basis for each of the feed slurry compositions and then subtracted from the observed gas yields from the coal slurry experiments in order to derive the hydrocarbon yields arising directly from the coal. The correction terms to be subtracted from the observed hydrocarbon gas yields are:

	Gas from solvent, wt % MAF coal		
	20% coal	30% coal	40% coal
815°F	1.4	0.8	0.5
850°F	4.6	2.7	1.7

The estimated hydrocarbon gas yields from the coal slurry experiments are graphed in Figure 10. These values represent our best estimate of the coal-derived hydrocarbon gas yield. Although this estimated gas yield is constant at 850°F over the 20-40 wt % range of coal concentration, it varies to a large, but seemingly random extent at the 815°F reaction temperature. This suggests that the yield of hydrocarbon gas derived from coal is not a function of coal concentration.

The heteroatom gas yield in relation to coal concentration in Figure 11 shows random fluctuations that are apparently due to experimental error. Heteroatom gas includes CO, CO₂, H₂S, and NH₃. The heteroatom gas yield ranged from 1.8 to 2.9 wt % of the MAF coal and was generally larger at 850°F than at 815°F. Since Wilsonville solvent by itself has a

negligible heteroatom gas yield, a correction for the heteroatom gas from the solvent would not alter these results significantly.

The water yields also display considerable scatter, as is evident from Figure 12. The water yield varies between 1.5 and 3.5 wt % on an MAF coal basis. Water yield increases slightly as reaction temperature increases from 815 to 850°F. Except for the 850°F point at 40 wt % coal concentration, these data suggest that water yield is reduced by increasing the coal concentration in the feed.

Distillate Yield. Because of fluctuations in the distillation cut points, the yields of the various liquid fractions are highly uncertain. For completeness, the yields of the individual liquid fractions are reported in Tables 10 and 11, although we do not have great confidence in these values. The total yield of IBP-780°F distillate is graphed in Figure 13 as a function of coal concentration and reaction temperature. The total distillate yield shows up generally higher at a reaction temperature of 815°F than at 850°F, but the data are really not consistent enough for drawing conclusions. Note, however, that total distillate yield was always positive.

A clearer picture is obtained if the total distillate yield is added to the SRC oils yield to give the total yield of heptane-soluble oils. This eliminates errors introduced by imprecision in the distillation cut points; the accuracy is wholly dependent upon the precision to which the heptane-soluble oils in the SRC can be measured.

This total oil yield is depicted in Figure 14. It increases fairly sharply, from 3.2 to 11.8% on an MAF weight percent basis, as the coal concentration is doubled from 20 to 40 wt % at a reaction temperature of 815°F.

The same trend is noted at the 850°F reaction temperature, although the oil yield shown for the 20 wt % coal slurry looks a bit high. Significantly, an increase in the reaction temperature from 815 to 850°F reduced the total oil yield. Since the Wilsonville Pilot Plant distills to a higher cut point (typically 850°F) in their continuous still than we can achieve in our laboratory still, this total oil measure probably corresponds fairly closely to a Wilsonville total distillable liquid yield. Based on our heptane-soluble oil determination procedure, Wilsonville SRC contains only a few percent of oils.

Another means of leveling out errors caused by fluctuating distillation cut points is to use the GC-simulated distillation of the distillable product to define the yield of a solvent over a narrow boiling range—one sufficiently removed from the 780°F cut point so that imprecision in that cut point will not affect the quantity of material within a narrow solvent boiling range.

A review of GC-simulated distillation results suggested that 450-700°F was an appropriate standard boiling range for the calculation of a solvent yield that would not be affected by distillation errors. The yields of 450-700°F solvent by GC are reported at the bottom of Tables 10 and 11, and graphed in Figure 15. Again, although there is some scatter in these data, the trends are reasonably clear. The yields of 450-700°F solvent are 6 to 15 wt % (MAF basis) higher at 815°F than at 850°F.

Increasing the coal concentration markedly increases the solvent yield, which agrees with the conclusion based upon total oil yield. At a reaction temperature of 815°F the solvent yield increased from 5.9 to 15.9 wt % (MAF basis) upon doubling the coal concentration in the feed from 20 to 40 wt %. However, the correspondence between the yield of full-range 420-850°F solvent and the yield of this 450-700°F solvent fraction may be tenuous.

Preasphaltene Yield. Probably the most sensitive indicator of coal conversion and/or regressive polymerization reactions is the net yield of the toluene-insoluble, pyridine-soluble preasphaltenes. The preasphaltene yield is graphed in Figure 16. At both reaction temperatures the preasphaltene yield was roughly the same for the 40 wt % coal slurry as

for the 20 wt % slurry. However, the preasphaltene yield was inexplicably higher at the 30 wt % coal slurry concentration.

The preasphaltene yield was lower at 850°F than at 815°F, indicating that this increase in reaction temperature enhanced the net conversion of preasphaltenes. This suggests that regressive polymerization reactions are not a serious problem at reaction temperatures of 850°F or less. The reduction in oil yield with increased reaction temperature can be explained by the increased cracking of oils to produce product gases as the reaction temperature is increased.

Kinetic Constants. Based upon the simplified sequential first-order kinetic model illustrated below, volumetric kinetic constants, based upon *grams* conversion per unit volume, for the conversion of coal, preasphaltenes, and asphaltenes were calculated.

This is an overly simplified model; for example, it ignores gas formation from coal, preasphaltenes, and asphaltenes. The experimental kinetic constants, and the formula for calculating them, are shown in Table 12. Surprisingly, these observed kinetic constants show virtually no temperature dependence. Increasing the coal concentration seems to increase the kinetic constants for preasphaltene and asphaltene conversion.

Reactions of Coal Slurries Including Mineral Residue

The purpose of this part of Run XCL-21 was to ascertain whether the addition of mineral-rich Wilsonville liquefaction residues enhanced the coal liquefaction reactions via mineral catalysis of solvent hydrogenation or other coal conversion reactions.

Two mineral residues were studied: Indiana V filter cake and Kerr-McGee ash from Kentucky #9/11 coal. The Kerr-McGee ash was evaluated both with and without the previously described 300°F precooking step. In each case, the residue concentration in the feed slurry was 10 wt %. The concentration of Pyro Kentucky #9 coal in the feed slurry was 30 wt %. Reaction conditions were identical to those studied with the coal slurries in the preceding section: 2,000 psig; 815, 850°F; LHSV = 2 hours⁻¹; H₂ rate, 2.2 wt % of total feed; Wilsonville recycle solvent (Run 166).

The results from the experiments at 850 and 815°F are reported in Tables 13 and 14. Data derived from the liquefaction of a 30 wt % coal slurry without added residue are also included in these tables as points of comparison with the results of adding residue.

The data indicate that filter cake exerts a catalytic action in the coal conversion reactions, causing an increased hydrogen consumption and a more favorable net product slate. Filter cake addition also increases the hydrogen content of the recovered recycle solvent. The effects of adding Kerr-McGee ash, apart from increased net coal conversion, are less significant and less consistent.

Coal Conversion. The net coal conversion to pyridine-soluble products is plotted in Figure 17. In calculating conversion, the pyridine-insoluble carbonaceous material in the added residues was assumed to be inert. As will be discussed below, this causes the net coal conversion to be understated, since our past work with residues plus solvents has shown that some conversion of the pyridine-insolubles in the residue does occur.

Filter cake addition had little effect upon conversion, which increased from 87.9 to 89.1% at 815°F but did not change at 850°F. The addition of Kerr-McGee ash or cooked

ash markedly increased conversion to a high of 96.5%. This increased conversion did not necessarily arise from any catalytic action on the part of the coal minerals in the residue. Rather, it may have resulted simply from the increased weight of coal charged to the reactor. Coal includes the unconverted coal present in the residue additives, which is treated as potentially reactive feed coal.

The total coal loadings in the 850°F experiments are listed in Table 15. Addition of 10 wt % of Kerr-McGee ash or cooked ash to the feed slurry is seen to increase the concentration of potentially reactable coal by 11.3%. Addition of an equal quantity of filter cake increases the coal concentration by only 7.9%.

The second row in this table lists the relative quantities of unconverted coal recovered from the product slurry of each of these experiments. In each case, residue addition resulted in a substantial increase in the quantity of unconverted coal in the product. The net yield of unconverted coal is calculated by subtracting the unconverted coal in the added residue from the unconverted coal in the product.

Solvent Hydrogen Content. The hydrogen concentration in the 420-780°F solvent recovered from the product slurries is shown in Figure 18. The addition of Kerr-McGee ash or cooked ash reduced the recovered solvent's hydrogen content by 0.1-0.2 wt %, while the addition of filter cake increased the hydrogen content of the recovered solvent by 0.1 wt % at 850°F and by 0.4 wt % at 815°F. The starting solvent contained 9 wt % hydrogen.

As we have noted, addition of 14% filter cake to 86% Wilsonville solvent at the same identical reaction conditions resulted in a reduction in solvent hydrogen content of 0.3 wt % at 850°F. Furthermore, the reaction of 30% Kentucky #9 coal/70% Wilsonville solvent resulted in no change in solvent hydrogen content—0 wt % at 815°F and a reduction of only 0.1 wt % at 850°F. But the reaction of solvent alone resulted in a reduction in hydrogen content—0.1 wt % at 815°F and 0.2 wt % at 850°F. Therefore, coal appears to facilitate solvent hydrogenation, either by acting as a catalyst or by reacting directly with molecular hydrogen and then possibly transferring hydrogen to the solvent—but this needs further study.

Increasing the reaction temperature reduces the hydrogen content of the recovered solvent. However, the change was significant only for the experiments with filter cake.

Hydrogen Consumption. The H_2 gas consumption can be computed by performing a hydrogen elemental balance between the feed slurry and the total product streams, with the increase in product hydrogen content being equated to gaseous H_2 consumption. Figure 19 shows that this gaseous H_2 consumption increased slightly on addition of 10 wt % Kerr-McGee ash to the feed and increased markedly on addition of filter cake. Increasing the reaction temperature generally caused a slight increase in the H_2 gas consumption.

At a reaction temperature of 850°F, the addition of 10 wt % filter cake resulted in an increase in the H_2 gas consumption from 1.3 wt % of the MAF coal to 2.4 wt %. At 815°F the increase was more dramatic: from 1.1 wt % to 3 wt % of the MAF coal. This latter value appears to be high, but it is consistent with the observed increase in solvent hydrogen content as determined by separate analyses of the 550-780°F solvent reaction and the full-range 420-780°F solvent.

As a double-check of these values, the H_2 gas consumption was also calculated from an H_2 gas balance between the feed and product gas streams. The results of this calculation, which is generally less reliable than the above method, are presented in Figure 20. The conclusions to be drawn from the two sets of data differ significantly. Here filter cake and Kerr-McGee ash exert the same minor degree of catalysis upon the consumption of H_2 gas. Additionally, these results show a much stronger effect of reaction temperature upon H_2

gas consumption. Future experiments should confirm which trend is correct, but past experience suggests that the data in Figure 19 are more reliable.

Since the experiments were conducted with non-steady-state, once-through solvent, the solvent can be either a net donor or a net consumer of hydrogen. Therefore, the total quantity of hydrogen consumed by the coal conversion reactions is the sum of the H_2 gas consumption and the net donation of hydrogen by the solvent, which may be negative. This total hydrogen consumption, which is shown in Figure 21, is believed to represent the best approximation possible of the hydrogen consumption (from gas) that would occur in closed-loop operation (solvent recycle) at these reaction conditions.

The addition of both Kerr-McGee ash and filter cake increases total hydrogen consumption to a moderate extent, with filter cake causing a somewhat larger increase. At a reaction temperature of 815°F the total hydrogen consumption is increased from 1.2 wt % with no additive to 1.5-1.7 wt % with Kerr-McGee ash and to 2.1 wt % with filter cake. A similar trend is observed at the 850°F reaction temperature. In all cases, the total hydrogen consumption was higher (by 0.3-0.6 wt %) at 850°F than at 815°F.

Gas Yield. The yield of hydrocarbon gases is plotted in Figure 22. The addition of mineral residue caused little change. At 815°F, the yield was 2.4 wt % of the MAF coal without residue added and 2.7-4.3 wt % with residue added. The largest gas yield was observed when filter cake was the residue.

At 850°F, the hydrocarbon gas yield was 7.1 wt % without residue and 6.7-8.3 wt % with residue. In this case, the largest gas yield accompanied the addition of cooked Kerr-McGee ash.

None of the residue additives significantly increased hydrocarbon gas yield at both reaction temperatures. All the additives seemed to contribute slightly to hydrocarbon gas yield. However, this increased yield may result from cracking of constituents in the residue rather than from mineral catalysis of solvent cracking. As observed before, the yield of hydrocarbons gases is very temperature-sensitive.

The yield of heteroatom gases (CO , CO_2 , H_2S , NH_3) is graphed in Figure 23. The heteroatom gas yield is not strongly affected by either reaction temperature or the addition of mineral additives. In fact, within experimental precision, there is no effect of residue addition upon heteroatom gas yield.

Water Yield. Both filter cake and cooked Kerr-McGee ash appear to significantly increase the water yield; however, uncooked Kerr-McGee ash has little or no effect on water yield. At 815°F, the water yield is increased from 1.6 wt % of the MAF coal to 2.1 wt % upon the addition of 10 wt % of cooked Kerr-McGee ash—and increased to 3.7 wt % upon the addition of an equal quantity of filter cake. At 850°F, the increase is from 1.7 to 3.7 and 5.5 wt %, respectively, upon the addition of cooked Kerr-McGee ash and filter cake. These trends are shown clearly in Figure 24.

Distillate Yield. As noted, imprecise distillation cut points have introduced significant error into the calculated yields for the various distillate fractions—and the effect of residue addition is difficult to judge with confidence.

The total distillate liquid yield is graphed in Figure 25. With the exception of the data points where filter cake was added, increasing the reaction temperature increased the distillate yield. However, for the reaction of coal alone plus solvent, the distillate yield had increased with reaction temperature only for the 30 wt % coal slurry (Figure 16). Residue addition had no consistent effect upon distillate yield.

The total oil yield (distillate plus SRC oils) was reasonably constant at 815°F (and at 850°F if the Kerr-McGee ash data point was taken as erroneous). Without residue addition,

the total oil yield decreased with increasing reaction temperature. When Kerr-McGee ash was added, however, the total oil yield increased along with an increase in reaction temperature. (The oil yield at 815°F with uncooked Kerr-McGee ash is suspect.) With added filter cake, the total oil yields again inversely varied with reaction temperature. This data is graphed in Figure 26. Residue addition appears to increase the total oil yield by a small amount.

Figure 27 shows the yield of the standard 450-700°F distillate cut as determined via GC-simulated distillation. Except for the data points where Kerr-McGee ash was added, the yield of this solvent fraction varied inversely with reaction temperature.

The three different approximations of solvent yield in Figures 25, 26, and 27 all show significant scatter in the data. Taking the data as a whole, residue addition seems to have little or no effect upon solvent yield. Filter cake addition may have a small positive effect, based upon total oil yield. However, more data are required to definitively assess the effect of residue addition upon solvent yield.

Preasphaltene Yield. The effect of residue addition upon preasphaltene yield is much clearer (see Figure 28). Filter cake addition substantially reduces the net yield of preasphaltenes. At a reaction temperature of 815°F, the preasphaltene yield was 43% of the MAF coal without added filter cake and 35% with filter cake. At 850°F, the addition of filter cake reduced the preasphaltene yield from 39 to 29%. The addition of uncooked Kerr-McGee ash also reduced the preasphaltene yield, but mixed results were obtained when cooked Kerr-McGee ash was added.

In all cases, an increase in reaction temperature reduced the preasphaltene yield.

Kinetic Constants. Based upon the first-order, sequential reaction model outlined above, experimental kinetic constants for coal conversion, preasphaltene conversion, and asphaltene conversion were calculated from the data. The experimentally derived kinetic constants are tabulated in Table 16.

The reactant concentration of unreacted coal used in the calculation of the kinetic constant for coal conversion is the weight percent of insoluble organic matter (IOM) in the product slurry. This includes IOM from both the feed coal and the added residue. The ratio of reactive vitroplast plus vitrinite to the relatively unreactive fusinite and coke should be lower in the residue addition experiments. This is because of the disproportionately large quantity of fusinite in the residue, compared to the fusinite content of feed coal.

The kinetic constants calculated for the 850°F point with added uncooked Kerr-McGee ash do not agree with the constants calculated for the other three data points with added Kerr-McGee ash. Aside from this, however, the addition of cooked or uncooked Kerr-McGee ash is seen to have no effect upon the kinetic rate constants. Filter cake, however, does significantly enhance the kinetic rate constants for both preasphaltene and asphaltene conversion. This suggests that the minerals present in the filter cake have a significant catalytic activity, whereas those present in the Kerr-McGee ash do not—which is plausible, since the mineral particles in the Kerr-McGee ash are entrapped in a matrix of preasphaltenes and are probably not accessible to reactants.

Much of the calculated catalytic action of filter cake toward asphaltene conversion may be an artifact of the simplistic kinetic model—the model assumes gases and water arise from oils and, hence, have asphaltene precursors, whereas a significant portion of this gas and water yield may arise from coal or preasphaltenes. The combined gas and water yield is significantly increased by filter cake addition.

SUMMING UP

The preliminary data reported here show that the reacted coal minerals present in dissolver solids can exert a significant catalytic action during coal liquefaction, particularly upon preasphaltene conversion and hydrogen consumption.

The carbonaceous content of the solids appears to affect their activity, e.g., the high preasphaltene content of the Kerr-McGee ash seems to block mineral catalysis of hydrogen consumption and preasphaltene conversion while promoting the conversion of pyridine-insolubles present in the solids themselves to a greater extent than occurs with filter cake. More data, particularly at demonstration plant conditions, are required in order to quantify the catalytic action of these solids. The next two CPDU runs should provide the information. However, we can tentatively conclude that the absence of dissolver solids in the demonstration plant dissolver will result in reduced volumetric reaction rates, for at least some of the coal conversion reactions, in comparison to Wilsonville.

Three unexpected results were obtained during the first experiments. Of greatest significance was the observation that increasing the reaction temperature from 815 to 850°F, in the absence of the simulated dissolver solids, causes a decreased yield of oils or solvent. This is a tentative conclusion that will be subjected to further investigation in future experiments. If it were confirmed, it would be directly opposite to the design team's approach for the demonstration plant of increasing reaction temperature and pressure in order to improve solvent yield. Even if the next two runs confirm this conclusion, it still must be determined whether this is unique to Pyro Kentucky #9 coal or applicable to Kentucky #9 in general. The experimental program would have to be expanded to answer the question definitively.

The second unexpected result was the observation that the addition of coal to solvent or to a solvent/mineral residue slurry significantly increased the rate of solvent hydrogenation. Under reaction conditions at which Wilsonville solvent, with or without added mineral residue, suffered a decrease in solvent hydrogen content, a net solvent hydrogenation was achieved with a coal/mineral residue/Wilsonville solvent slurry. This suggests one of two conclusions: (1) coal minerals are much better hydrogenation catalysts than reacted coal minerals, or (2) the carbonaceous portion of the coal can catalyze solvent hydrogenation, either by dissociating hydrogen molecules or by reacting with the hydrogen gas and then transferring hydrogen to the solvent.

The third result, closely related to the second, was that increasing the coal concentration in the feed slurry increased the absolute gaseous hydrogen consumption and resulted in a more favorable net product slate (less gas, more solvent). If this were confirmed, it would indicate that the demonstration plant should be operated at the highest possible coal concentration, and scale-up should be based upon slurry LHSV rather than coal loading (pounds per cubic foot per hour).

A final caveat. In addition to being preliminary conclusions requiring confirmation, all of the above are based upon open-loop experiments with non-steady-state solvent. The most important conclusion—concerning the catalytic effect of the mineral residues—will be checked by closed-loop solvent recycle experiments. The effect of reaction temperature may also warrant double-checking in closed-loop experiments.

LITERATURE CITED

Skinner, R. W. 1981. Pages 121-125 in SRC-I monthly technical reports, July 1979-December 1979. International Coal Refining Co., Allentown, Pa.

Table 1

Summary of XCL-21 Samples^a

Feed slurry composition	Temperature (°F)			
	780	815	850	885
Wilsonville recycle solvent (WRS)		X	X	X
WRS + 14% Kerr-McGee ash concentrate (K-MAC)		X	X	X
WRS + 14% cooked K-MAC		X	X	
SRC + 14% Indiana V filter cake			X	X
Creosote + 25% Emery filter cake	X	X	X ^b	X
WRS + 20% Kentucky #9		X	X	
WRS + 30% Kentucky #9		X	X	
WRS + 40% Kentucky #9		X	X	
WRS + 30% Kentucky #9 + 10% K-MAC		X	X	
WRS + 30% Kentucky #9 + 10% cooked K-KMAC		X	X	
WRS + 30% Kentucky #9 + 10% Indiana V filter cake		X	X	
Hydrotreated creosote + 40% inert Kentucky #6		0	X	
Hydrotreated creosote + 40% normal Kentucky #6		0	X	

^aX indicates analyses were completed; 0 indicates sample was not fractionated. Constant reaction conditions were: 2,000 psig; liquid hourly space velocity (LHSV) = 2 hours⁻¹; H₂ rate, 2.2 wt % of total feed.

^bData were also collected at 1,000-psig system pressure.

Table 2

Summary of XCL-23 Samples without Coal^a

Feed slurry composition	Reaction Temperature (°F)			
	780	815	815b	885
Creosote solvent	X	X	X	X
Creosote + 25% Kentucky #9 filter cake	X	X	X	X

^aConstant reaction conditions: 2,000 psig; LHSV = 2 hours⁻¹; H₂ rate, 2.2 wt % of total feed.

^bData were also collected at 1,000-psig system pressure.

Table 3A^a
Feed Materials Composition

	Coal samples and laboratories						
	Ky #9 coal Pyro Mine APCI	Ky #9 coal Pyro Mine PETC	Ky #9 coal Pyro Mine Huffman	Ky #6 coal air-dried APCI	Ky #6 coal air-dried Huffman	Ky #6 inert-prep APCI	Ky #6 inert-prep Huffman
Moisture (wt %)	<u>1.8</u>	4.3	1.5	2.4		1.7	
ASTM ash (wt %)	<u>10.1</u>	14.4	12.8, 13.4, 13.1	6.5	<u>9.3</u>	7.2	<u>9.2</u>
Sulfate ash (wt %)	<u>13.5</u>		13.4, 13.7	9.5	<u>8.7</u>	9.3	<u>9.5</u>
Volatiles (wt %)	<u>37.9</u>	34.4	36.1	37.3		38.5	
Fixed carbon (wt %)	49.4	46.9	50.4	52.8		50.2	
Carbon (wt %)	<u>69.3</u>		70.4	71.6		73	
Hydrogen (wt %)	<u>4.7</u>		4.8	4.8		4.8	
Nitrogen (wt %)	<u>0.9</u>	1.9	1.5	1.4		1.3	
Sulfur (wt %)	3	3	<u>3.3</u>	2.9		3	
Sulfates (wt %)	<u>0.04</u>	0	0.1	0.3		0.04	
Pyrites (wt %)	1.8	1.6	1.6	1		1.6	
Oxygen (wt %)			6.1				
Aluminum (wt %)	1.5	1.5		1.1		1	
Silicon (wt %)		3.7					
Iron (wt %)	1.5	1.5		0.9		1.1	
Titanium (ppm)	570	1,000		340		570	
Boron (ppm)	590			1,500		1,400	
Chlorine (ppm)	2,400			2,500		2,500	
Calcium (ppm)	90	1,900		60		60	
Magnesium (ppm)	850	980		470		720	
Potassium (ppm)	2,700	2,900		1,800		1,600	
Sodium (ppm)	470	460		360		280	
Pyridine soluble (wt %)	16.5			17.0		17.4	

^aUnderlined values were used for material-balance calculations.

Table 3B^a
Feed Materials Composition

	Residue additive samples and laboratories				
	K-MAC APCI	Indiana 5 filter cake APCI	Emery filter cake APCI	Ky #9 filter cake APCI	Ky #9 filter cake Huffman
ASTM ash (wt %)	37.2	65.3	29.6	50.9	<u>55.1</u> , 57.6
Sulfate ash (wt %)	55.0	59.8			
Carbon (wt %)	50.7	21.9	60.1		34.1
Hydrogen (wt %)	2.7	1.5	3.1		2.3
Nitrogen (wt %)	0.8	0.5	1.1		0.5
Sulfur (wt %)	5.2	5.3			4.0
Oxygen (wt %)					5.3
Aluminum (wt %)	4.4	6.5	3.4	4.5	
Iron (wt %)	3.2	7.4	1.09	5.7	
Titanium (ppm)	1,400	930	200	15	
Boron (ppm)	4,500		100	2,400	
Chlorine (ppm)	1,600	700	300	7,200	
Calcium (ppm)	150	1,600	7,700	60	
Magnesium (ppm)	1,500	6,600		2,200	
Potassium (ppm)	6,700	10,000	700	8,700	
Sodium (ppm)	1,700	4,600	8,500	23,000	
Pentane solubles (wt %)	3.0			9.2	
Toluene solubles (wt %)	4.2	4.7		10.1	
Pyridine solubles (wt %)	29.0	9.1		14.7	
Analysis of pyridine insolubles:					
Carbon (wt %)	34.3	20.6			
Hydrogen (wt %)	1.7	1.3			
Nitrogen (wt %)	0.9	--			
Sulfate ash (wt %)	55.0	70.0			

^aUnderlined values were used for material-balance calculations.

Table 3C
Feed Materials Composition

	Wilsonville recycle solvent	Solvents	
		Hydrotreated creosote	Creosote
Solvent drum ID	F-198, F-199	P-27	--
IBP-420°F (wt %)	1.3	9.1	0.4
Carbon (wt %)	84.8	89.0	89.9
Hydrogen (wt %)	9.9	10.7	7.6
Nitrogen (wt %)	0.4	0.2	0.3
Sulfur (wt %)	0.2	--	--
420-550 °F (wt %)	53.9	43.3	38.5
Carbon (wt %)	87.5	91.1	90.7
Hydrogen (wt %)	9.3	8.6	6.8
Nitrogen (wt %)	0.4	0.1	1.2
Sulfur (wt %)	0.3 ^a	--	--
550-780 °F (wt %)	32.6	46.6	54.4
Carbon (wt %)	88.4	92.1	91.6
Hydrogen (wt %)	8.5	7.3	5.8
Nitrogen (wt %)	1.1	0.1	0.6
Sulfur (wt %)	0.3 ^a	--	--
850°F (wt %)	12.2	1.0 ^b	7.0
Carbon (wt %)	86.6	87.0 ^b	89.4
Hydrogen (wt %)	7.4	6.0 ^b	5.0
Nitrogen (wt %)	1.6	--	2.1
Sulfur (wt %)	0.7	--	0.7
Heptane soluble (wt %)	78.0	100.0	--
Toluene soluble (wt %)	92.9	--	--

^a Analyzed as combined fractions.

^b Assumed value; sample insufficient.

Table 7

Gas Yield from Wilsonville Process Solvent Experiments^a

Solid additive	Wt % of feed	Wt % of solvent		
		815°F	850°F	885°F
None	0	0.30	1.0	2.4
Kerr-McGee ash residue	14	0.3	0.6	2.6
Cooked Kerr-McGee ash	14	0.5	1.4	--
Indiana V filter cake	14	--	1.8	2.6

^aConditions: 2,000 psig; LHSV = 2 hours⁻¹; H₂ rate = 2.2 wt % of feed.

Table 8

Gas Yield from Creosote Oil

Gas yield ^a	Temperature (°F) and pressure (psig)				
	780 2,000	815 2,000	850 2,000	850 1,000	885 2,000
From creosote oil	0	0	0 ^b	0.07	0.2
From creosote oil and 25% FC (Ky #9)	0.15	0.21	0.36	0.61	1
From creosote oil and 25% Emery FC	0.23	0.53	1.48	1.16	2.4

^aGases included hydrocarbons, carbon oxides, hydrogen sulfide, and ammonia, although virtually no H₂S or NH₃ was present.

^b845°F.

Table 5

Catalysis of Wilsonville Process Solvent Hydrogenation by Ash Residue^a

Ash	Concentration in feed (wt %)	Hydrogen content in solvent (wt %)			
		Start	815°F	850°F	885°F
None	0	8.88	8.78	8.66	8.51
Kerr-McGee ash	14	8.98	8.84	8.86	8.69
Cooked Kerr-McGee ash	14	8.88	8.64	8.68	--
Filter cake	14	8.70 ^b	--	8.41	8.28

^aConditions: 2,000 psig; LHSV = 2 hours⁻¹; H₂ rate = 2.2 wt % of feed.^bLower hydrogen level reflects up to 6% creosote oil contamination in feed.

Table 6

Hydrogenation of Creosote Oil without Residue Addition^a

Sample	FL	FL	FL	PL	PL	PL	PL	PL
Temperature (°F)	--	--	--	780	815	845	850	885
Pressure (psig)	--	--	--	2,000	2,000	2,000	1,000	2,000
Hydrogen (wt %)	5.97	5.93	5.93	5.91	6.01	5.98	5.96	5.95
Sulfur (wt %)	0.59	0.60	NA	0.59	0.58	0.57	0.60	NA
Mol wt	178	178	180	174	175	180	175	182
Gas yield (wt %)	--	--	--	0	0	0	0.07	0.20

^aConditions: LHSV = 2 hours⁻¹; H₂ rate = 5.5 wt % of feed. FL = unreacted feed liquid (Allied 24 CB creosote oil); PL = recovered product liquid.

Table 4

Summary of Data Points from Run XCL-21^a

Feed slurry composition used during balance period	Reaction Temperature (°F)			
	780	815	850	885
Wilsonville recycle solvent (WRS)		62	50	56
WRS + 14% Kerr-McGee ash concentrate (K-MAC)		71	77	82
WRS + 14% cooked K-MAC		144	137	
WRS + 14% Indiana V filter cake (FC)			251	244
WRS + 20% Kentucky #9 coal		306	298	
WRS + 30% Kentucky #9 coal		280	288	
WRS + 40% Kentucky #9 coal		195	203	
WRS + 30% Kentucky #9 + 10% K-KMAC		270	262B	
WRS + 30% Kentucky #9 + 10% cooked K-KMAC		155	163	
WRS + 30% Kentucky #9 + 10% FC		182	175	
Creosote	5 ^b	10 ^b	15 ^b	25 ^b
Creosote + 25% Emery FC	236B	232	214	226
Creosote + 25% Kentucky #9 FC	225 ^b	231 ^b	237 ^b	250 ^b
Hydrotreated creosote + 40% inert- prep Kentucky #6		NA ^c	323	
Hydrotreated creosote + 40% inert- prep air-dried Kentucky #6		NA ^c	334	

^aThe numbers in the right-hand columns are sample numbers that identify the balance periods of data points. Conditions: 2,000 psig; LHSV = 2 hours⁻¹; H₂ rate = 500 standard liters per hour.

^bSample from Run XCL-23.

^cNA, sample not analyzed.

Table 9

Petrographic Analysis of Reacted Kerr-McGee Ash Concentrate Samples

Number	Pre-cooked?	Reaction temp (°F)	wt % calculated carbon removals as:		Qualitative petrographic analysis		
			IOM	Preasphaltenes	Major constituents (25 vol %)	Minor constituents (5-25 vol %)	Trace constituents (5 vol %)
XL-21-75-FL	No	--	0	(20)	A. Vitroplast (50% cenosphere) B. Granular residue	A. Unconverted vitrinite B. Pyrrhotite	A. Semi-coke, 1% B. Unconverted fusinite C. Quartz D. Clay
XCL-21-142-F1	Yes	--	0	(10)	A. Vitroplast (50% cenosphere) B. Granular residue	A. Unconverted vitrinite B. Pyrrhotite	A. Semi-coke, 1% B. Unconverted fusinite C. Unconverted liptinite D. Clay E. Quartz
XCL-21-71-PL	No	815	13	51	A. Granular residue B. Vitroplast (30% cenosphere)	A. Unconverted vitrinite B. Pyrrhotite	A. Semi-coke (50% mesophase) B. Unconverted fusinite C. Quartz D. Clay
XCL-21-143-PL	Yes	815	--	--	A. Granular residue B. Vitroplast (50% cenosphere)	A. Unconverted vitrinite B. Pyrrhotite	A. Semi-coke (50% mesophase) B. Unconverted fusinite C. Clay D. Quartz
XCL-21-77-PL	No	850	17	59	A. Granular residue B. Vitroplast (3% cenosphere)	A. Semi-coke (50% mesophase) B. Unconverted vitrinite C. Pyrrhotite	A. Unconverted fusinite B. Quartz C. Clay
XCL-21-83-PL	No	885	20	81	A. Granular residue B. Vitroplast (3% cenosphere)	A. Semi-coke (50% mesophase) B. Unconverted vitrinite C. Pyrrhotite	A. Unconverted fusinite B. Clay C. Quartz

Table 10

Effect of Coal Concentration at 815°F

	Sample No.		
	21-306	21-280	21-195
Coal in feed slurry (wt %)	20	30	40
Ash balance (wt %)	99	93	108
Coal conversion (% MAF)	86.5	87.9	89.7
Hydrogen content of recovered solvent (wt %)	9	8.9	8.7
Hydrogen consumption			
From H ₂ gas (% MAF)	1.2	0.8	0.8
From H ₂ gas (g/L-hr)	4.7	4.7	6.3
From solvent (% MAF)	0.2	0.4	0.6
Total (% MAF)	1.4	1.2	1.4
Net product slate (% MAF wt basis)			
Hydrocarbon gas	3.5	2.4	3.5
CO, CO ₂ , H ₂ S, NH ₃	1.7	2.4	1.8
Water	3.2	1.6	1.5
Liquid	18.5	10.9	21.7
IBP-420°F	(1.6)	2.5	1.2
420-550°F	8.3	16.4	7.4
550-780°F	11.7	(7.9)	13.1
SRC	59.7	71	60.9
Oil	(21.7)	(6.6)	(9.9)
Asphaltene	42.2	34.2	33.5
Preasphaltene	39.2	43.4	37.3
IOM	13.5	12.1	10.3
Total oil	(3.2)	4.3	11.8
450-700°F solvent by GC	5.9	7.4	15.9

Table 11
Effect of Coal Concentration at 850°F

	Sample No.		
	21-298	21-288	21-203
Coal in feed slurry (wt %)	20	30	40
Ash balance (wt %)	106	100	104
Coal conversion (% MAF)	88.7	88.3	89.7
Hydrogen content of recovered solvent (wt %)	8.9	8.9	9
Hydrogen consumption			
From H ₂ gas (% MAF)	1.1	1.1	1.4
From H ₂ gas (g/L-hr)	3.9	8.1	10.9
From solvent (% MAF)	0.7	0.5	0.1
Total (% MAF)	1.8	1.8	1.5
Net product slate (% MAF wt basis)			
Hydrocarbon gas	8.8	7.1	5.9
CO, CO ₂ , H ₂ S, NH ₃	2.9	2.4	2.4
Water	3.5	1.7	2.4
Liquid	1.9	16.7	10.4
IBP-420°F	1.9	11.0	3.7
420-550°F	6.7	14.1	4.2
550-780°F	(6.7)	(8.4)	2.5
SRC	71.3	60.6	68.7
Oil	(3.0)	(16.9)	(2.1)
Asphaltene	38.1	38.4	35.1
Preasphaltene	36.1	38.8	35.1
IOM	11.3	11.7	10.3
Total oil	(1.1)	(0.2)	8.3
450-700°F solvent by GC	8.0	1.6	0.3

Table 12
Kinetic Constants (k) for Coal-Solvent Reactions^a

	Wt % coal concentration @ 815°F			Wt % coal concentration @ 850°F		
	20	30	40	20	30	40
Coal conversion	15	17	20	19	17	20
Preasphaltene conversion	2.6	2.3	3.2	3.0	2.8	3.4
Asphaltene conversion	0.6	0.6	1.2	0.7	0.6	1.2

^aCoal → preasphaltene → asphaltene → oil. k has the dimension of hours⁻¹.

$$k = \frac{(\text{yields of downstream products}) (\text{fraction coal in feed}) (\text{LHSV})}{(\text{wt \% reacting species in product stream})}$$

Table 13

Effect of Residue Addition at 850°F

	Sample No. and residue			
	21-288 None	21-262B K-MAC	21-163 Cooked K-MAC	21-175 Filter Cake
Ash balance (wt %)	100	98	86	88
Coal conversion (% MAF)	88.3	96.5	92.3	88.3
Hydrogen content of recovered solvent (wt %)	8.9	8.7	8.7	9
Hydrogen consumption				
From H ₂ gas (% MAF)	1.3	1.7	1.3	2.4
From H ₂ gas (g/L-hr)	8.1	9.9	8.1	13.8
From solvent (% MAF)	0.4	0.6	0.7	0.1
Total (% MAF)	1.8	2.3	2	2.5
Net product slate (% MAF wt basis)				
Hydrocarbon gas	7.1	6.7	8.2	7.4
CO, CO ₂ , H ₂ S, NH ₃	2.4	2.4	2.7	2.7
Water	1.7	2.3	3.7	5.5
Liquid	16.7	13.8	14.5	12.5
IBP-420°F	11	4.9	4	4.5
420-550°F	14.1	14.7	(3)	6.2
550-780°F	(8.4)	(5.8)	13.5	1.8
SRC	60.6	71.3	63.6	60.1
Oil	(16.9)	5.1	(12.5)	(10.4)
Asphaltene	38.4	36.8	41.1	41.3
Preasphaltene	38.8	29	35.1	29.2
IOM	11.7	3.5	7.7	11.7
Total oil	(0.2)	18.9	2	2.1
450-700°F solvent by GC	2.5	0.7	0.9	(0.3)

Table 14

Effect of Residue Addition at 815°F

	Sample No. and residue			
	21-280 None	21-270 K-MAC	21-155 Cooked K-MAC	21-182 Filter Cake
Ash balance (wt %)	93	97	94	93
Coal conversion (% MAF)	87.9	90.7	92.6	89.1
Hydrogen content of recovered solvent (wt %)	9	8.9	8.8	9.5
Hydrogen consumption				
From H ₂ gas (% MAF)	1.1	1.3	1.2	3
From H ₂ gas (g/L-hr)	6.2	7.4	6.9	17.7
From solvent (% MAF)	0.2	0.2	0.6	(0.9)
Total (% MAF)	1.2	1.5	1.7	2.1
Net product slate (% MAF wt basis)				
Hydrocarbon gas	2.4	2.7	2.8	4.3
CO, CO ₂ , H ₂ S, NH ₃	2.4	1.6	2.2	2
Water	1.6	1.4	2.1	3.7
Liquid	11	(4.2)	7.4	21.2
IBP-420°F	2.5	2.2	3.4	2.7
420-550°F	16.4	9.6	0	9.6
550-780°F	(7.9)	(16)	4	8.9
SRC	71	89.3	78.2	57.8
Oil	(6.6)	11	(5.8)	(14.9)
Asphaltene	34.2	36.9	40.2	37.3
Preasphaltene	43.4	41.4	43.8	35.4
IOM	12.1	9.3	7.4	10.9
Total oil	4.4	6.8	1.6	6.3
450-700°F solvent by GC	8.3	(0.6)	0.3	12.1

Table 15

Comparison of Coal Loadings
850°F Data Points^a

	Coal	Coal with K-MAC	Coal with cooked K-MAC	Coal with filter cake
Feed (coal with unconverted coal)	100	111.3	111.3	107.9
Product (coal unconverted)	11.7	14.6	18.4	19.6
Net unconverted coal	11.7	3.3	7.1	11.7

^aBasis: 100 units of fresh feed coal. Unconverted coal is pyridine-insoluble carbonaceous portion of the added residue (K-MAC or filter cake).

Table 16

Kinetic Constants for Coal Liquefaction Reactions^a

	815°F				850°F			
	None	K-MAC	Cooked K-MAC	Filter cake	None	K-MAC	Cooked K-MAC	Filter cake
Coal conversion	17	10	11	10	17	13	10	10
Preasphaltene conversion	2.3	2.2	2.1	3.2	2.8	3.9	2.9	4.2
Asphaltene conversion	0.6	0.7	0.4	0.9	0.6	1.7	0.8	0.9

^ak has dimension of hours⁻¹.

$$k = \frac{(\text{yields of downstream products}) (\text{fraction coal in feed}) (\text{LHSV})}{(\text{wt \% reacting species in product stream})}$$

Figure 1
Boiling Point Distribution of Wilsonville Recycle Solvent

Figure 2
Boiling Point Distribution of Hydrotreated Creosote Oil

Figure 3

Boiling Range Distribution of Standard Distillation Cuts

Boiling Range Distribution of Product Liquid Fractions From Sample 21-323

Figure 4
Change in Solvent Hydrogen Content vs Reaction Temperature

Figure 5
R Cracking of Wilsonville Process Solvent
in the Presence of 14 wt. % Filter Cake

Figure 6
Coal Conversion

Figure 7
Hydrogen Content of Recovered Solvent

Figure 8
Gaseous Hydrogen Consumption

Figure 9
Hydrocarbon Gas Yield (C₁ - C₄)

Figure 10
Estimated Hydrocarbon Gas Yield From Coal

Figure 11
Heteroatom Gas Yield

Figure 12
Water Yield

Figure 13
Yield of IBP - 780°F Distillate

Figure 14
Total Oil Yield

Figure 15
Yield of 450 - 700°F Solvent

Figure 16
Preasphaltene Yield

Figure 17
Coal Conversion

Figure 18
Hydrogen Concentration in Recovered Solvent

Figure 19
H₂ Gas Consumption (via H Elemental Balance)

Figure 20
H₂ Gas Consumption (via H₂ Balance)

Figure 21
Total Hydrogen Consumed by Coal

Figure 22
Hydrocarbon Gas Yield

Figure 23
Heteroatom Gas Yield

Figure 24
Water Yield

Figure 25
Total Distillate Liquid Yield

Figure 26
Total Oil Yield

Figure 27
Yield of 450 - 700°F Distillate

Figure 28
Preasphaltene Yield

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EFFECTS OF ACCUMULATED SOLIDS ON DISSOLVER PERFORMANCE (JULY-SEPTEMBER 1980)

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I. S. Kingsley,* and F. K. Schweighardt***

The preceding article in this Quarterly Technical Report describes the results of Run XCL-21, the first of three open-loop coal process development unit experiments. Important tentative conclusions were:

- (1) Liquefaction residues can catalyze coal liquefaction reactions, particularly H₂ consumption and preasphaltene conversion.
- (2) The preasphaltenes contained in Kerr-McGee ash concentrate (K-MAC) cannot be removed by heating to 300°F in Wilsonville solvent; they are converted to toluene solubles at 850°F. Because of its higher preasphaltene content, K-MAC displayed less catalytic activity than filter cake. Therefore, K-MAC may not be as good a substitute for dissolver solids.
- (3) In the absence of added residue, solvent yield varies inversely with reaction temperature (for Pyro Kentucky #9 coal).

Run XCL-23, reported here, was designed to test the validity of conclusions 1 and 3 above. We used filter cake exclusively to simulate the dissolver solids because of its superior catalytic activity.

We experienced several problems using a new product fractionation procedure during this period. Therefore, many values are questionable and conclusions are tentative. However, our results on filter-cake addition are consistent with the preliminary conclusions drawn in the preceding article. Specifically, filter cake addition reduces preasphaltene yield, increases hydrogen gas consumption, and increases the hydrogen content of the recovered solvent.

We tentatively conclude the following:

- (1) Results obtained with the addition of only 5 wt % filter cake were very similar to the results achieved with 13 wt % added filter cake, suggesting that the process response to solids addition is nonlinear.
- (2) Filter cake addition appeared to suppress coke formation.
- (3) The product "solvent" fraction isolated by distillation differs significantly in its chem-

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ical and physical properties from the "solvent" oils isolated by solvent separation. The solvent-separated oils contain more nitrogen bases and only half the phenolics found in the distillate.

- (4) The number-average molecular weights of the product oil fractions were significantly less than those of the oil in the starting Wilsonville recycle solvent (WRS).
- (5) The product oils also contained significantly less saturates and alkyl substituents than the WRS oil fraction, which may account for the observed molecular weight reduction.

Two of our tentative conclusions contradict results from the previous run.

- (1) In the present study, filter cake addition generally increased the net coal conversion, presumably because unconverted coal macerals in the filter cake reacted to yield pyridine solubles. Previously, filter cake had no effect, although a different one was used.
- (2) All of the product fractions from this run contained less hydrogen than the oil fraction of the starting solvent. In the previous run, at reaction conditions nearly identical with those here, there was net solvent hydrogenation or no change in solvent hydrogen content.

Statistically, the errors in the concentrations of the various fractions in the product slurry do not follow a normal Gaussian distribution. Although most of the duplicate analyses agreed very well, both the product sampling and the solvent separation procedure caused large errors randomly affecting about one-fifth of the samples. Therefore, all future data points should be sampled and analyzed in duplicate, to protect against these large random errors. If the duplicates are not in reasonable agreement, a third analysis should be performed and the odd analysis rejected. (These duplicate analyses can be discontinued when samples are collected and analyzed more precisely.)

EXPERIMENTAL PROGRAM

Open-loop (i.e., no solvent recycle) CPDU Run XCL-23 was completed during November 1979, after product samples from 42 reaction conditions were collected during the 281 hr the unit was on stream.

A broader range in reaction temperatures and filter cake concentrations was examined. Conditions were: 2,000 psig; LHSV = 2.0; 25 M scf H₂/ton of coal; 780, 815, 850, and 885°F; 30 wt % coal in feed; and 0, 5, and 13 wt % filter cake in the feed. The product slurries from this run were fractionated primarily by a new solvent separation procedure, whereas distillation was used previously.

Reaction conditions for the 16 data points are shown in Table 1. The Wilsonville recycle solvent (WRS) and Pyro Kentucky #9 coal are the same as those used in Run XCL-21, but Kentucky #9 filter cake replaced Indiana V filter cake. A wide temperature range was used to measure the activation energies for the coal liquefaction reactions. Unfortunately, the data are not sufficiently accurate to permit these calculations.

Materials

Analytical data on Kentucky #9 coal from three laboratories are listed in Table 2A. If results conflict for the same analysis, the value used for our calculations is underlined.

Analytical data for Kentucky #9 and Indiana V filter cakes are summarized in Table 2B. Note that the Kentucky #9 filter cake contains about 20% less ash and iron than the Indiana V filter cake, and over twice the concentration of toluene-soluble¹ organic constituents, most of which are also pentane soluble. The 9.2 wt % of pentane-soluble oils contain 9.35% hydrogen and are presumed to be IBP-450°F Wilsonville wash solvent. Both filter cakes have a preasphaltene (toluene-insoluble, pyridine-soluble) content of about 4.5%.

WRS, the same as used previously, was fractionated both by distillation and solubility into the standard fractions shown in Table 2°C. Elemental analyses are reported for both the overall solvent and the fractions, except for the preasphaltene sample, which was lost.

Conditions

Product samples, including those feed slurries that did not include coal, were collected at 42 different sets of reaction conditions; these conditions are described in Tables 3A and 3B and identified by balance-period number. The 16 coal-containing slurry samples that have been analyzed thus far are underlined; the remaining samples have been retained but will not be fractionated or analyzed.

Operation

The CPDU design was not modified, although main receiver samples were collected differently than reported previously because the solvent separation procedure can handle only 5- to 8-g samples. The main-receiver product sample is limited to 75-150 g, which is the maximum size that can be resampled accurately in the laboratory.

Receiver samples for distillation-based fractionation (1,500-g dilution sample, 1,000-g prime sample) were collected as usual. The sample for solvent fractionation was collected in a steel sampling flask by first draining the main receiver completely until product gas broke through (so that about 100 g of fresh product slurry could accumulate in the receiver) and then completely draining the receiver into the sample flask. On the basis of calculated ash balances, a representative mix of solids and liquid in the slurry sample was not always achieved; sometimes the ash balance was in error by more than 50%. Such errors are certainly beyond the range where a forced ash balance can give reasonably valid results, since we suspect that the liquid adhering to the residue particles is enriched in preasphaltenes relative to the bulk liquid.

Sampling errors are exemplified by deviations in residue concentrations determined for three separate samples (see Table 4). After a 100-g sample collected during balance period 23-163 was resampled and fractionated four times via the solvent fractionation technique, residue determinations varied by less than ± 0.7 from the mean value of 7.9 wt %. This suggests that the 100-g main receiver sample can be resampled and analyzed with adequate precision. However, a second 100-g main receiver sample, which was collected 1 hr later, contained 12.9 wt % residue. Thus, these two 100-g samples of a fixed-com

¹Later in this paper certain analytical methods are described that use benzene rather than toluene, to give benzene solubles and insolubles. These data were collected during a switch from use of toluene to benzene to permit freeze-drying of asphaltenes. The results should be similar.

position product stream contain grossly different residue concentrations, presumably because the solid residue fraction settles out of suspension in the main receiver and is difficult to sample on such a small scale. A 1,000-g sample was also collected immediately before the 100-g sample and was fractionated via distillation, filtration, and pyridine digestion. It was found to contain 6.3 wt % of residue. Since distillation usually gives a somewhat smaller residue yield than solvent fractionation, this result is reasonably consistent with the 7.9 wt % residue concentration in the first sample. A comparison of distillation and solvent separation samples for balance period 23-158 (see Table 12) also reveals a sampling error of equal magnitude.

Because of these sampling errors some of the data from this run must be discounted. Subsequent to Run XCL-23, a hemispherical bottom was installed in the main receiver, which should increase the accuracy of sampling small amounts in the future.

Product Work-up

Distillation. The distillation work-up for sample 23-158 followed the procedure used in the preceding article. Other fractionations followed an abbreviated procedure that does not isolate an SRC sample for analysis and is designed only as a double-check of solvent and residue yields. Since the SRC is not isolated, asphaltene and preasphaltene yields are not determined and the hydrogen consumption cannot be calculated. In the short distillation procedure, 300 g of product slurry was vacuum-distilled in a 6 in. X 11 in. heli-pack, 15-plate, packed-glass column at 10/1 reflux. The IBP-420°F, 420-550°F, and 550°F-EP distillate cuts were isolated and weighed. The precision of these distillation cuts (shown in Figure 1) is superior to that achieved by the previous distillation procedure (see Figure 3 of preceding article). The end point of the final cut is not fixed; as much distillate as possible is recovered overhead. The distillation flask is heated by a temperature-controlled heating mantle, the column is insulated by a vacuum-jacket, and the portion of the distillation flask above the heating mantle is wrapped with insulation. Distillate end points of about 760°F are achieved by this technique.

An increased end point was achieved by "forced-flash" distillation, where both the pot and the column were heated to 650°F under a vacuum of 0.5 torr. The temperature was increased slowly to keep the pot temperature only slightly hotter than the liquid, and then was held at 650°F until no more distillate could be recovered, which required 15 min. By the end of this interval, significant product cracking had occurred and the vacuum degraded to 1.1 torr. Although heating the column eliminates liquid holdup, the overhead vapors are superheated and the dew point is not known. Hence, the corrected atmospheric end point cannot be determined during the distillation. However, a GC-simulated distillation indicated that the "forced-flash" procedure gave a distillate cut having an 869°F end point (98% overhead).

Sample 23-169 was distilled three times by short distillation and once by the "forced-flash" procedure (see results in Table 5). The short procedure gave a distillate yield of 65.2 ± 0.4 wt %, while the forced flash yielded 72.2 wt % of distillate, an increase of 7 wt %. If increased slurry heating in the forced-flash procedure had caused any repolymerization of SRC to pyridine-insoluble coke, the ash content of the resulting residue would be reduced. Since the residue fractions from both procedures contain about 59 wt % ash, the forced-ash procedure does not cause extraneous coke formation and will yield reliable values for the residue yield. The forced-flash procedure gives a larger distillate yield, which corresponds more closely to the Wilsonville cut point.

Statistical Analysis of Distillation Precision. Table 6 shows a variance analysis of the concentrations determined by short distillation. Replicate distillations were performed at 6 sets of reaction conditions, involving a total of 14 data points. This represents only 8 degrees of freedom (summation of $n - 1$) on which to estimate variance.

The estimated variance, S^2 , is equal to the sum of squares of deviations, SS, divided by the total degrees of freedom. For any set of replicated data points, SS is computed with the equation:

$$SS = \sum X^2 - \frac{(\sum X)^2}{n}$$

where X is the experimentally determined weight percent of distillate. The $\bar{X}$ values in Table 6 are the means of the weight-percent distillate determination at each set of reaction conditions. Note that S^2 is an estimate of the true variance, because of the small sample size. For a sufficiently large sample population that follows a normal distribution, the standard deviation will be equal to the square root of the variance.

The estimated variance for the distillate determinations is $S^2 = 4.0$. Note that two of the six sets of distillate analyses account for virtually all of the variance. In fact, within a 97.5% probability, the variance for points (27-50, 56) is not the same as that for points (27-188, 192) and (21-288, 23-164, 27-106). Hence, these points should not even be included within the same pooled variance.

Since the experimental errors do not resemble a normal distribution but consist of a few, large, sporadic errors in a population of small errors, the pooled-variance approach described above is not strictly correct. The proper approach would be to make all of our data comparisons based upon duplicate data points, using triplicate analyses and discarding the outlying data point when large discrepancies are encountered. Unfortunately, the product samples from Run XCL-23 were not and cannot be distilled in duplicate. Therefore, the best way to estimate their statistical significance is to use the pooled variances to calculate the smallest difference between two data points that is statistically valid at any assumed confidence level. The following calculations show the size of the least significant difference in distillate yield for comparing duplicated or nonduplicated data points.

Using the Student's t test, we can calculate the least significant difference, at a 90% confidence level, between the means of duplicate distillate determinations. Using the pooled variance $S^2 = 4.0$ for 8 degrees of freedom (df):

$$LSD_{90} = t_{0.1(8 \text{ df})} S_d$$

where

$$S_d = S \left(\frac{1}{n_1} + \frac{1}{n_2} \right)^{1/2} = (4.0)^{1/2} \left(\frac{1}{2} + \frac{1}{2} \right)^{1/2} = 2.0$$

Since $t_{0.1(8 \text{ df})} = 1.397$:

$$LSD_{90} = 2(1.397) = 2.8$$

Therefore, using pooled variance, two product slurries containing 70 and 72.8 wt % distillate, based on duplicate analyses, are barely distinguishable at the 90% confidence level. If only single analyses were performed, the distillate concentrations would have to differ by 4.0 wt % to be statistically significant; this difference corresponds to a difference

in distillate yield of 16 wt % MAF (moisture and ash free) for a 30 wt % coal slurry feed. None of the distillate concentration determinations for Run XCL-23 were duplicated, and the differences in distillate yield among the seven reaction conditions where the product was distilled were all within this experimental error.

Solvent Separation. All of the primary XCL-23 product slurry samples (Tables 3A and 3B) were fractionated using a modification of the solvent separation procedure (see Chart 1) developed by F. Schweighardt at the Pittsburgh Energy Technology Center [Schweighardt, 1980 (modified method); Schweighardt and Thames, 1978]. This procedure reduced the fractionation time from 4 to 1.5 technician days, and recovered asphaltene and preasphaltene fractions. Four product fractions were isolated for analysis: pentane-soluble oils; pentane-insoluble, benzene-soluble asphaltenes; benzene-insoluble, pyridine-soluble preasphaltenes; and a pyridine-insoluble residue.

The major disadvantage of the new procedure is that the sample size is only 5-7 g, making collection of a representative sample very difficult. The size of the CPDU sample can be increased to a maximum of 100-150 g by first homogenizing the main-receiver sample in a Bronson sonicator, but this was still too small to be reliably collected with our original main receiver design. After Run XCL-23 was completed, we installed a rounded bottom in the main receiver to facilitate the collection of small samples.

Table 7 shows the varying residue concentrations obtained in multiple solvent-separation analyses of the same 100-g main-receiver sample. The 9 samples represent a total of 24 residue analyses, which constitute 15 degrees of freedom for calculation of the estimated variance. The reproducibility of this analysis was good and the estimated variance is only 0.4, which means that, even for unreplicated data points, a difference in residue yield of 0.9 wt % is significant at the 90% confidence level. However, this does not include errors introduced by sampling the main receiver.

Statistical Analysis of Solvent-Separation Precision. To ascertain the relative importance of these sampling errors, we should estimate the variance for the residue analysis based upon the residue concentrations determined for different main-receiver samples collected at identical process conditions and, therefore, having the same residue content if sampled and analyzed perfectly. This variance will be equal to the sum of the variances due to sampling and analytical error.

In the only population of residue analyses that we can compare, the residue concentration was determined by different analytical methods, which could influence the amount of organic material counted as residue but should not affect the quantity of ash that is counted as residue. We can, therefore, calculate the variance in ash concentration as a result of sampling error. This analysis is shown in Table 8. Based upon 6 degrees of freedom, the estimate of the variance is $S_2 = 0.96$. The variance has the following multiplicative property: if $Y = bX$, where X and Y are variables and b is a constant, then $S^2(Y) = b^2 S^2(X)$. Note that $S^2(Y)$ means the estimated variance of variable Y . We will, therefore, approximate the variance of the residue concentration by assuming that the ash concentration in each of the residues equals the average ash fraction of 0.55. Then:

$$S^2(\text{residue}) = \frac{1}{(0.55)^2} S^2(\text{ash}) = 3.1$$

Therefore, the residue variance arising from main-receiver sampling (3.1) is about 6 times the variance arising from analysis (0.4). This indicates that improving the main-receiver design is the best way to improve the quality of this data.

Variances have been estimated for oil and preasphaltene analyses in main-receiver samples, as determined by multiple analyses of the same sample. Table 9 reports an estimated variance of 5.7 in the oil determination, based upon 23 analyses constituting 13 degrees of freedom. If only the 7 most recent analyses (23-163 and 23-169) are considered, the variance estimate is reduced to 1.7 based upon 5 degrees of freedom, probably because these studies were performed 1 month or more after the previous analyses and reflected greater precision due to increased operator experience. Nonetheless, for the current data a difference of 13% MAF in oil yield is required to establish a statistically significant (90% confidence) difference between duplicated samples. A difference of 18% MAF is required without duplicates.

In Table 10 an estimated variance of 6.9 for the preasphaltene analysis is derived, based upon 10 degrees of freedom. As above, if only the most recent data are used, an estimated variance of 1.9 is computed, but this represents only 5 degrees of freedom. This also indicates that the precision of this analysis has improved as operator experience increased. The reader is cautioned that these oil and preasphaltene variances relate only to errors in the laboratory sampling and analysis and do *not* include the errors introduced in sampling the main receiver. Since the bulk of the variance results from a few grossly incorrect data points, adequate data precision can be achieved by running all data points in duplicate. A third analysis will be required only when the duplicates differ significantly.

Measuring Solvent Yield. Many techniques have been employed to measure solvent yield, but the only true way is to use a continuous distillation column for solvent recovery in a closed-loop solvent recycle run. The Wilsonville Pilot Plant operates in that way and so will the demonstration plant.

The best that we will be able to do is to recover solvent in a 7-gal batch still during a closed-loop run, so that, as repeated distillations are performed, the effect of still holdup will become negligible. Presently, however, our "solvent" yields must be calculated by analyzing samples from open-loop runs.

Table 11 compares "solvent" concentrations found in the product slurry by four analytical procedures: solvent separation; solvent precipitation; short distillation; forced-flash distillation. These procedures, depicted in Charts 1-3 (Kingsley, 1980), give very different definitions of the concentrations of solvent present in a product slurry. Also, the differences are not consistent from sample to sample.

Both solvent separation (Method 1) and forced-flash distillation (Method 4) give about 72% "solvent" in the product slurry. In solvent precipitation (Method 2), additional asphaltene-derived oils (ADO) were recovered by dissolving the asphaltenes in benzene and then reprecipitating them with pentane, making the solvent composition 85/15 pentane/benzene. This yielded an additional 1.5 wt % of pentane-insoluble "solvent" dissolved in the pentane/benzene mixed solvent. Short distillation (Method 3) yielded ca. 7 wt % less "solvent" than the other techniques, and both distillations gave lower residue concentrations than the solvent-separation methods, probably because boiling pyridine rather than ambient-temperature pyridine was used and because of the co-solubility effects of the SRC accompanying the boiling pyridine.

The first three fractionation techniques were also compared (Table 12) for Sample 23-158, which was generated at a very high reaction severity (885°F). Forced ash as well as uncorrected concentrations of the various fractions are reported, the former values appearing more reliable. Unlike Sample 23-169, equivalent "solvent" concentrations were measured by solvent separation and distillation. Solvent precipitation concentrations were 10% higher than results from the other methods. The relatively low "solvent"-separation

yield could be caused by experimental error or by the chemical and/or physical properties of this sample, owing to the very high reaction temperature.

These two data sets definitely show that we cannot assume the four product fractionation techniques will give oil yields differing by a fixed absolute or relative amount. The Method 1 pentane extraction yields an oil fraction where roughly 5% of the material boils above 800°F, whereas the vacuum distillation (Method 3) produces a composite liquid in which 95 wt % of the liquid boils below 720°F and virtually none boils above 800°F.

The distillates and oils also differ chemically. Silica/alumina column separation following HCl precipitation of the nitrogen bases gave the following fractionation (numbers are the average weight percent obtained in duplicate column separation experiments):

	Fraction from 885°F product slurry	
	Oils	Distillate
Saturates	3	4
Aromatics	67	60
Phenolics	16	34
N-bases	14	2

Phenolic and N-base concentrations differed significantly.

Finally, while the aromatic fraction from the oils is a translucent, dark-orange liquid, that from the distillate is a light-yellow, transparent liquid of slightly lower viscosity. The starting solvent contained 8 wt % saturates; therefore, about half of the initial saturates were destroyed during the reaction. Cracking of saturates may be a major contributor to hydrocarbon gas yield.

RESULTS

Results from the 16 prime data points will be discussed in three sections. The first, which includes data points collected at a constant pressure of 2,000 psig, examines reaction-temperature effects upon net product slate and hydrogen consumption for 30 wt % slurries of coal in Wilsonville recycle solvent (WRS) without added filter cake and with 5 and 13 wt % filter cake. The second section, which includes data points collected at a constant reaction temperature of 850°F, examines the effect of system pressure for a 30 wt % coal slurry both with and without 13 wt % filter cake. The last section discusses changes in solvent quality and asphaltene and preasphaltene molecular weights as functions of reaction conditions.

Detailed product-gas analyses, weights and elemental compositions of feed and product slurries, corrected weight percents, net product slates, hydrogen consumptions, and boiling point distributions are not included in this report.

Effect of Reaction Temperature

Reaction temperatures of 780, 815, 850, and 885°F were explored for feed slurry compositions of both 30% Pyro coal/70% WRS and 30% Pyro coal/13% filter cake/57%

WRS. (For 30% Pyro coal/5% filter cake/65% WRS, only the 815 and 850°F data points were examined.) In each case the system pressure was 2,000 psig, the superficial liquid space velocity was 2.0 hr⁻¹, and the hydrogen feed rate equalled 2.2 wt % of the slurry feed rate.

The 30% Pyro coal/13% filter cake/57% WRS feed slurry was expected to contain 15 wt % filter cake. However, analysis of two feed slurry samples indicated that the actual feed did not contain enough ash or pyridine insolubles for a 30% coal/15% filter cake slurry. Therefore, the feed slurry composition was altered to reflect the actual analysis.

Interpretation of the data was complicated by errors introduced by the new solvent fractionation procedure. Several poor ash balances indicate sampling problems that also reduce data precision. Forced-ash balance is expected to correct some of this sampling error.

Coal Conversion. Filter cake addition increases the apparent coal conversion. As shown in Figure 2 for the forced-ash balance, the yield of insoluble organic material (IOM), which equals 100% conversion, was generally reduced when 5 or 13 wt % filter cake was added. This effect was especially pronounced at the higher reaction temperatures, where a 6 to 17% reduction in IOM yield was noted.

Without added filter cake, an increase from 780 to 850°F raised the IOM yield from 12 to 16%, and at 885°F IOM yield jumped to 25 wt %. This could be due to coking, since the residue sample from the 885°F data point contained 37 vol % coke. Thus, coking increased the IOM yield by about 15% (MAF coal basis) at 885°F. When filter cake was added, at either concentration, an increase in reaction temperature had no significant impact on IOM yield, which varied only between 7 and 9 wt %. These forced-ash IOM yields should not be significantly affected by product sampling errors.

We also calculated IOM yield on an ash-free basis; these results (Figure 3) are fairly similar to those with forced-ash balance. Up to 850°F without filter cake there was no temperature effect on IOM, but at 885°F IOM yield more than doubled, from 14 to 39% of the MAF coal. At each temperature except 780°F, the filter cake addition reduced the IOM yield, i.e., increased coal conversion.

Overall, these data suggest that:

- Filter cake addition enhances net coal conversion.
- Temperature has little impact on coal conversion at 815-850°F.
- Filter cake addition markedly reduces coke formation at very high reaction temperature (885°F).

The Kentucky #9 filter cake used in this run has a significantly higher carbon content than the Indiana V filter cake used during Run XCL-21. Data from that run showed that addition of Kerr-McGee ash concentrate enhanced net coal conversion, whereas filter cake had no effect. However, because Kentucky #9 filter cake has a higher carbon content, it may contain more reactive coal macerals and vitroplast than Indiana V filter cake. Therefore, the enhancement of coal conversion we observed at reaction temperatures of 850°F and below need not be ascribed to catalytic action by coal minerals.

We also studied the reaction of Kentucky #9 filter cake in creosote oil at the same conditions used above. The extent to which toluene-insoluble constituents in the filter cake were converted to toluene-soluble products was calculated for each reaction temperature. We used the results to calculate how much of the increased net coal conversion with 13 wt % added filter cake was due simply to conversion of the filter cake itself. Expressed on

an MAF coal basis, these values are: 780°F, 0.1 wt %; 815°F, 2.6 wt %; 850°F, 4.3 wt %; 885°F, 6.3 wt %.

Conversion of the toluene-insoluble organic constituents of the filter cake accounts for about one-half of the observed enhancement in coal conversion at 815 and 850°F, but leaves unexplained fully 10% (MAF) of the difference in coal conversion at 885°F. Thus the coal minerals in the filter cake appear to suppress coking by increasing the supply of hydrogen available to terminate free radicals, either by catalyzing solvent hydrogenation or by adsorbing hydrogen on their surface in an activated form.

Preasphaltene Yield. Addition of filter cake to the feed slurry also appears to significantly reduce preasphaltene yield. On the basis of the forced-ash balance, the addition of 5 or 13 wt % filter cake reduced preasphaltene yield from 5 to 14 wt % at the four reaction temperatures studied (Figure 4). The addition of 13 wt % filter cake reduced the preasphaltene yield from 51.5 to 41% at 815°F and from 36.5 to 28.5% at 850°F. The magnitude of the reduction was not significantly affected by the quantity of filter cake added. The decrease in both residue and preasphaltene yields due to filter cake addition considerably improves the overall product slate. Increasing reaction temperature typically reduced preasphaltene yield.

Calculating yield on an ash-free basis (shown in Figure 5) gave identical results. Sampling errors may have had at least a small impact upon the calculated yield.

Oil Yield. As we noted previously for Run XCL-21, the effects of reaction temperature and filter cake addition upon solvent yield cannot be clearly discerned. In the solvent fractionation product work-up procedure, the yield of pentane-soluble oils is expected to correspond to the combined yield of solvent plus lighter boiling organic liquids.

Based upon the forced-ash balance (Figure 6) without filter cake addition, temperature increases generally reduced the oil yield: from 11 wt % of the MAF coal at 780°F to -20 wt % at 885°F. The ash-free balance (Figure 7) indicates a sharper drop from a positive oil yield of 8 wt % at 780°F to a 31 wt % loss at 885°F.

We did not expect this inverse relationship between oil yield and reaction temperature nor was it predicted by the kinetic model used by the demonstration plant design team. The sharp drop in oil yield from 850 to 885°F is understandable since hydrocarbon gas increased substantially and since substantial coking occurred at 885°F. However, the decrease in oil yield between 780 and 815-850°F does not seem reasonable and may well be caused by data error. Indeed, the distillate yield for the same data points follows the opposite trend.

Another concern with these data is the negative oil yield calculated above 780°F. Taken at face value, these data indicate that solvent in the demonstration plant will be significantly out of balance, especially since these yields include IBP-420°F organics, which are not usable as solvent. Fortunately, the distillate yields for all of these data points were positive. Since solvent recovery in the demonstration plant will be based on distillation rather than solvent separation, the reader should not overreact to the negative oil yields.

Positive oil yields were achieved for each data point in which filter cake was added to the feed slurry. Filter cake addition had little impact upon oil yield at 780°F, but it increased oil yield by a progressively larger amount as the temperature increased to 815°F and above. The 30 wt % improvement in oil yield at 850°F seems too large to ascribe to filter cake catalysis, especially since we found that filter cake had minimal effects on oil yield in preliminary results from Run XCL-27 (discussed in the following article). This is further cause to question the accuracy of the data.

We used gas chromatography to simulate the boiling point distribution for the product oils, converting the forced-ash oil yields to yields of arbitrarily defined "450-700°F solvent"

and "850°F solvent" (presented in Figures 8 and 9, respectively). Except for negative values at 780 and 815°F for the feed slurry containing 13 wt % filter cake, the computed yields resembled those that were unadjusted.

Distillate Yield. The distillate yields for these data points were all positive; 13 wt % filter cake always increased the oil yield, but its effect cannot be quantified because of serious data scatter. The distillate yields without filter cake showed little dependence on temperature, varying over the narrow range of 0.2-4.4 wt % (Figure 10), while those with filter cake varied erratically from 4.4 to 16.5 wt %. The smallest and largest yield increases with filter cake addition were ~2 and 16 wt %, respectively.

We compare distillate and oil yields without filter cake in Figure 11. The distillate yields exceeded the oil yields by about 15 wt %, except at 780°F the oil yield is 10 wt % larger. The yield disparity could result from inherent differences in the fractionation techniques or from experimental error, because the distillation and pentane-extraction steps do not recover the same compounds as "solvent."

Since sampling errors also might be responsible, the ash material balances were calculated for the data points shown in Figure 11. They are poorer for the solvent separation points, which is reasonable since that procedure uses a smaller sample size (Figure 12). However, there is a consistent bias in the data: the solvent separation points had ash balances ranging from 98 to 152%, while those for the distillation points ranged from 87 to 100%. If, as we expect, the ash-containing residue particles are coated with liquid containing more preasphaltenes than bulk liquid, then the preasphaltene yields for the solvent separation points would be artificially high and the oil yields would be low.

Gas Yield. Hydrocarbon yields are affected by reaction temperature, not filter cake addition (see Figure 13). They increase from 1.1-1.5 wt % of the MAF coal at 780°F to 6.2-7.8% at 850°F to 12.6-14.8 wt % at 885°F. The large increase between 850 and 885°F partially reduces oils and distillates over that same temperature range.

As shown in Figure 14, the yield of heteroatom gases (i.e., CO, CO₂, H₂S, NH₃) is relatively insensitive to both reaction temperature and the presence or absence of filter cake. When the reaction temperature increases from 780 to 885°F, this yield increases by about 1 wt % of the MAF coal feed (from just under 2 wt % to slightly over 3 wt %).

All of the gas yields should be unaffected by sampling error.

Hydrogen Consumption. We calculated hydrogen consumption by performing an elemental hydrogen balance between the summation of the product streams and the feed slurry, using both the forced-ash (Figure 15) and ash-free balance product slates (Figure 16). Both yield negative values for the 30% Pyro coal/WRS slurry without added filter cake, at 780 to 850°F. Since these are the first negative H₂ consumptions observed, we doubt their validity. An error probably exists either in product sampling or in the feed slurry composition, since a threefold repetition of an analytical error of this magnitude (probably about 0.5% in overall hydrogen content of the products) seems unlikely and a gas-phase hydrogen balance (H₂ in minus H₂ out) showed positive hydrogen consumption for these points (Figure 17).

Results were positive for runs with filter cake; hydrogen consumption increased with increasing reaction temperature, except at 885°F, which could be dictated by thermodynamic equilibrium for the solvent hydrogenation reaction. Hydrogen consumption with 13% filter cake was significantly higher at 815 and 850°F than that with only 5 wt % added filter cake.

For all of these data points, the solvent was a net donor of hydrogen to the coal liquefaction reactions, i.e., the recovered oil fraction from the product slurries contained less hydrogen than the starting solvent. The net solvent hydrogen consumed by the coal generally

increased as the reaction temperature was raised and decreased upon addition of filter cake to the feed slurry at each temperature (Figures 18 and 19). Hydrogen consumption for the 5 wt % filter cake slurry was intermediate between the values observed without filter cake and with 13 wt % filter cake.

The sum of the hydrogen gas and solvent hydrogen consumptions generally increased with a rise in reaction temperature (Figures 20 and 21) and with the addition of filter cake.

The hydrogen content of the oil fraction recovered from the product slurries is plotted in Figure 22. The hydrogen content of the oil fraction from Sample 95 (780°F, 13 wt % filter cake) is not accurately known, because the oils were contaminated by the pentane-fractionating solvent, which was not fully flashed from the sample. In general, the oils recovered from the experiments with 13 wt % added filter cake contain about 0.1 and 0.2 wt % more hydrogen than the oils from runs with only 5 wt % added filter cake and without filter cake, respectively. Also, as the reaction temperature was increased, the product oils contained less hydrogen.

SRC Quality. Measured as the weighted average sulfur content of the asphaltene and preasphaltene product fractions (Figure 23), the SRC sulfur content decreased as reaction temperature increased. For most of the data points the SRC contained over 1 wt % sulfur, which is an unacceptably large value. The addition of filter cake had an inconsistent effect: the slurry with 5 wt % added filter cake resulted in SRC with the highest sulfur content, while 13 wt % filter cake gave the lowest.

The ratio of the net yield of asphaltene to preasphaltene is another major criterion of SRC quality; a higher ratio improves SRC recovery in the Kerr-McGee deashing step. Filter cake addition seems to increase this ratio at low reaction temperatures (815°F or less), but has a negative or no effect at higher temperatures (Figure 24). Note that all of these ratios are considerably lower than the demonstration plant design ratio of 1.75.

Results with Creosote Oil Solvent. Our previous data (Run XCL-21) and the present results indicate that, without added filter cake, the oil yields obtained from slurries of Pyro Kentucky #9 coal in WRS generally varied inversely with reaction temperature. To determine if this inverse temperature effect was solvent dependent, data were gathered using 30 wt % Kentucky #9 coal in creosote oil, rather than Wilsonville recycle solvent, under identical reaction conditions at 815 and 850°F.

The hydrocarbon gas yield is significantly lower with creosote oil solvent (Table 13). As reported in the preceding article, WRS is more prone to thermal cracking than is creosote oil. Heteroatom gas and water yields are also lower with creosote oil.

However, there was a significant difference in oil yield: a net loss of oil was experienced at both temperatures using WRS, but yields of 16-25 wt % of the MAF coal were achieved with creosote oil. Earlier work with Kentucky #9/14 coal from the Colonial Mine of PAMCO showed slightly better distillate yields from WRS than from creosote oil. Although we are unable to explain this discrepancy, it might be related to differences in the way distillation and solvent separation procedures distinguish between molecules in defining a "solvent" cut. Further work is needed, particularly in correlating solvent-fractionation and distillation data. However, this result certainly makes the solvent-separation data for the 30% coal/70% WRS feed more suspect.

Coal conversion was improved by the substitution of creosote oil for WRS: at 850°F, the IOM yield was 16 wt % of the MAF coal with WRS, but only 8.8 wt % with creosote oil. Although this trend is similar to our earlier work, the magnitude of the effect is much larger in the current work.

The very large consumption of hydrogen gas that occurred at both temperatures for the 30% coal/70% creosote oil slurry was expected. Creosote oil is very hydrogen deficient,

and the solvent hydrogenation rate appears to vary inversely with the concentration of naphthenic hydrogen in the solvent. Interestingly, the 2.4 wt % hydrogen gas consumption calculated for the 850°F data point (creosote oil solvent) is virtually identical with the 2.5 wt % consumption found in the earlier study using Kentucky #9/14 coal.

Effect of Reaction Pressure

We designed experiments to determine the effect of reaction pressure upon hydrogen consumption, net product slate, and product quality, and to determine if the presence of dissolver solids altered the pressure dependency of these variables. The only feed slurry compositions tested were 30% Pyro coal/70% WRS and 30% Pyro coal/13% filter cake/57% WRS. All of the product samples were collected at a reaction temperature of 850°F for a liquid hourly space velocity of 2.0 hr^{-1} and a hydrogen feed rate equal to 2.2 wt % of the slurry feed. Although product samples were collected at system pressures of 1,000, 1,500, 2,000, and 2,500 psig, the 1,500-psig samples were not analyzed. Surprisingly, pressure did not have a significant and consistent effect upon most of the dependent variables. In fact, coal conversion (IOM yield) was the only variable that correlated against pressure.

Coal Conversion. The yield of IOM was inverse to reaction pressure, both with and without added filter cake. A reduction in IOM yield from 23 to 12%, on an MAF coal basis, accompanied an increase in system pressure from 1,000 to 2,500 psig for the experiment in which no filter cake was added (Figure 25). A similar reduction from 13.5 to 5% was observed in the experiment with 13 wt % added filter cake. Hence, increased system pressure definitely improves coal conversion, possibly by suppressing retrograde polymerization reactions. Note also that the data are consistent with the conclusion that filter cake addition improves the net coal conversion. IOM yields were the same with or without forced-ash balance (Figure 26).

Preasphaltene Yield. Filter cake significantly reduced preasphaltene yield at 1,000 and 2,000 psig, but no effect was noticed at 2,500 psig. Since filter cake minerals increase the quantity of solvent and/or activated adsorbed hydrogen available for reaction, their effect should be less evident at higher reaction pressures, where solvent hydrogen is more plentiful. Nevertheless, the "no filter cake" data point at 2,500 psig (Figure 27) appears to be erroneous.

If this single point is ignored, then a mild trend toward increased preasphaltene yield at increased system pressure is observed. However, this does not mean that increased pressure hinders preasphaltene conversion, since any increase in preasphaltene yield is smaller than the concomitant increase in coal conversion. Thus, preasphaltene yield may be larger not because of any reduction in conversion rate but simply because the quantity of preasphaltenes formed from coal has increased. Figure 28 shows that very similar results are obtained if the ash balance is not forced.

Oil Yield. At each of the three system pressures studied by forced-ash balance, the addition of filter cake improved oil yield (Figure 29).

Hydrocarbon Gas Yield. Hydrocarbon gas yield covers a fairly narrow range, with random variations that are probably due to experimental error rather than reaction pressure or filter cake (Figure 30).

Hydrogen Consumption. Because solvent hydrogenation is supposed to be first order in hydrogen partial pressure, we expected a large rise in hydrogen consumption as

the system pressure increased by a factor of 2.5 from 1,000 to 2,500 psig. Our data, although of poor quality, did not reflect this. The hydrogen consumption determined from the elemental hydrogen balance (Figure 31) showed large experimental errors, and no trend is discernible, except that filter cake addition did increase hydrogen consumption.

A gas balance between the inlet hydrogen and product gas streams showed that hydrogen gas consumption increased by only about 50% as the pressure increased by 150% (Figure 32). Hence, a linear relation between pressure and hydrogen consumption is not substantiated.

Solvent Hydrogen Content. For all of these data points, the solvent was a net donor of hydrogen to the coal liquefaction reactions. The consumption of solvent hydrogen (expressed as a weight percent of the MAF coal feed) generally decreased as the reaction pressure increased (Figure 33) and always decreased when filter cake was added to the feed slurry.

In these open-loop experiments the total hydrogen consumed by the coal equals the sum of H_2 gas consumed plus solvent hydrogen consumed. If the solvent recovered from the product slurries were used to prepare fresh feed slurry, then a steady-state solvent concentration would eventually be attained. At that time, the solvent hydrogen consumption would be zero and the total hydrogen consumed by the coal would be identical with the hydrogen gas consumption. Our results (Figure 34) revealed no trends for total hydrogen consumption.

SRC Quality. The sulfur content of the SRC product seems to increase slightly as the system pressure is increased, although the differences are too small to draw any conclusion (Figure 35). Such a trend is plausible, however, since an increase in system pressure also increases the partial pressure of hydrogen sulfide.

Increasing the system pressure appears to beneficially increase the asphaltene/preasphaltene yield ratio, especially with a feed slurry containing 13 wt % filter cake (Figure 36).

Additional Product-Quality Analyses

The number-average molecular weight of the oil constituents was determined by vapor phase osmometry, and -OH oxygen and -NH nitrogen concentrations were measured by near-infrared (near-IR). Solvent hydrogen distribution among three classes was analyzed by proton nuclear magnetic resonance spectroscopy (1H NMR) [chemical shift is measured as parts per million from the internal standard tetramethylsilane (TMS)]: H_{ar} = 5.5-9.5 ppm; H_{α} = 2.0-4.7 ppm; H_o = 0.3-2.0 ppm.

NMR. H_{ar} counts those hydrogens that are attached to the carbons of aromatic rings. H_{α} counts hydrogens attached to carbons that are one carbon removed from an aromatic ring. This class includes most of the naphthenic hydrogens as well as the hydrogens of the first carbon in an alkyl substituent on an aromatic ring, such as the methyl hydrogens in toluene. H_o counts the hydrogens from alkanes and from hydrogens on carbons two or more carbons away from an aromatic ring. This class includes most of the hydrogens on alkyl side chains but also a portion of the naphthenic hydrogens (half of the donatable naphthenic hydrogens in octahydrophenanthrene would be classed as H_o). At present, even with these errors the absolute concentration of H_{α} is our best gauge of the hydrogen donor capacity of a solvent and is reasonable provided that the solvents being compared are structurally similar. H_o is our best measure of the combined concentrations of alkyl substituents and alkanes.

Temperature effects on hydrogen distribution in the product oils are shown in Figure 37. The top graph plots H_{ar}/H_{α} as a function of reaction temperature. As the temperature increases this ratio also tends to increase, indicating that the product oils become more and more aromatic in character at higher reaction temperatures.

This increase can be produced either by dehydrogenation of hydroaromatic structures or by the loss of substituents or aromatic rings. Heteroatom removal will also increase this ratio. For example, when a phenol group is removed from an aromatic ring, it is replaced by an aromatic hydrogen, thus increasing H_{ar}/H_{α} . A better estimate of aromaticity, taken from a modified Brown-Ladner calculation, will be discussed later. The addition of 13 wt % filter cake to the feed slurry does not significantly affect the product oil H_{ar}/H_{α} , which was usually higher than the feed oil ratio.

The middle graph of Figure 37 shows the absolute concentration of H_{α} as a function of temperature. The data seem to scatter around the H_{α} concentration of the oils from the feed solvent, but there is no consistent effect of either temperature or filter cake addition.

The bottom graph shows a significant inverse relationship between the absolute concentration of H_O in the oils and reaction temperature. All of the recovered oils contained less H_O than did the oil separated from the starting Wilsonville recycle solvent, indicating that for the reaction conditions studied in Run XCL-23, WRS differed substantially from an "equilibrium" steady-state solvent. The H_O concentration could be reduced during coal liquefaction by cracking of alkyl substituents from the oil molecules. Filter cake seems to moderate this H_O loss.

Figure 38 depicts the effect of reaction pressure upon product oil hydrogen distribution for a constant reaction temperature of 850°F. The top graph shows that H_{ar}/H_{α} varies inversely with pressure when filter cake is not present, which is expected since both the kinetic solvent hydrogenation rate and the chemical equilibrium ratio of naphthenics/aromatics will vary directly (but not necessarily first order) with hydrogen partial pressure. However, the data for the feed slurry containing 13 wt % filter cake do not follow a clear trend as system pressure increases; in all cases H_{ar}/H_{α} of the product oil equalled or exceeded the ratio for the feed. This is consistent with a reduction in either substituents or naphthenic hydrogen.

The middle graph shows the variation with system pressure of the absolute weight percent of α -hydrogen in the product oil: without filter cake, H_{α} concentration varies directly with pressure, and the highest concentration was observed. At 2,000 and 2,500 psig, the product oil contained more H_{α} than the feed oil. With filter cake, H_{α} was not significantly affected by pressure.

When filter cake is not present, H_O varies inversely with pressure. No trend is evident for the experiment with added filter cake (bottom graph).

Oil Molecular Weight. The number-average molecular weight determinations are accurate to within ± 10 amu (Figure 39). All of the product oil number-average molecular weights were significantly less than 221, the molecular weight measured for the oils in the undistilled starting solvent.

The top graph shows that, with the exception of one data point where the reaction mixture coked extensively, the oil's molecular weight was progressively reduced as the reaction temperature increased. In one extreme case molecular weight decreased from 221 to 184 between the feed and product, which could be due to cracking of alkyl substituents. Product oil molecular weights were generally higher with 13 wt % added filter cake in the feed than with the coal/WRS feed slurry. Changes in reaction pressure did not significantly or consistently influence product oil molecular weight.

Near-Infrared (NIR). The -OH oxygen and -NH nitrogen concentrations in the product oils were determined by measuring the NIR absorptions at 2,790 and 2,890 nm (Table 14).

The absolute concentration of phenolic oxygen in the product oils varied from 1.21 to 1.43%, while it was 1.35% in the feed solvent oil fraction. The variation in -OH analyses among the samples appears to equal the precision of this determination. About 45% of the total oxygen in the oils is phenolic oxygen.

The -NH nitrogen content of the product oils ranged from 0.09 to 0.17%, which is 10-25% of the total nitrogen content.

Brown-Ladner Calculations. The NMR, IR, and elemental analyses of the oils were used with modified Brown-Ladner equations (Retcofsky et al., 1977) to calculate average structural parameters for the oil molecules. The modification corrects for the phenolic content of the solvent. The structural parameters calculated were: σ , the substitution fraction of the aromatic edge carbons; f_a , the carbon aromaticity fraction; and H_{ar}/C_{ar} , the hydrogen to carbon ratio that pertains to the corresponding aromatic compounds *without* substituents. H_{ar}/C_{ar} values, useful indicators of the degree of compound condensation, are: 1.0 for a single-ring compound such as toluene; 0.8 for naphthalenes; 0.71 for the three-ring anthracenes and phenanthrenes; 0.67 for chrysene (four-ring, orthocondensed); and 0.63 for pyrene (four-ring, pericondensed).

The following equations were used:

$$f_a = \frac{\frac{C}{H} - \frac{H_{\alpha}^*}{X} - \frac{H_O^*}{Y}}{\frac{C}{H}} \quad (1)$$

$$\sigma = \frac{\frac{H_{\alpha}^*}{X} + \frac{O}{H}}{\frac{H_{\alpha}^*}{X} + \frac{O}{H} + H_{ar}^* - Z \frac{O}{H}} \quad (2)$$

$$\frac{H_{ar}}{C_{ar}} = \frac{H_{ar}^* - Z \frac{O}{H} + \frac{O}{H} + \frac{H_{\alpha}^*}{X}}{\frac{C}{H} - \frac{H_{\alpha}^*}{X} - \frac{H_O^*}{Y}} \quad (3)$$

Z is the fraction of oxygen as phenolic O; Y is the average number of H_O hydrogen atoms on the carbon atoms that are two or more carbons away from the aromatic ring (2.0 worked best in these calculations). X, the average number of hydrogen atoms on carbons α to an aromatic ring, was found by iteration using equations 1 and 4.

$$X_{\text{best}} = \frac{H_{\alpha}^* + H_O^*}{\frac{C}{H} - \frac{C}{H} f_a} \quad (4)$$

The calculated X_{best} values all ranged around 2.0 ± 0.2 .

These simplified equations assume that bridgehead hydrogens are an insignificant fraction of the total hydrogen and that all of the oxygens are attached directly to the ring, either as phenols or as cyclic ethers. This is a good estimate since the bridgehead hydrogens are less than about 5% of the total hydrogens.

The calculated values for the structural parameters are also listed in Table 14. σ 's varied from 0.30 to 0.33 and did not seem to be a function of the reaction conditions.

f_a varied from 0.57 to 0.63. Only the starting solvent and the 780°F sample from the 30% coal/WRS experiment had an aromaticity of 0.57; all of the other product oil aromaticities were higher than that of the oil from the starting solvent. Increasing the reaction temperature tended to raise the carbon aromaticity (upper panel of Figure 40), while the addition of filter cake reduced it slightly.

$H_{\text{ar}}/C_{\text{ar}}$ for the product oils fell within the range 0.81 to 0.92, while the WRS oils had a ratio of 0.86, which is in the middle of that range. This ratio does not seem to vary systematically as a function of reaction conditions, and it indicates that the average number of condensed aromatic rings in the feed and product oils is 1.4-1.9.

SRC Molecular Weight. We used vapor phase osmometry to calculate number-average molecular weights for asphaltene and preasphaltene product fractions.

The asphaltene number-average molecular weights ranged from 363 to 532 but did not vary consistently as a function of reaction conditions (Figure 41).

The preasphaltene number-average molecular weights varied from 693 to 2,150 with changes in reaction temperature and pressure (Figures 42 and 43, respectively). Molecular weight decreased fairly sharply and consistently as the reaction temperature was increased. This is reasonable since coal conversion to preasphaltenes is sufficiently rapid that preasphaltenes can almost be viewed as the first reactant in the reaction series:

As the reaction severity increases, a greater fraction of the large preasphaltene molecules will split into smaller preasphaltenes and asphaltenes. Barring regressive polymerization reactions, there is no source to replenish these large preasphaltenes since coal conversion is almost complete at all of these temperatures.

The effect of system pressure upon the average preasphaltene molecular weight is shown in Figure 43 for an 850°F reaction temperature. The very high molecular weight average at 1,000 psig is not surprising, since regressive polymerization reactions could be significant at this low a pressure. However, we cannot explain why the molecular weight average should be significantly greater at 2,500 psig than at 2,000 psig. In this figure the curves for the experiments with and without added filter cake virtually overlap, indicating no effect of filter cake addition. The temperature study in Figure 42 also shows no significant effect of filter cake addition upon the average molecular weight of the preasphaltene product. Recall, however, that filter cake addition does significantly reduce the total yield of preasphaltenes.

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Table 1

Experimental Variable Space^a

Feed slurry composition	780°F 2,000 psi	815°F 2,000 psi	850°F 1,000 psi	850°F 2,000 psi	850°F 2,500 psi	885°F 2,000 psi
30% Pyro KY #9 coal in Wilsonville recycle solvent (WRS)	X	X	X	X	X	X
30% Pyro KY #9/ 5% KY #9 filter cake in WRS		X		X		
30% Pyro KY #9/ 15% KY #9 filter cake in WRS	X	X	X	X	X	X
30% Pyro KY #9 coal in creosote oil		X		X		

^aAll data at LHSV = 2.0; 2.2 wt % H₂ based on total feed.

Table 2A

Feed Materials Composition
Feed Coal
(KY #9, Pyro Mine)

Analysis	Laboratory		
	Air Products	PETC	Huffman
Moisture (wt %)	<u>1.8</u>	4.3	1.5
ASTM ^a ash (wt %)	10.1	14.4	12.8, 13.4 <u>13.1</u>
Sulfate ash (wt %)	13.5		13.4, 13.7
Volatiles (wt %)	37.9	34.4	36.1
Fixed carbon (wt %)	49.4	46.9	50.4
Carbon (wt %)	<u>69.3</u>		70.4
Hydrogen (wt %)	<u>4.7</u>		4.8
Nitrogen (wt %)	0.9	1.9	<u>1.5</u>
Sulfur (wt %)	<u>3.0</u>	3.0	3.3
Sulfates (wt %)	0.04	0	0.1
Pyrites (wt %)	1.8	1.6	1.6
Oxygen (wt %)			6.1
Aluminum (wt %)	1.5	1.5	
Silicon (wt %)		3.7	
Iron (wt %)	1.5	1.5	
Titanium (ppm)	570	1,000	
Boron (ppm)	590		
Chlorine (ppm)	2,400		
Calcium (ppm)	90	1,900	
Magnesium (ppm)	850	980	
Potassium (ppm)	2,700	2,900	
Sodium (ppm)	470	460	
Pyridine soluble (wt %)	16.5		

^aASTM, American Society for Testing and Materials.

Table 2B

Feed Materials Composition
Residue Additive

	KY #9 filter cake Air Products	KY #9 filter cake Huffman	Indiana V filter cake Air Products
ASTM ^a ash (wt %)	50.9	55.1, 57.6	65.3
Sulfate ash (wt %)		(56.3)	69.8
Carbon (wt %)		34.1	21.9
Hydrogen (wt %)		2.3	1.5
Nitrogen (wt %)		0.5	0.5
Sulfur (wt %)		4.0	5.3
Oxygen (wt %)		5.3	
Aluminum (wt %)	4.5		6.5
Iron (wt %)	5.7		7.4
Titanium (ppm)	15		930
Boron (ppm)	2,400		
Chlorine (ppm)	7,200		700
Calcium (ppm)	60		1,600
Magnesium (ppm)	2,200		6,600
Potassium (ppm)	8,700		10,000
Sodium (ppm)	23,000		4,600
Pentane solubles (wt %)	9.2		
Toluene solubles (wt %)	10.1		4.7
Pyridine solubles (wt %)	14.7		9.1
Analysis of pyridine insolubles:			
Carbon (wt %)			20.6
Hydrogen (wt %)			1.3
Nitrogen (wt %)			--
Sulfate ash (wt %)			70.0

^aASTM, American Society for Testing and Materials.

Table 2C

Feed Materials Composition
Wilsonville Process Solvents
(Drum No. F-198, F-199)

IBP-420°F (wt %)	1.3	Oils (wt %)	95.8
Carbon (wt %)	84.8	C (wt %)	87.26
Hydrogen (wt %)	9.9	H (wt %)	8.88
Nitrogen (wt %)	0.4	O (wt %)	2.52
Sulfur (wt %)	0.2	N (wt %)	0.76
420-550°F (wt %)	53.9	S (wt %)	0.58
Carbon (wt %)	87.5	Asphaltenes (wt %)	1.4
Hydrogen (wt %)	9.3	C (wt %)	82.69
Nitrogen (wt %)	0.4	H (wt %)	6.26
Sulfur (wt %)	0.3 ^a	O (wt %)	7.23
550-780°F (wt %)	32.6	N (wt %)	2.20
Carbon (wt %)	88.4	S (wt %)	1.61
Hydrogen (wt %)	8.5	Preasphaltenes (wt %)	2.8
Nitrogen (wt %)	1.1	Sample lost, no analyses	
Sulfur (wt %)	0.3 ^a	Overall solvent (as received)	
780°F+ (wt %)	12.2	C (wt %)	87.25
Carbon (wt %)	86.6	H (wt %)	8.85
Hydrogen (wt %)	7.4	O (wt %)	2.61
Nitrogen (wt %)	1.6	N (wt %)	0.76
Sulfur (wt %)	0.7	S (wt %)	0.58
Heptane soluble (wt %)	78.0		
Toluene soluble (wt %)	92.9		

^aAnalyzed as combined fractions.

Table 3A

Summary of XCL-23 Data Points^a

Feed slurry composition for balance period	Reaction temperature (°F)			
	780	815	850	885
(1) Creosote oil (CO)	5	10	15	25
(2) 25% KY #9 filter cake (FC)/CO	225	231	237	250
(3) 20% Pyro KY #9 coal/CO		298	306	
(4) 30% Pyro KY #9 coal/CO		<u>276</u>	<u>282</u>	
(5) 40% Pyro KY #9 coal/CO		267	261	
(6) 30% Pyro KY #9 coal/15% FC/CO		316	323	
(7) 40% KY #9/14 coal in Wilsonville recycle solvent (WRS)		52	47	
(8) 30% Pyro KY #9 coal/WRS	<u>195</u>	<u>189</u>	<u>163</u>	<u>158</u>
(9) 30% Pyro KY #9 coal/5% FC/WRS		<u>204</u>	<u>210</u>	
(10) 30% Pyro KY #9 coal/15% FC/WRS	<u>95</u>	<u>102</u>	<u>108</u>	<u>132</u>

^aThose samples that have been analyzed thus far are underlined. All data points in this table at 2,000 psig, LHSV = 2 hr⁻¹, 2.2% H₂. Numbers in the table are the sample numbers, i.e., balance-period numbers.

Table 3B

Summary of XCL-23 Data Points
(All Data Points at 850°F)

Feed slurry composition for balance period	LHSV = 2 1,000 psig	LHSV = 2 1,500 psig	LHSV = 2 2,000 psig	LHSV = 2 2,500 psig	LHSV = 3 2,000 psig
(1) Creosote oil (CO)	20		15		
(2) 25% KY #9 filter cake (FC)/CO	242		237		
(4) 30% KY# 9 coal/CO	288		282		
(6) 30% Pyro KY #9 coal/ 15% FC/CO	329		323		
(7) 40% KY #9/14 coal/ Wilsonville recycle solvent (WRS)			47		37
(8) 30% Pyro KY #9 coal/WRS	<u>182</u>	175	<u>164</u>	169	
(9) 30% Pyro KY #9 coal/ 5% FC/WRS	215		<u>210</u>		
(10) 30% Pyro KY #9 coal/ 15% FC/WRS	<u>120</u>	126	<u>108</u>	<u>114</u>	

Table 4

Product Sampling Problem
(Calculated Weight Percent of Product Fraction in Slurry)

Data point	Size of sample (g)	Distillate	SRC	Residue	Oil	Asph	PA	Residue
23-163	100				68.2	10.4	13.6	7.8
					69.5	11.7	10.3	8.5
					67.0	13.8	12.1	7.2
					<u>69.7</u>	<u>11.1</u>	<u>11.1</u>	<u>8.1</u>
				Average	68.6	11.8	11.8	7.9
23-164	1,000	65.4	28.3	6.3				
23-164	100				63.0	10.7	13.4	12.9

Table 5

Comparison of Distillation Yields

Distillation procedure	Distillate (wt %)	Ash in residue (wt %)
Short	65.2	59.1
Short	65.5	58.9
Short	64.8	60.4
Forced-flash	72.2	59.1

Table 6

Variance in Distillate Yield by Linwood Determination

Sample	Wt % distillate data points	n	df	ΣX	ΣX^2	$\bar{X}$	SS
27-50,56	69.3, 69.4	2	1	138.7	9,619	69.35	0.01
27-277,284	68.0, 69.2	2	1	137.2	9,413	68.6	0.72
27-188,192	57.5, 63.2	2	1	120.7	7,300	60.35	16.25
27-122,129	57.9, 56.9	2	1	114.8	6,590	57.4	0.50
26-169	65.2, 65.5, 64.8	3	2	195.5	12,740	65.2	0.25
a	65.4, 68.0, 70.8	<u>3</u>	<u>2</u>	204.2	13,914	68.1	<u>14.59</u>
		14	8				32.32

$$s^2 = \frac{32.32}{8} = 4.01$$

^a = 21-288, 23-164, 27-106, which have identical reaction conditions.

Table 7

Variance in Laboratory Residue Determination for CPDU Samples

Sample	Data points	n	df	ΣX	ΣX^2	$\bar{X}$	SS
23-102	17.0, 16.4	2	1	33.4	558	16.7	0.18
23-108	17.0, 17.5	2	1	34.5	595	17.25	0.13
23-120	20.2, 19.1	2	1	39.3	773	19.65	0.61
23-158 ^a	16.7, 14.4	2	1	31.1	486	15.55	2.65
23-163	7.8, 8.5, 7.2, 8.1	4	3	31.6	251	7.9	0.90
23-169 ^a	7.6, 7.4, 7.9, 7.0, 8.1, 7.8	6	5	45.8	350	7.63	0.77
23-189	9.0, 8.6	2	1	17.6	155	8.8	0.08
23-204	12.1, 12.1	2	1	24.2	293	12.1	0
23-210	11.8, 10.7	<u>2</u>	<u>1</u>	22.5	254	11.25	<u>0.61</u>
		24	15				5.93

$$s^2 = \frac{5.93}{15} = 0.40$$

^a Ash concentration, converted to residue by dividing average weight percent ash to keep separation techniques used at Wilsonville comparable.

Table 8

Variance in Ash Determination among Different
CPDU Samples of Same Product Stream

Sample	Data points	n	df	ΣX	ΣX^2	$\bar{X}$	SS
23-158	6.0, 3.8	2	1	9.8	50	4.9	2.42
23-164	5.5, 4.0, 3.7	3	2	13.2	60	4.4	1.86
23-170	4.2, 4.3, 5.3	3	2	13.8	64	4.6	0.74
23-195	4.7, 3.5	<u>2</u>	<u>1</u>	8.2	34	4.1	<u>0.72</u>
		10	6				5.74

$$s^2 = \frac{5.74}{6} = 0.96^a$$

^aThis is equivalent to an S^2 for residue of about $(0.96/0.55)^2 = 3.1$ or over seven times as large a variance as for laboratory separation (0.55 is the average ash fraction in residue).

Table 9

Sample Variance for Oil Determination

Sample	Data points	n	df	ΣX	ΣX^2	$\bar{X}$	SS
23-163	68.2, 69.5, 67, 69.7	4	3	274.4	18,828.6	68.6	4.8
23-169	70.7, 72.0, 73.4	3	2	216.1	15,570.1	72.03	3.7
23-102	57.5, 59.7	2	1	117.2	6,870.3	58.6	2.4
23-108	65.9, 64.7	2	1	130.6	8,529	65.3	0.7
23-120	54.6, 64.4	2	1	119.0	7,128.5	59.5	48.0
23-189	63.7, 67.8	2	1	131.5	8,654	65.75	8.4
23-204	65.3, 67.4	2	1	132.7	8,807	66.35	2.2
23-210	68.7, 71.2	2	1	139.9	9,789	69.95	3.1
23-95	58.4, 58.5	2	1	116.9	6,833	58.45	0.0
23-164	63.0, 62.1	<u>2</u>	<u>1</u>	125.1	7,825	62.55	<u>0.4</u>
Total		23	13				73.7

A. Consider all data points

Pooled error SS = SS = SS = 73.7

$$S^2 = MS_E = \frac{73.7}{13} = 5.7$$

B. Consider only 23-163, 23-169 (most recent data)

SS = 8.5

df = 5

$$S^2 = \frac{8.5}{5} = 1.7$$

Table 10

Sample Variance for Preasphaltene Determination

Sample	Data points	n	df	ΣX	ΣX^2	$\bar{X}$	SS
23-163	13.6, 10.3, 12.1, 11.1	4	3	47.1	561	11.78	6.1
23-169	10.3, 10.8, 8.3	3	2	29.4	292	9.80	3.5
23-102	14.2, 12.0	2	1	26.2	346	13.1	2.4
23-108	10.9, 9.5	2	1	20.4	209	10.2	1.0
23-120	8.1, 18.2	2	1	26.3	397	13.15	51.0
23-189	16.6, 13.9	2	1	30.5	469	15.25	3.7
23-210	8.9, 10.4	<u>2</u>	<u>1</u>	19.3	187	9.65	<u>1.1</u>
		17	10				68.8

A. Consider all data points

Pooled error $SS = SS = SS = 68.8$

$$s^2 = MS_E = \frac{68.8}{10} = 6.9$$

B. Consider just 23-163, 23-169 (most recent data)

$SS = 9.6$ $df = 5$

$$s^2 = \frac{9.6}{5} = 1.9$$

Table 11

Comparison of Product Fractionation Techniques
(Sample 23-169)

Procedure used	Oil or solvent	Asphaltene	Preasphaltene	Residue
Solvent fractionation	70.7	11.6	10.3	7.4
	72.0	10.0	10.8	7.2
	<u>73.4</u>	<u>10.3</u>	<u>8.3</u>	<u>8.0</u>
Avg	72.0	10.6	9.8	7.5
Solvent precipitation	73.8	7.4	10.9	8.1
	73.4	8.8	9.4	8.4
	<u>73.4</u>	<u>7.0</u>	<u>12.1</u>	<u>8.1</u>
Avg	73.5	7.7	10.8	8.2
Short distillation	65.2		29.7	5.1
	65.5		27.9	6.6
	<u>64.8</u>		<u>28.7</u>	<u>6.5</u>
Avg	65.2		28.7	6.1
Forced-flash distillation	72.2		21.9	5.9

Table 12

Comparison of Product Fractionation Techniques
(Sample 23-158)

Fractionation technique	Concentration of product fraction, wt % ^a			
	Oil or distillate	Asphaltene	Preasphaltene	Residue
Solvent separation	61.9 (66.4)	10.4 (11.1)	10.8 (11.5)	17.0 (11.1)
Solvent precipitation	74 (76.8)	5 (5.2)	6.8 (7.0)	14.2 (10.6)
Distillation	66.8 (66.1)		24.0 (23.6)	9.2 (10.3)

^aForced-ash balance concentrations in parentheses.

Table 13

Comparison of Results between Creosote Oil and Wilsonville Solvents
Forced-Ash Balance

Sample	189	276	163	282
Solvent	WRS	Creosote	WRS	Creosote
Temperature (°F)	815	815	850	850
Ash balance	124	112	97	158
Net product slate (wt % MAF)				
Hydrocarbon gas	3.5	1.9	6.9	3.2
CO, CO ₂ , H ₂ S, NH ₃	2.7	2.2	2.6	2.2
Water	1.8	0.9	2.9	1.7
Oil	(7.0)	16.3	(4.4)	24.7
Asphaltene	35.8	26.4	40.3	24.5
Preasphaltene	51.7	42.3	36.5	35.1
IOM	12.2	10.0	16.0	8.8
Hydrogen consumption (wt % MAF)				
From gas	(0.4)	2.3	(0.1)	2.4
From solvent	0.9	(0.7)	1.2	(1.1)
Total	0.6	1.6	1.1	1.3
SRC quality				
Sulfur (wt %)	1.2	1.2	1.1	1.4
Asphaltene/preasphaltene ratio	0.7	0.6	1.1	0.7

Table 14

Oil and Asphaltene Characterization

% FC	Sample ID	¹ H NMR analysis			NIR analysis		No. avg mol wt	Atomic fraction (%)					OH/O	X	σ	H _{ar} /C _{ar}	f _a
		H _{ar}	H _α	H _o	OH	NH		C	H	O	N	S					
					(wt % O)	(wt % N)											
	Wilsonville solvent - oils	28.4	23.7	47.9	1.35	0.15	221	44.55	54.04	0.96	0.33	0.11	0.54	2.09	0.32	0.86	0.57
	Wilsonville solvent - asph.						384						0.17				
0	23-195-Oil (780, 2000)	27.7	23.3	49.0	1.24	0.13	195	45.34	53.0	1.27	0.28	0.123	0.38	2.2	0.32	0.85	0.57
	23-195-Asph.				3.06	0.20	424										
0	23-189-Oil (815, 2000)	28.8	23.6	47.6	1.30	0.09	192	45.63	52.92	0.97	0.36	0.12	0.52	2.05	0.32	0.81	0.59
	23-189-Asph.				2.64	0.22	391						0.48				
0	23-164-Oil (850, 2000)	34.3	26.9	38.8	1.33	0.15	184	46.06	52.29	1.09	0.45	0.12	0.48	1.95	0.33	0.87	0.62
	23-164-Asph.				2.65	0.33	363						0.52				
0	23-158-Oil (885, 2000)	35.8	24.6	39.6	1.29	0.13	201	46.50	51.87	1.12	0.39	0.13	0.46	1.88	0.32	0.85	0.63
	23-158-Asph.				2.03	0.21	458						0.46				
0	23-169-Oil (850, 2500)	34.8	29.0	36.2			190	44.65	53.86	1.04	0.35	0.11		2.10	0.33	0.92	0.58
	23-170-Asph.				2.76	0.30	395						0.47				
0	23-182-Oil (850, 1000)	34.1	21.8	44.1	1.28	0.13	190	45.99	52.13	1.17	0.61	0.10	0.44	1.97	0.30	0.81	0.62
	23-182-Asph.				1.97	0.19	523						0.36				
13	23-95-Oil (780, 2000)	Contaminated with pentane															
	23-95-Asph.																
13	23-102-Oil (815, 2000)	28.9	24.5	46.6	1.21	0.12	201	44.85	53.81	0.88	0.31	0.15	0.53	2.08	0.32	0.86	0.58
	23-102-Asph.				2.50	0.23	407						0.47				
13	23-108-Oil (850, 2000)	31.3	22.3	46.4	1.38	0.10	208	45.09	53.40	1.04	0.37	0.10	0.51	2.04	0.30	0.86	0.60
	23-108-Asph.				2.15	0.18	532						0.40				
13	23-132-Oil (885, 2000)	33.2	24.6	42.2	1.43	0.17	188	46.23	52.33	1.04	0.30	0.11	0.55	1.99	0.32	0.81	0.62
	23-132-Asph.				2.32	0.26	384						0.47				
13	23-114-Oil (850, 2500)	32.2	25.2	42.6	1.31	0.14	203	45.62	52.83	1.09	0.36	0.10	0.47	2.07	0.32	0.84	0.61
	23-114-Asph.				2.53	0.21	529						0.49				
13	23-120-Oil (850, 1000)	32.6	24.4	43.0	1.36	0.10	193	45.89	52.61	0.94	0.44	0.11	0.42	2.03	0.31	0.84	0.62
	23-120-Asph.				2.38	0.33	496						0.47				
5	23-210-Oil (850, 2000)	30.0	23.8	46.0	1.36	0.14	194	45.45	53.08	1.05	0.32	0.11	0.51	2.05	0.32	0.83	0.60
	23-210-Asph.				2.75	0.35	422						0.54				

SRC-I QTR—APRIL-JUNE 1981

Chart 1
Product Liquid Separation
Method 1
(Solvent Separation)

Chart 2
Product Liquid Separation
Method 2
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Chart 3
Product Liquid Separation
Methods 3 or 4

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EFFECTS OF ACCUMULATED SOLIDS ON DISSOLVER PERFORMANCE (OCTOBER-DECEMBER 1980)

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This article presents results from the final open-loop run through the coal process development unit (CPDU), which evaluated the catalytic activities of filter cake and Kerr-McGee ash concentrate (K-MAC) (simulating dissolver solids) at demonstration plant conditions. Also, the effect of sodium carbonate addition was determined and the liquefaction behaviors of Pyro and Lafayette Kentucky #9 coals were compared.

Many tentative conclusions from previous runs were substantiated by this run; however, there was an increase in oil yield as the reaction temperature increased that was not observed previously. The addition of either type of solid, filter cake or K-MAC, substantially increased H₂ gas consumption and solvent hydrogenation, but did not affect the hydrocarbon gas yield. Thus, dissolver solids appear to catalyze the solvent hydrogenation reaction.

The results indicate that (1) dissolver solids catalyze preasphaltene conversion and solvent hydrogenation and (2) an SRC process using residue recycle can improve net coal and preasphaltene conversions without increasing gas yield. Improved preasphaltene conversion is economically significant because the Kerr-McGee critical solvent deashing (CSD) unit cannot efficiently recover preasphaltenes as products.

EXPERIMENTAL PROGRAM

Product slurry samples were collected at 18 sets of reaction conditions; at each, distillable solvent yield and quality were determined. A solvent separation procedure was used to predict the complete product slate and the quantity of hydrogen consumed at 10 of the reaction conditions. The solvent separations were generally performed in duplicate, to avoid the spurious results seen in the preceding run.

Materials

The Pyro Kentucky #9 coal was identical with that used previously (Runs XCL-21 and -23) (Table 1), but filter cake and Kerr-McGee ash residues differed (Table 2). The filter cake, which was produced during Wilsonville Run 175 using Kentucky #9 feed coal, contains

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only 50.7 wt % ash, compared to 53.1 and 65.3% for the filter cakes tested in Runs XCL-23 and XCL-21, respectively. The Kerr-McGee ash concentrate (K-MAC) contained 26.4% ash, significantly less than the 37.2 wt % ash tested during Run XCL-21.

The Wilsonville recycle solvent (WRS) used here contained only 8.13 wt % hydrogen, whereas that used previously contained 8.85 wt % hydrogen (Table 3). Also, this run used solvent containing 97.5 wt % oils and was 95.7% distillable, whereas the previous solvent contained 95.8 wt % oils and was only 87.8% distillable by our laboratory batch distillation procedure. The solvents also had contrasting hydrogen distribution, as determined by proton nuclear magnetic resonance (^1H NMR). The values given below are for the oil fraction of the solvent:

	Run 179 XCL-27 WRS	Run 166 XCL-21,23 WRS
% H as H_{ar}	36.4	28.4
% H as H_{α}	27.9	23.7
% H as H_{O}	35.7	47.9

The current solvent is more aromatic and has fewer side chains and/or saturates than the previous WRS, which should be reflected in a reduced hydrocarbon gas yield and slightly increased coal conversion.

The Wilsonville solvent quality test shows that the Wilsonville Run 179 solvent used in Run XCL-27 is significantly superior to the Wilsonville Run 166 solvent used previously. Microautoclave solvent quality numbers were 67.5 on July 2, 74.1 on July 3, 65.3 on July 4, 69 on July 9, and 55 on July 10, suggesting that the Run 166 solvent collected on July 3 has a solvent quality number of about 67. The Run 179 solvent was collected at Wilsonville on November 26, 1979. A sample analyzed on November 24 and two from November 29 show solvent quality numbers of 75.9, 73.6, and 72.5, respectively. Thus, the Run 179 solvent quality number is about 74, compared to only 67 for the Run 166 solvent.

Operation

Our only significant operational problem was the inability to obtain a reasonable gas-phase hydrogen balance. Either the inlet hydrogen rate or the product gas rate was in error by about 10%.

The only major equipment change since Run XCL-23 was the installation of a conical bottom in the main product receiver, which greatly improved the precision of the ash material balance.

Product Work-up

Product slurry distillations were carried out on 300-g samples using a packed column equal to 15 plates. This column, the standard short distillation procedure, and the solvent fractionation procedure are described in the preceding article in this report. In view of the occasional spurious results seen with this technique, most of the product slurry samples from Run XCL-27 were fractionated in duplicate. If the first two analyses disagreed significantly, the separation was run a third time.

Statistical analysis of the variation in analytical results indicates that the improved precision achieved on the final samples from Run XCL-23 has continued, but little further improvement was seen, and that errors are due to the solvent fractionation procedure rather than CPDU sampling.

Statistical Analysis of Solvent Separation Precision

Solvent separation analyses were duplicated at seven of the XCL-27 reaction conditions. Several replicates analyzed separate product samples collected at constant reaction conditions, while the remainder were multiple analyses of the same sample. Since the most recent data from XCL-23 (samples 163 and 169) showed similar precision, they were included in the analysis.

Results are reported in Table 4. Although estimated "standard deviations" are included for comparison, the data represent only 12-17 degrees of freedom (df) and are not adequate to determine a true standard deviation. The Student's *t* test distribution was used for all data comparison. Note that determination of the oil fraction concentration is the least precise analysis; the standard deviation of 1.6% corresponds to a standard deviation of 6.3% moisture and ash free (MAF) in oil yield.

RESULTS

The product slurry was separated into four fractions: (1) pentane-soluble oils; (2) pentane-insoluble, benzene-soluble asphaltenes; (3) benzene-insoluble, pyridine-soluble preasphaltenes; and (4) pyridine-insoluble residue.

Each fraction was analyzed for C, H, O, N, S, and ash, so that elemental balances and hydrogen gas consumption could be computed. The ash balances were forced by adjusting the quantity of residue in the product slurry. Since the ash balances were generally excellent, only those results are discussed.

Distillate was determined by batch distillation to give an independent measure of solvent yield, which may be more representative of the solvent yield achieved in the demonstration plant than the solubility-defined oil yield can be. Unfortunately, the laboratory distillation gave only a 750-780°F end point instead of the 850°F end point expected from the plant's continuous distillation columns. Because of this difference in end points, our batch distillation might not be a good indicator of demonstration plant solvent yield. Therefore, a new procedure has been developed that will achieve an 850°F end point on future samples.

Improper sampling of the distillation bottoms resulted in some very poor ash balances. Since analysis of the smaller solvent separation samples showed that the ash balances were actually very good, the distillation yield calculations were not based on a forced-ash balance.

Effect of Residue Addition at Demonstration Plant Conditions

To estimate the catalytic activity of dissolver solids, the liquefaction behaviors of slurries consisting of (1) 30% coal/70% WRS, (2) 30% coal/15% filter cake/55% WRS, and (3) 30% coal/15% K-MAC/55% WRS were compared at demonstration plant conditions [2,000 psig, 840°F, liquid hourly space velocity (LHSV) = 1.4, and a hydrogen feed rate equal to 3.0 wt % of the slurry feed rate].

Two separate product slurry samples were collected for each feed slurry and analyzed independently. Analyses of two of the samples were repeated in an effort to overcome data scatter. The results are summarized in Table 5. Table 6 shows the statistical significance of the changes in liquefaction behavior caused by residue addition. Changes that are statistically significant at a 95% confidence level are underlined. Residue addition reduced preasphaltene yield, increased oil plus asphaltene yield, increased hydrogen gas and total hydrogen consumptions, and increased the solvent hydrogen content.

Effect upon Product Slate. The combined net yield of oil plus asphaltenes increased by about 11% MAF when 15 wt % filter cake was added and by about 24% MAF when an equal quantity of K-MAC was added. Although both of these changes are significant at the 95% confidence level, they do not prove that the coal minerals in the residues are catalytic. Unlike true dissolver solids, the residue additives contain reactive organic materials such as preasphaltenes and coal macerals. Thus, the net oil plus asphaltene yield could conceivably increase simply because of the increased concentration of reactants. Simplified kinetic rate constants for preasphaltene conversion (presented in detail later) show that at least part of the increase in oil plus asphaltenes is due to residue mineral catalysis of the preasphaltene conversion step:

The preceding discussion indicates that the net yield of preasphaltenes should decrease. This proved true. Filter cake addition reduced the preasphaltene yield by 10.3% MAF, while K-MAC addition reduced it by 16.3% MAF. As will be demonstrated later, K-MAC's effect upon preasphaltene yield is caused not by catalysis, but rather by reaction of the large quantity of preasphaltene (45% by weight) contained in the K-MAC.

Adding K-MAC significantly reduced net residue yield, from 10.2 to 1.1% MAF, probably because K-MAC coal macerals were converted. In contrast, the small reduction in net residue yield following filter cake addition is not statistically significant, even at the 80% confidence level. Since the filter cake contains a greater concentration of both coal macerals and coal minerals than K-MAC, this difference in behavior is somewhat puzzling. One possible explanation is that the intimate contact of coal macerals with preasphaltenes in the K-MAC renders those macerals more reactive.

The data suggest that residue addition increased oil yield by about 8-10 wt % (MAF), but this change is not statistically significant. Oil yield is one measure of solvent yield; the net yield of distillate (Figure 1) is another. Although filter cake had no effect upon distillate yield, K-MAC residue addition increased distillate yield from 4 to 14-25 wt % (MAF). Thus, the data indicate that filter cake and, presumably, dissolver solids do not affect solvent yield. However, K-MAC addition may increase solvent yield, because the preasphaltenes in K-MAC partially convert to oil.

Effect upon Hydrogen Consumption. Hydrogen gas consumption, probably through solvent hydrogenation, appears to be strongly catalyzed by both residues. With filter cake it increased by a factor of 2.5, from 1 to 2.5 wt % of the MAF coal, and K-MAC caused almost as large an increase, to 2.3 wt % MAF. Both of these changes are twice as large as needed to be statistically significant at the 95% confidence level.

Because of the large increase in hydrogen gas consumption, the hydrogen content of the product solvent increases relative to the starting solvent. When no residue was added, the product oils contained only 7.90 wt % hydrogen compared to 8.22 wt % in the WRS oil fraction. This decrease constitutes a net donation of hydrogen to the coal equal to 0.8

wt % of the MAF coal feed. In contrast, when filter cake was added, the hydrogen content of the product oils increased to an average of 8.29 wt %, while with K-MAC, the product oils had the same hydrogen content as the WRS oils.

Filter cake addition caused a 1.0 wt % (MAF) decrease in the net quantity of solvent hydrogen consumed by the reactions, while K-MAC caused an 0.8 wt % MAF decrease. Both of these changes are statistically significant at a 95% confidence level.

As seen in Figure 2, residue addition also increased the hydrogen content of the product distillate, although K-MAC rather than filter cake had the larger effect. Thus, by either method of defining the solvent, residue addition increases solvent hydrogenation.

The concept of net donation or consumption of hydrogen by the process solvent must be considered here only because these are open-loop experiments with a nonequilibrium process solvent. At Wilsonville or the demonstration plant, in a closed-loop, solvent-recycle configuration, the process solvent will eventually assume a fixed steady-state composition, provided the reaction conditions are held constant. At that time, the solvent will neither gain nor lose hydrogen in the course of the reaction, and the total hydrogen consumed in converting the coal will equal the hydrogen gas consumption. By definition, an equilibrium solvent's composition is unchanged between feed and product streams. Although very close to an equilibrium solvent for Wilsonville, WRS cannot be an equilibrium solvent for each CPDU reaction condition, and its composition changes in the CPDU.

Future CPDU runs will be closed-loop runs in which the steady-state solvent composition, product slate, and hydrogen consumption will be determined both with and without added filter cake. Meanwhile, we can only approximate the quantity of hydrogen that the coal will consume at steady-state conditions by totalling the hydrogen gas and solvent hydrogen consumptions.

The total hydrogen consumption is 1.8 wt % of the MAF coal feed without residue addition, and 2.3 wt % of the MAF coal with either filter cake or K-MAC. This 0.5 wt % (MAF) change in total consumption is statistically significant at a 95% confidence level, even though the difference is only half the observed change.

Although the data clearly show that the mineral-rich residues catalyze hydrogen gas consumption by coal slurries, the mechanism is unclear. Earlier data showed that residues had little impact upon solvent hydrogenation/dehydrogenation in the absence of coal. This complex interaction between coal, solvent, hydrogen, and residue certainly needs to be better understood. Free radicals generated from the coal may play an essential role in solvent hydrogenation.

Our data also show a slight trend toward increased oil yield and decreased sulfur concentration in the SRC product when either residue is added to the feed. As shown in Table 6, however, neither of these trends is significant at a 90% confidence level.

Calculations of Kinetic Rate Constants. Comparison of calculated kinetic rate constants is useful for isolating true catalytic effects from changes due to variations in reactant concentration. This method is essential for assessing the catalytic activity of the minerals in K-MAC. Its high preasphaltene concentration should substantially enhance the rate of preasphaltene conversion simply by increasing the preasphaltene concentration in the dissolver. This has a ripple effect: conversion of some of the extra preasphaltene will increase the asphaltene concentration and thus affect the absolute rate of asphaltene conversion. Our CSTR is particularly suited for the calculation of rate constants since the concentration of each species in the reactor equals its concentration in the exit stream (ignoring volatilization of light solvent constituents).

Properly calculated kinetic constants can remove the effects of variations in reactant concentrations that might obscure catalytic effects. However, the accuracy depends on the

validity of the kinetic model used to make the calculation. We have assumed the following simple, first-order, sequential kinetic model:

Although we have not proven the validity of the above model, it fit our past data reasonably well over a wide range of reaction conditions. Addition of a parallel reaction step for conversion of preasphaltene to oil did not significantly improve the model's ability to fit that data.

The most arbitrary feature of the model is its handling of product gas formation. About half of the hydrocarbon gas actually arises from cracking of the oil fraction. Asphaltenes are considered to be the source of heteroatom gases and water, based upon the observation that asphaltenes and preasphaltenes have about the same heteroatom (O, N, S) content. Oils contain much fewer heteroatoms. These details of the model may seriously affect the kinetic constants for asphaltene and oil conversion but should not affect the coal and preasphaltene kinetic constants.

The rate constants computed from the data using our kinetic model are shown in Table 7. Although considerable data scatter is evident, the statistics (Table 8) show that filter cake catalyzes preasphaltene conversion.

The mean value of the experimental kinetic rate constant for preasphaltene conversion increased from 2.7 to 4.2 hr^{-1} when filter cake was added. This better than 50% increase is statistically significant at a 95% confidence level. Although K-MAC addition also increased the mean rate constant, the change was much smaller and not statistically significant. Even though the same coal-derived minerals, notably pyrrhotite and clays, are found in both filter cake and K-MAC, this difference in catalytic activity is reasonable: first, the absolute concentration of minerals was almost twice as high in the filter cake as in K-MAC; second, the large quantity of preasphaltenes present in K-MAC probably obstructs much of the free mineral surface area, further reducing catalytic activity.

The mean kinetic rate constant for asphaltene conversion increased slightly from 1.3 hr^{-1} with no additive, to 1.5 hr^{-1} with filter cake, to 1.4 hr^{-1} with K-MAC. These increases are not statistically significant, which suggests that the coal minerals found in these residues, as well as in dissolver solids, do not significantly catalyze asphaltene conversion. However, the reader is cautioned that the rate constant for asphaltene conversion is particularly dependent upon the nature of the kinetic model. If the parallel reaction pathway

is significantly rapid, then the rate constant for asphaltene conversion should be smaller, and the observed effects of adding residue minerals could be magnified. This should be investigated, since it is unreasonable that coal minerals catalyze preasphaltene and not asphaltene conversion. Preasphaltenes and asphaltenes are rather arbitrarily defined quantities "lumped" in the same series of compounds, where molecular weight increases and stability of the scissile bonds decreases in going from asphaltenes to preasphaltenes.

When we computed the rate constants for coal conversion, all of the pyridine-insoluble organic matter in the product slurries was counted as reactive coal. This is incorrect, because unreactive fusinite macerals and the small amount of coke that may be present are then counted as reactants. Since filter cake and K-MAC are liquefaction residues, they are relatively rich in unreactive organic species. This is probably why the reaction rate constant

for coal conversion decreased when either residue was added to the feed. When petrographic analyses of the feed coal and residues, as well as the product residues, are available, these rate constants should be recalculated based upon the concentrations of reactive macerals plus vitroplast in the product slurry stream, not upon all pyridine-insoluble organic matter.

Residue addition had little or no effect upon the kinetic constant for the conversion of oil to hydrocarbon gas. A statistical analysis of this quantity is not possible because the duplicate product analyses used the same values for product gas rate and composition.

Effect of Reaction Temperature

The liquefaction behaviors of the 30% coal/70% WRS and the 30% coal/15% filter cake/55% WRS slurries were evaluated at 815 and 865°F, as well as at demonstration plant design temperature (840°F). All other reaction conditions were equal to demonstration plant design.

Oil Yield. As shown in Figure 3, oil yield increases at higher reaction temperatures both with and without filter cake. However, earlier data showed a decreased oil yield at higher reaction temperatures without residue addition. Those data were based on a lower superficial slurry residence time of 30 min, a lower hydrogen feed rate, and use of a different batch of Wilsonville recycle solvent.

Without filter cake addition, the oil yield increased from 14.5 wt % MAF at 815°F to 23.5 wt % MAF at 865°F. A somewhat larger temperature effect was observed with filter cake: from 20.3 wt % MAF at 815°F to 33.5 wt % MAF at 865°F. Note that, although there is data scatter, particularly at 840°F, filter cake addition always increases oil yield.

Distillate Yield. Without residue addition, distillate yield was independent of reaction temperature and equalled 4-5 wt % of the MAF coal. This lack of temperature sensitivity is contrary to the trend observed for oil yield. Thus, batch distillation and pentane extraction give different measures of solvent yield that vary with changes in reaction conditions.

When filter cake was added to the feed, the distillate yield increased markedly with increases in reaction temperature, from only 2 wt % (MAF) at 815°F, to 4 wt % at 840°F, to 18 wt % at 865°F. This follows the same trend observed for oil yield. Adding K-MAC to the feed slurry increased distillate yield at each reaction temperature (compared to no residue addition) to 14-25 wt % (MAF); however, distillate yield did not vary consistently with reaction temperature.

By combining the distillation yields with a gas chromatographic (GC) simulated distillation of the distillates, yields of a standard 450-700°F distillate cut were calculated (Figure 4). The yield of this fraction appears to go through a maximum of about 840°F for the feed slurries with no residue and with 15% added K-MAC. Adding K-MAC increased the yield at each temperature. In contrast, filter cake addition reduced the yield at 815 and 840°F. This is reasonable, because filter cake contains much less reactive SRC than does K-MAC. This suggests that the presence of dissolver solids will not increase solvent yield.

Preasphaltene Yield. Higher reaction temperature significantly decreased preasphaltene yield, whether or not filter cake was added (Figure 5): without filter cake, the decrease was from 38 wt % MAF at 815°F to 28 wt % at 865°F; with filter cake, these values are 28 and 20 wt % MAF, respectively. Filter cake consistently reduced the net preasphaltene yield at each reaction temperature.

Residue Yield. Without filter cake, an increase in reaction temperature reduced residue yield only slightly, from 10.5 wt % MAF at 815°F to 9.6 wt % MAF at 865°F (Figure

6). The temperature sensitivity was larger with filter cake, showing a decline from 9.2 wt % MAF at 815°F to 6.5 wt % MAF at 865°F. The decline is a good indication that coking is not significant, even at 865°F. Unlike the results discussed in the two preceding articles, filter cake addition consistently reduced residue yield.

Gas Yield. As in the previous runs, hydrocarbon gas yield increased sharply at higher reaction temperatures, from 3 wt % MAF at 815°F to 9.6 wt % MAF at 865°F without filter cake (Figure 7). Temperature sensitivity seems to be slightly reduced by filter cake addition, the yield only rising from 4.5 wt % MAF at 815°F to 8.3 wt % MAF at 865°F.

Yields of heteroatom gases (CO, CO₂, H₂S, and NH₃) depended slightly on temperature and were unaffected by filter cake (Figure 8).

Water yield increased moderately at higher reaction temperatures, and, at each temperature, the net water yield was higher with filter cake (Figure 9).

Oil plus Asphaltene Yield. The combined net yield of oils and asphaltenes conveniently compares the desirability of two product slates and assesses the extent of coal conversion. This quantity is simply the yield of benzene-soluble products minus the yield of unwanted by-product gases and water. Thus, it represents the yield of the most desirable product fractions.

The combined oil plus asphaltene yield increased modestly at higher reaction temperatures, with or without filter cake (Figure 10). Filter cake improved this combined yield at all reaction temperatures, by a margin of 7-11 wt % MAF. Differences of this magnitude should certainly be economically significant, since oils and asphaltenes are recovered almost quantitatively in the Kerr-McGee critical solvent deashing unit, while substantial preasphaltene is rejected along with the residue.

Hydrogen Gas Consumption. The more desirable product slates achieved by filter cake addition are at the expense of increased hydrogen gas consumption. As expected, consumption increased with reaction temperature for both the nonadditive and filter cake experiments. However, temperature sensitivity was lower with filter cake present, a pattern that is consistent with the hydrocarbon gas yields (Figure 11). Without additive, H₂ consumption increased from 0.92 wt % MAF at 815°F to 1.95 wt % at 865°F, whereas with filter cake the increase was only from 1.95 to 2.52 wt % at 815 and 865°F, respectively. Although the 840°F filter cake data point shows unacceptably large scatter in H₂ consumption, the above trends are clear.

Total Hydrogen Consumption. Solvent (oil) hydrogen concentration was relatively unchanged in the experiments with added filter cake, but it decreased by 0.1-0.3% in the reactions without filter cake. The net quantity of hydrogen donated by the solvent to the coal is expressed on an MAF coal basis (Figure 12). Where this quantity is negative, the solvent was a net consumer of hydrogen.

Without additive, the solvent was a significant net hydrogen source for coal conversion, but with filter cake the net transfer of hydrogen to or from the solvent was insignificant. Because of this, total hydrogen consumption (gas H₂ plus solvent hydrogen) by the coal was not as strongly affected by filter cake addition as was hydrogen gas consumption (Figure 13). Filter cake increased this total hydrogen consumption from 1.15 to 1.8 wt % MAF at 815°F, but had a progressively smaller impact as the temperature increased. At 865°F, the difference was only from 2.5 to 2.6 wt % MAF. We believe that this total hydrogen consumption is the best available estimate of what the hydrogen gas consumption would be in a closed-loop, solvent-recycle experiment at these reaction conditions.

Kinetic Constants. The sequential first-order kinetic model discussed earlier was used to calculate kinetic constants for preasphaltene, asphaltene, and oil conversion.

The volumetric reaction rate for preasphaltene conversion is given by:

$$\text{rate} = k_{pA} C_{pA} \text{ (g/L-hr)}$$

where k_{pA} is the first-order kinetic constant (hours^{-1}) and C_{pA} is the preasphaltene concentration in the reactor effluent (grams/liter).

The mean values of the experimentally determined rate constants (k_{pA}) at each reaction condition are (hours^{-1}):

	<u>815°F</u>	<u>840°F</u>	<u>860°F</u>
No additive	2.0	2.7	3.7
15% filter cake	3.2	4.2	4.9

From an Arrhenius plot of these kinetic constants (Figure 14), the rate constants were found to fit the following equations:

$$k_{pA}(\text{no additive}) = 1.52 \times 10^{-7} \exp(-20,200/T)$$

$$k_{pA}'(\text{filter cake}) = 8.04 \times 10^{-4} \exp(-12,900/T)$$

The activation energy for this reaction is reduced by filter cake addition, as expected if the filter cake is catalyzing the reaction. However, based upon the magnitude of the scatter in the experimentally determined kinetic constants, these activation energies are not very precise.

The kinetic constants for asphaltene conversion (k_A) that were computed from the data show little evidence of catalytic action by the filter cake minerals. The mean values of the experimental kinetic constants, with and without filter cake, were increased by only 25% by filter cake addition:

	<u>815°F</u>	<u>840°F</u>	<u>865°F</u>
No additive	0.95	1.3	2.1
Filter cake	1.2	1.5	2.6

This change is statistically significant only at an 80-90% confidence level.

The Arrhenius plots of the experimental kinetic constants (Figure 15) show that filter cake addition does not affect the activation energy for asphaltene conversion (about 29 kcal/mol in either case). The kinetic constants as functions of temperature are given by:

$$k_A(\text{no additive}) = 1.22 \times 10^9 \exp(-26,800/T)$$

$$k_A'(\text{filter cake}) = 1.10 \times 10^9 \exp(-26,400/T)$$

where temperature (T) is in degrees rankine.

Kinetic constants (hours^{-1}) for the conversion of oils (k_O) to hydrocarbon gases were also calculated from the data at each of three reaction temperatures:

	<u>815°F</u>	<u>840°F</u>	<u>865°F</u>
No. additive	0.0165	0.0341	0.0529
Filter cake	0.0304	0.0373	0.055

The mean values are based on the assumptions that all of the hydrocarbon gas arises from the cracking of oil molecules and that this reaction is first order. The activation energy for the case with no additive is 43 kcal/mol. The activation energy with filter cake addition has not been calculated, because the 815°F data point appears to be in error.

Lafayette Kentucky #9 Coal

A 30 wt % slurry of Lafayette Kentucky #9 coal in Wilsonville recycle solvent was reacted at 865°F under the same conditions used with Pyro coal. This test was performed because Wilsonville reported an appreciable increase in solvent yield after simultaneously switching from Pyro to Lafayette coal and adding sodium carbonate to the feed slurry. Additionally, the closed-loop experiments under this contract will be conducted with Lafayette coal.

Lafayette coal does not yield more solvent than Pyro coal. At demonstration plant conditions (840°F), each coal gave a distillate yield of 4 wt % (MAF). Oil yield was actually larger, 23-25 wt % vs. 14 wt % for Pyro coal. As shown in Table 9, the product slates from these two coals are quite similar. Although the data suggest a lower hydrogen consumption using Lafayette coal, this should not be accepted without confirmation.

Sodium Carbonate Addition

Addition of 1.1 wt % Na_2CO_3 to a feed slurry of 30% Pyro coal in WRS at demonstration plant reaction conditions (Table 10) did not increase distillate yield; it was 3.9-9.0 wt % MAF with sodium carbonate and 3.9-7.1 wt % MAF without. Also, Na_2CO_3 did not improve oil yield, and asphaltene yield was unaffected. The only appreciable difference in the net product slates was in residue yield, which was about 10 wt % MAF without Na_2CO_3 and 13.0 wt % MAF with Na_2CO_3 . When we calculated residue yield, the Na_2CO_3 was treated as Na_2O residue plus CO_2 heteroatom gas. A portion of the increase in residue yield could arise either from the reaction of H_2S with Na_2O to form sodium sulfide or from the presence of unreacted Na_2CO_3 in the product.

The hydrogen content of the product oil fraction from the Na_2CO_3 addition experiment was 8.3 wt %, slightly more than the 8.2 wt % hydrogen in the starting solvent. Without sodium carbonate, the hydrogen concentration in the product oils declined to 7.9 wt %, while with Na_2CO_3 hydrogen gas consumption substantially increased, as calculated from the solvent separation data. Again, this result should not be accepted without confirmation.

Check of XCL-23 Results without Added Residue

The results from Run XCL-23 for the 30% Pyro coal/70% WRS feed slurry were suspect for several reasons: (1) oil yields were generally negative and varied inversely with reaction temperature, (2) corresponding distillate yields were positive, and (3) the calculated hydrogen gas consumptions were generally negative. As a check on these results, the 850°F data point at 2,000 pounds per square inch gage (psig) and LHSV = 2 was repeated. The distillate yield reproduced reasonably well, 14 wt % MAF for the Run 27 sample compared to 9 wt % MAF for the Run 23 sample. The same reaction conditions during Run 21 gave a 17 wt % MAF distillate yield. These values are the same within experimental error.

However, the yields based on solvent separation did not agree well (Table 11). The oil yield is positive for sample 27-106 and about 20 wt % MAF higher than the previous negative result obtained for 23-163. Furthermore, the difference is caused not by the oil/asphaltene cut point, since the asphaltene yields are about equal, but rather by the lower preasphaltene and residue yields for sample 27-106. These results suggest that either retrograde reactions and coking were significant during the production of sample 23-163 or else the solvent separation procedure was grossly in error. Since the WRS used during Run 27 was a superior solvent to that used during Run 23, retrograde reactions could conceivably be significant in Run 23 but not in Run 27, but they could not account for the wide differences between oil and distillate yield in Run 23.

Although the difference in hydrocarbon gas yields suggests a difference in reaction temperature, it can be explained by differences in solvent composition.

As expected, the hydrogen gas consumption for Sample 27-106 was positive. The total hydrogen consumption is also somewhat larger than for the Run 23 data points.

Effect of Residence Time upon Distillate Yield

Since the distillate yield was shown to be reasonably reproducible from run to run, data from all three runs were combined to show the effect of the superficial slurry residence time (Figure 16). Up to at least 850°F, the distillate yield was higher at 30-min than at 40-min residence. Although the difference between individual data points is about equal to the estimated standard deviation of the distillation procedure, that difference is observed consistently and is probably significant. The drastic decrease in distillate yield at 885°F and 30-min residence time is probably associated with product coking at those conditions.

Comparison of Oil and Distillate Yields

The results from Run 23 typically showed higher distillate than oil yields for a given sample, but this trend is reversed in the current results (Figure 17). Except for one data point, the oil yield always exceeded the distillate yield, which was expected since the pentane-solubility criterion used as the cut point between oil and asphaltenes is believed to correspond to a distillation cut point of about 900°F. Naturally, this is not strictly correct and our earlier work shows that phenolic compounds and nitrogen bases respond differently to the two fractionation techniques.

Although oil yield is virtually always greater than distillate yield, the two do not seem to vary in a consistent pattern. Therefore, in future work distillate yield should be measured, since it cannot be calculated from oil yield and since oil yield is not a conservative estimate of distillate yield. However, if the new batch distillation achieves an 850°F cut point, then oil and distillate yields should be more nearly equal.

¹H NMR Analysis of Product Solvent

The fraction of total hydrogen in the product oil that occurs as aromatic hydrogen, H_{ar} , was reduced by about 4% when filter cake was added to the feed slurry. As seen in Figure 18, the reaction temperature did not strongly influence H_{ar} . The fraction of aromatic hy-

drogen in the feed oil was intermediate between the fraction seen in the product oils, with and without filter cake. Figure 19 shows very similar results for the product distillate. The only difference is that the distillate H_{ar} increased with temperature when residue was absent.

The α -hydrogen fraction was not strongly affected by either filter cake addition or changes in reaction temperature (Figures 20 and 21). This suggests that H_{α} may not be as good an indicator of solvent composition and quality as we had suspected.

Hydrogen atoms in saturated compounds or on carbon atoms that are two or more carbons away from an aromatic ring (H_O) are good indicators of the combined concentrations of alkyl side chains and saturates, and seem to predict the tendency for solvents to crack to hydrocarbon gases. In the starting solvent, 37.4% of the hydrogen was H_O , but all of the product distillates contained less, some 31% (see Figure 22). Residue addition increased the H_O fraction by about 1-4%.

Similarly, the H_O fraction in the product oils increased by 5% upon filter cake addition, but was not affected by reaction temperature. The H_O fractions in the oils from the starting solvent and in the product oils from filter cake addition were virtually identical (Figure 23).

Filter cake addition increased the total weight percent of hydrogen in the product oils by 0.1-0.3 wt % (Figure 24). The effect of temperature is ambiguous; with filter cake present, the hydrogen content of the oils declined slightly with increasing temperature, but without additive, the change in hydrogen content was erratic.

Note that the oils lost 0.3 wt % hydrogen at the demonstration plant temperature of 840°F without filter cake, but had unchanged hydrogen content during the reaction with added filter cake.

By multiplying the total weight percent of hydrogen in the product oils by the percent of that hydrogen occurring in each NMR classification (Figures 18, 21, and 23), we computed the absolute weight percent of H_{ar} , H_{α} , and H_O in the product oils (Figures 25-27). As also seen in Run 23, filter cake addition increased the absolute concentration of H_O , by about 0.4 wt %. Although H_O concentration did vary inversely with reaction temperature, the magnitude of the change is far smaller than was previously observed.

Filter cake addition also reduced the concentration of H_{ar} by about 0.3 wt %. Neither temperature nor filter cake affected the H_{α} concentration, which suggests that either solvent quality is relatively constant or H_{α} is a much poorer indicator of quality than we suspected.

Molecular Weights of Product Fractions

We used vapor pressure osmometry to determine the number-average molecular weights of the product oil, asphaltene, and preasphaltene fractions. Since several product slurry samples were subjected to duplicate fractionation and analysis, an estimate of the precision of these molecular weight determinations is possible. However, since the variations between duplicate analyses of the same sample exceed differences among samples, these data will not be reported here. The estimated variance and estimated standard deviation are reported in Table 12.

The most serious errors [estimated standard deviation of 580 atomic mass units (amu)] occur for the preasphaltene molecular weight. In half the cases, pyridine contamination of the preasphaltenes was evident. In the other instances, which included the largest error, the elemental analyses of the duplicates agreed excellently and the error must have arisen in the osmometry experiment. These results point out the danger of relying upon unreplicated molecular weight determinations.

CONCLUSIONS

Our earlier work (Runs XCL-23 and -21), conducted at shorter residence times and lower gas rates than those planned for the demonstration plant, resulted in nine tentative conclusions.

- (1) Liquefaction residues and, presumably, dissolver solids catalyze certain coal conversion reactions, particularly H_2 consumption and preasphaltene conversion.
- (2) The large concentration of preasphaltenes in K-MAC was not removed by simple pretreatment; instead, preasphaltenes were largely converted to toluene solubles at reaction conditions.
- (3) K-MAC catalytic activity is reduced compared to that of filter cake, apparently because K-MAC's large preasphaltene concentration blocks the mineral surface.
- (4) The addition of either 5 or 13 wt % filter cake produced similar catalytic enhancement.
- (5) Filter cake addition suppresses coke formation; presumably, dissolver solids function similarly.
- (6) Both filter cake and K-MAC contain vitropast and coal macerals, which are converted to pyridine solubles during the reaction. While this does not relate to catalysis by dissolver solids, it does suggest that a second-generation SRC-I process with residue recycle would be beneficial.
- (7) Increasing the reaction temperatures reduces solvent yield, unless a liquefaction residue is added to the feed.
- (8) Product "solvents" isolated by distillation differ markedly in physical and chemical properties from those isolated by solvent fractionation.
- (9) The product solvents from the CSTR experiments are of lower molecular weight and contain fewer saturates and alkyl substituents than the Wilsonville recycle solvent.

Most of these tentative conclusions were either substantiated (#1, 3, 6, 8, 9) or not addressed by Run XCL-27. The only exception is the inverse relationship between oil (solvent) yield and reaction temperature for feed slurries not containing added mineral residue; unlike the earlier results, Run XCL-27 shows an increase in oil yield as reaction temperature increases. Increased slurry residence time, increased hydrogen feed rate, and better process solvent in Run XCL-27 could be responsible for this difference. Thus, both observations on the effect of temperature upon solvent yield could be correct.

Filter cake addition increased the kinetic rate constant for preasphaltene conversion by about 50%; it also increased solvent hydrogenation and raised the H_2 gas consumption rate by a factor of 2.5. Analysis of replicates indicates that these differences are statistically significant at a 95% confidence level.

Kerr-McGee ash concentrate, in which the mineral particles are embedded in preasphaltene, did not increase the rate constant for preasphaltene conversion. However, since most of the preasphaltenes in the K-MAC were converted to benzene solubles, the net yield of preasphaltenes was reduced. Hydrogen gas consumption increased by more than a factor of 2.0.

Although addition of filter cake or K-MAC residues substantially increased H_2 gas consumption, the hydrocarbon gas yield did not change. Instead, the extra hydrogen increased the solvent hydrogen content, improved preasphaltene conversion, converted coal macerals

contained in the residues (which improves net coal conversion), and slightly increased solvent yield and heteroatom removal.

The above results strongly indicate that (1) dissolver solids will catalyze preasphaltene conversion and solvent hydrogenation and (2) a second-generation SRC process employing residue recycle would improve the net coal and preasphaltene conversions without increasing gas yield. The extent of preasphaltene conversion is of great economic significance, because the Kerr-McGee critical solvent deashing process cannot recover preasphaltenes efficiently.

The current work also shows that the product slates to be expected from Pyro and Lafayette Kentucky #9 coals are very similar and that sodium carbonate does not improve solvent yield.

FUTURE WORK

The next two coal process development unit runs will be closed-loop, solvent-recycle experiments conducted under demonstration plant conditions, with and without the addition of filter cake to the feed. These experiments will be continued until a steady-state solvent composition is achieved. Extensive characterization of these steady-state solvents should better elucidate the impact that filter cake and, presumably, dissolver solids have on solvent composition and quality. These recycle runs should accurately determine the net product slates expected at steady-state demonstration plant conditions. By mathematically compensating for the lesser back-mixing at the plant, these data should permit us to predict performance with and without dissolver solids accumulation.

Table 1
Feed Coal Analyses

Analysis	Kentucky #9 coal	
	Pyro	Lafayette
Moisture (wt %)	1.8	
Volatiles (wt %)	36.1	
Fixed carbon (wt %)	50.4	
ASTM ^a ash (wt %)	13.1	9.8
Carbon (wt %)	70.4	72.9
Hydrogen (wt %)	4.8	5.1
Nitrogen (wt %)	1.5	1.4
Sulfur (wt %)	3.3	2.7
Sulfate S (wt %)	0.04	0.09
Pyrite S (wt %)	1.6	0.80
Oxygen (wt %)	6.1	8.1
Aluminum (wt %)	1.5	1.0
Silicon (wt %)	3.7	2.3
Iron (wt %)	1.5	1.1
Titanium (ppm)	570	1,300
Boron (ppm)	590	<100
Chlorine (ppm)	2,400	2,790
Calcium (ppm)	90	1,800
Magnesium (ppm)	850	
Potassium (ppm)	2,700	3,500
Sodium (ppm)	470	2,200
Pyridine soluble (wt %)	16.5	

^aASTM, American Society for Testing and Materials.

Table 2

Residue Analyses

Analysis	Residue type and Wilsonville run no.		
	Dissolver solids ^a	Filter cake	K-MAC
	204	175	167
Elemental analysis			
Carbon (wt %)	36.2	38.2	62.0
Hydrogen (wt %)	1.8	2.7	3.7
Nitrogen (wt %)	0.6	0.6	1.5
Sulfur (wt %)	8.1	3.3	2.3
Oxygen (wt %)	4.5	4.3	5.2
ASTM ash (wt %)	48.9	50.7	26.4
Iron (wt %)	21.9	6.16	2.75
Titanium (wt %)	0.22	0.11	0.11
Silicon (wt %)	6.03		
Aluminum (wt %)	3.09	5.59	2.46
Boron (ppm)	17,200	8,400	9,100
Calcium (ppm)	300	30	20
Magnesium (ppm)	2,100	300	980
Sodium (ppm)	26,600	17,600	15,900
Potassium (ppm)	9,100	14,700	4,800
Chlorine (ppm)	11,800		
Solubility fractions (wt %)			
Oils	0.0	16.0	0.0
Asphaltenes	0.0	3.0	2.0
Preasphaltenes	?	5.0	45.0
Residue		76.0	53.0

^aMethylene chloride washed, normalized from 112%.

Table 3

Analysis of Wilsonville Process Solvent^a

Total solvent analysis		Solvent fractionation results	
C (wt %)	87.5	Oils (wt %)	97.5
H (wt %)	8.13	C (wt %)	87.5
O (wt %)	2.7	H (wt %)	8.22
N (wt %)	1.1	O (wt %)	2.8
S (wt %)	0.52	N (wt %)	1.1
Mol wt	182	S (wt %)	0.38
Fractionation by distillation		Asphaltenes (wt %)	1.9
IBP-420°F (wt %)	1.4	Preasphaltenes (wt %)	0.7
420-550°F (wt %)	48.6	Analysis of distillate bottoms	
550-852°F (wt %)	45.7	C (wt %)	82.6
Total distillable (wt %)	95.7	H (wt %)	6.8
Bottoms (wt %)	4.3	O (wt %)	4.3
Analysis of 420-852°F distillate		N (wt %)	1.7
C (wt %)	87.2	S (wt %)	1.0
H (wt %)	8.09	Ash (wt %)	4.5
O (wt %)	3.0		
N (wt %)	0.89		
S (wt %)	0.79		
Mol wt	200		

^aSolvent drum ID F-217 to F-220; this solvent is taken from Wilsonville Run 179.

Table 4

Statistical Analysis of Analytical and Fractionation Data Precision

Quantity measured	df ^a	Estimated variance, $\underline{s}^2$	Estimated standard deviation, $\underline{s}$
Oil concentration in product (wt %)	14	2.7	1.6
Asphaltene concentration (wt %)	14	1.8	1.35
(Oil + asphaltene) concentration (wt %)	14	1.3	1.15
Preasphaltene concentration (wt %)	14	1.3	1.15
Residue concentration (wt %)	17	0.23	0.50
H in product (wt %)	12	0.0073	0.09
Gas H ₂ consumed (% MAF) ^b	12	0.112	0.33
Solvent H consumed (% MAF)	12	0.073	0.27
Total H consumed (% MAF)	12	0.044	0.21
Sulfur in SRC (wt %)	10	0.017	0.13
Kinetic constants			
Preasphaltene conversion (hr ⁻¹)	9	0.47	0.69
Asphaltene conversion (hr ⁻¹)	9	0.17	0.42

^adf, degrees of freedom.^bMAF, moisture and ash free.

Table 5

Effect of Residue Addition at Demonstration Plant Conditions

Analysis	Sample no. and additive							
	50 None	50 None	122 FC ^a	129 FC	129-R FC	188 K-MAC	192 K-MAC	192-R K-MAC
Wt % in product								
Oil	71.5	72.6	62.2	59.4	53.9	60.9	57.3	61.2
Asphaltene	9.9	8.2	10.7	11.0	8.1	10.8	14.5	13.0
Preasphaltene	8.8	9.2	5.9	8.3	6.9	12.2	11.9	10.2
Residue	6.5	6.6	17.5	17.4	17.2	12.4	12.4	11.9
Hydrocarbon gas	1.4	1.4	1.3	1.5	1.5	1.4	1.4	1.4
Heteroatom gas	0.6	0.6	0.9	0.8	0.8	0.9	0.9	0.9
Water	1.0	1.0	1.2	1.2	1.3	1.3	1.1	1.1
Organic condensate	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Yield (wt % MAF)								
Total oil	13.5	18.1	25.5	14.6	30.5	29.6	15.5	30.7
Asphaltene	33.8	26.8	36.4	37.2	26.1	37.1	52.0	45.8
Preasphaltene	32.5	34.3	18.7	27.9	22.7	20.1	19.1	12.2
Residue	9.9	10.5	8.2	7.8	8.0	1.7	1.9	(0.3)
Hydrocarbon gas	5.7	5.7	5.1	5.8	5.8	5.7	5.5	5.5
Heteroatom gas	2.4	2.4	3.4	3.0	3.0	3.7	3.5	3.5
Water	2.0	2.0	2.6	3.0	3.0	2.7	2.3	2.3
Ash balance (%)	99	109	102	100	101	98	99	98
Wt % sulfur in SRC	1.1	0.9	0.5 ^b	1.1	0.9	0.7	0.8	1.0
Hydrogen consumed (% MAF)								
From H ₂ gas	1.0	1.0	3.1	1.9	2.4	2.4	2.4	2.1
From solvent	0.8	0.9	(0.5)	0.1	(0.1)	0.1	(0.2)	0.1
Total	1.8	1.9	2.6	2.0	2.3	2.5	2.2	2.3
Hydrogen in oil (wt %)	7.9	7.9	8.4	8.2	8.3	8.2	8.3	8.2

^aFC, filter cake.^b0.8 prior to correction for residue in SRC.

Table 6

Statistical Analysis of Significance of Observed Effects of
Residue Addition at Demonstration Plant Conditions

Quantity to be compared	Mean of data values		Least significant change at confidence level			
	No additive	Filter cake	Δ	95%	90%	80%
No additive vs. 15% filter cake						
Oil yield (% MAF)	15.8	23.6	7.8	12.4	10.0	7.7
Asphaltene yield (% MAF)	30.3	33.2	2.9	10.4	8.5	6.5
(Oil + asphaltene) yield (% MAF)	46.1	56.8	<u>10.7^a</u>	8.8	7.2	5.5
Preasphaltene yield (% MAF)	33.4	23.1	<u>10.3</u>	8.8	7.2	5.5
Residue yield (% MAF)	10.2	8.0	2.2	3.8	3.1	2.4
Gas H consumed (% MAF)	1.0	2.5	<u>1.5</u>	0.7	0.5	0.4
Solvent H consumed (% MAF)	0.8	(0.2)	<u>1.0</u>	0.5	0.4	0.3
Total H consumed (% MAF)	1.8	2.3	<u>0.5</u>	0.4	0.3	0.3
Sulfur in SRC (wt %)	1.01	0.95	0.06	0.29	0.24	0.14
No additive vs. 15% K-MAC						
Oil yield (% MAF)	15.8	25.3	9.5	12.4	10.0	7.7
Asphaltene yield (% MAF)	30.3	45.0	<u>14.7</u>	10.4	8.5	6.5
(Oil + asphaltene) yield (% MAF)	46.1	70.3	<u>24.2</u>	8.8	7.2	5.5
Preasphaltene yield (% MAF)	33.4	17.1	<u>16.3</u>	8.8	7.2	5.5
Residue yield (% MAF)	10.2	1.1	<u>9.1</u>	3.8	3.1	2.4
Gas H consumed (% MAF)	1.0	2.3	<u>1.3</u>	0.7	0.5	0.4
Solvent H consumed (% MAF)	0.8	0	<u>0.8</u>	0.5	0.4	0.3
Total H consumed (% MAF)	1.8	2.3	<u>0.5</u>	0.4	0.3	0.3
Sulfur in SRC (wt %)	1.01	0.83	0.18	0.26	0.22	0.16

^aChanges that are statistically significant at a 95% confidence level are underlined.

Table 7

Kinetic Rate Constants (Hours⁻¹) at Demonstration Plant Conditions

	Sample no., additive, and ash balance							
	50	56	122	129	129R	188	192	192R
	None	None	FC	FC	FC	FC	K-MAC	K-MAC
	99	109	102	100	101	98	99	98
Coal →	15	14	6.5	6.5	6.7	9.0	8.9	10.2
preasphaltene								
Preasphaltene →	2.8	2.6	5.2	3.2	4.1	2.9	2.9	3.8
asphaltene								
Asphaltene →	1.0	1.5	1.4	1.0	2.1	1.7	0.9	1.4
oil								
Oil →	0.035	0.034	0.034	0.040	0.037	0.041	0.042	0.039
hydrocarbon gas								

Table 8

Statistical Analysis of Significance of
Difference in Kinetic Constants

Kinetic constant for	Mean of data values			Difference in mean		Least significant change at		
	Additive	FC	K-MAC	No add., No add.,		confidence level		
				FC	K-MAC	95%	90%	80%
Preasphaltene conversion	2.7	4.2	3.2	1.5	0.5	1.4	1.2	0.9
Asphaltene conversion	1.3	1.5	1.4	0.2	0.1	0.9	0.7	0.5

Table 9

Comparison of Lafayette and Pyro Kentucky #9
Coal Liquefaction at 865°F

Analysis	Coal	
	Pyro	Lafayette
Net yields (wt % MAF)		
Oil	22.6-24.4	13.7
Asphaltene	24.0-24.7	32.0
Preasphaltene	26.2-29.5	26.6
Residue	9.2-10.1	11.4
Hydrocarbon gas	9.6	9.2
Heteroatom gas	3.1	2.7
Oil + asphaltene	47.3-48.4	45.7
Hydrogen consumption (wt % MAF)		
H ₂ gas	1.8-2.1	1.0
Solvent hydrogen	0.5-0.7	0.8
Total hydrogen	2.5-2.6	1.7

Table 10

Effect of Na_2CO_3 Addition upon Net Product
Slate at Demonstration Plant Conditions

Analysis	Added Na_2CO_3 (wt %)	
	0.0	1.1
Net product slate (% MAF)		
Oil	13.5-18.1	15.4
Asphaltene	26.8-33.8	28.4
Preasphaltene	32.5-34.3	31.3
Residue	9.9-10.5	13.0
Hydrocarbon gas	5.7	6.1
Heteroatom gas	2.4	2.3
Water	2.0	3.3
Oil + asphaltene	44.9-47.1	43.8
Hydrogen consumption (wt % MAF)		
H_2 gas	1.0	1.8
Solvent hydrogen	0.8-0.9	(-0.2)
Total hydrogen	1.8-1.9	1.6

Table 11

Check of XCL-23 Solvent Separation Results

Analysis	Sample no. and ash balance (wt %)		
	23-163 ^a	23-164	27-106
	97	135	97
Net yields (% MAF)			
Oil	(4.4)	(15.4)	16.0
Asphaltene	40.3	38.0	36.9
Preasphaltene	36.5	44.6	29.2
Residue	16.0	20.4	9.8
Hydrocarbon gases	6.9	6.8	4.2
Heteroatom gases	2.6	2.6	2.3
Water	2.9	2.9	1.6
(Oil + asphaltene)	35.9	22.6	52.9
Hydrogen consumption (% MAF)			
H ₂ gas	(0.1)	(0.6)	0.6
Solvent hydrogen	1.2	1.4	0.8
Total hydrogen	1.1	0.8	1.4

^a Average of four data points.

Table 12

Precision of Molecular Weight Determinations

Species	Data points	df	Estimated variance, $\underline{S}^2$	Estimate of standard deviation, $\underline{S}$
Oils	14	7	189	14
Asphaltenes	12	6	4,070	64
Preasphaltenes	14	7	334,000	580

Figure 1
Effect of Residues on Distillate Yield

Figure 2
Solvent Hydrogen Content

Figure 3
Effect of Temperature on Oil Yield

Figure 4
Effect of Residues on 450 - 700°F Distillate Yield

Figure 5
Temperature vs. Preasphaltene Yield

Figure 6
Residue Yield vs. Reaction Temperature

Figure 7
Hydrocarbon Gas Yield

Figure 8
Heteroatom Gas Yield

Figure 9
Water Yield

Figure 10
Oil + Asphaltene Yield vs. Temperature

Figure 11
Hydrogen Gas Consumption

Figure 12
Solvent Hydrogen Consumption

Figure 13
Total Hydrogen Consumption

Figure 15
Arrhenius Plot of Asphaltene Conversion K

Figure 16
Effect of Residence Time on Distillate Yield

Figure 17
Comparison of Oil and Distillate Yields

Figure 18
Fraction Aromatic H in Product Oil

Figure 19
Hydrogen Distribution - Fraction Aromatic

Figure 20
Hydrogen Distribution - Fraction H_{α}

Figure 21
Fraction Alpha H in Product Oil

Figure 22
Hydrogen Distribution - Fraction H_0

Figure 23
Fraction H_0 in Product Oil

Figure 24
Total Hydrogen Concentration in Oils

Figure 25
Aromatic Hydrogen Concentration in Oils

Figure 26
Alpha Hydrogen Concentration in Oils

Figure 27
H_o Concentration in Oils

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EFFECT OF SOLIDS ADDITION ON DISSOLVER PERFORMANCE

S. V. Joshi*

In the coal-processing runs [XCL-21 (21), XCL-23 (23), and XCL-27 (27)] described in the three preceding articles, solids were fed into the continuously stirred tank reactor (CSTR) of APCI's coal process development unit (CPDU). Because Wilsonville dissolver solids were not available in large quantities, filter cakes and Kerr-McGee ash concentrates (K-MAC) from Wilsonville were substituted.

Examination of the CPDU data results in the following general conclusions about the qualitative and quantitative effects of solids addition.¹ All conclusions are valid for the range of solids concentrations and the types of solids investigated.

- Hydrocarbon gas, heteroatom gas, and water yields are unaffected by solids.
- The net yield of preasphaltenes does depend on the nature and concentration of solids.
- The moisture- and ash-free (MAF) yield of preasphaltenes derived directly from coal decreases by about 7-10% absolute, seemingly independent of the kind or amount of solids.
- Oil yields increase by about 5-10 wt % MAF, apparently unaffected by the nature and amount of solids.
- Total hydrogen consumption increases by about 0.5 wt % absolute on a MAF basis and appears to be independent of the nature and amount of solids.

GENERAL COMMENTS ON THE DATA²

Characteristics of the Kentucky #9 coal used in all CPDU runs varied minimally (Table 1). The Wilsonville recycle solvent used in runs 21 and 23 differed from that used in run 27: 8.85 wt % hydrogen and 96 wt % pentane-soluble oils vs. 8.13 wt % hydrogen and 98 wt % oils, respectively. Three filter-cake and two Kerr-McGee ash concentrate residues added to the CPDU runs were analyzed (Table 2); in general, K-MAC samples contained considerably less ash and considerably more preasphaltenes than the filter cakes.

In all runs, coal concentration was maintained at 30 wt % of the feed slurry. Additive concentrations varied between 10 and 15 wt % of the feed slurry, except for a few data

*Air Products and Chemicals, Inc. (APCI).

¹Note that the liquefaction behavior of the particular coal/solvent systems without additives had already been established by examining data from various CPDU runs (Joshi, 1981).

²See also Skinner and Givens, 1981a,b; Skinner et al., 1981.

in run 23 that were obtained at 5 wt %. The coal-to-solvent ratio increased from 0.43 to 0.46-0.55 upon solids addition. For this report, it was assumed that ratios ranging from 0.43 to 0.55 would affect the yield insignificantly (Joshi, 1981; Skinner and Givens, 1981a). The addition of solids also increased the ash to MAF coal ratio from 0.16 to 0.27-0.45.

The nominal residence time of the coal slurry was 30 min in runs 21 and 23, and 40 min in run 27. Thirty-minute residence-time yields were corrected by a mathematical model (Skinner, 1979; Martin, 1979), so that all comparisons are based on a nominal residence time of 40 min. The corrections are explained in detail elsewhere (Joshi, 1981).

Total liquid products were analyzed by distillation II (a combination of filtration and distillation) in run 21 and by solvent separation in runs 23 and 27. Other analytical work (Joshi, 1981) indicated that (1) heptane-soluble yields determined by distillation II can be assumed to equal distillate yields from distillation I with a heated column and (2) distillate yields determined by distillation I are 3-4 wt % MAF absolute less than oil yields determined by solvent separation. Therefore, yields from run 21 were increased appropriately. Table 3 compares the reaction conditions for the three CPDU runs.

Data points mentioned in this report have ash-balance errors within $\pm 10\%$. All the yields were calculated on the basis of forced-ash balance, although any other balancing technique would yield essentially the same results. Based on available information, MAF yields of oils, asphaltenes, and preasphaltenes have a standard deviation of about 5 wt % absolute (Joshi, 1981).

YIELDS IN THE PRESENCE OF ADDITIVES

Yield structures can be calculated using equation 1:

$$\text{MAF yield of a fraction} = \frac{(\text{fraction})_{\text{product}} - (\text{fraction})_{\text{feed}}}{(\text{MAF coal})_{\text{feed}}} \quad (1)$$

Oil, asphaltene, preasphaltene, and insoluble organic matter (IOM) fractions can be determined. APCI used equation 1 to compute all the yields observed after adding filter cake or K-MAC (Skinner and Givens, 1981a,b; Skinner et al., 1981). Ideally, additives should be inert so that, when passed through the reactor/dissolver, they will not yield their own liquefaction products. For the process engineer, who is concerned only with net product slate, equation 1 provides sufficient information regardless of whether or not the added residue is inert. In contrast, for the reaction engineer, who wants to know whether the feed coal itself produced more or less of a fraction after residue addition, equation 1 may be misleading if the residue is active and yields its own products.

To alleviate this problem, product slates from coal and from additives were differentiated. Independently processed coal was assumed to have the product slate predicted by the computer model (Skinner, 1979; Martin, 1979), as shown in column two of Table 4. We also presumed that the net yield after recycling preasphaltenes could be calculated using the same computer model. Our implicit assumption was that recycled preasphaltenes from additives would react similarly to preasphaltenes from coal, and that the reactivity of coal preasphaltenes would not change even when preasphaltenes were recycled.

Column three of Table 4 shows the net product slate calculated by equation 1. Note the large difference in the two net product slates, even though the yields due to coal alone do not change. The largest differences are seen in the yields of two fractions: recycled

preasphaltenes and asphaltenes, which are the primary products of the recycled fraction in the sequential reaction mechanism. If the recycled preasphaltenes had been inert, the two net product slates would be identical.

Thus, to obtain the true yield structure of coal, the net product slate must be corrected whenever reactive fractions are recycled. Corrections to product yields after filter cake addition are insignificant, mainly because the filter cake contains minimal amounts of preasphaltenes and asphaltenes (see Table 2). On the other hand, corrections are necessary with K-MAC, as discussed in detail in the following sections.

Conversion

A separate study concluded that MAF conversion of Kentucky #9 coal is about 90% and is independent of solvent nature and reaction temperature (Joshi, 1981). Also, Skinner and Givens (1981b) determined that coal conversion increases significantly upon K-MAC addition but insignificantly upon filter cake addition. The increase was attributed to catalysis by the added solids, to reactivity of insoluble organic matter in the added solids, or to both. If the increase in apparent coal conversion is attributed solely to reactive insoluble organic matter in the residue, the resulting correlation between reactivity of the insoluble matter and its ash content is interesting (Figure 1). Insoluble organic matter in K-MAC appears to be more reactive than that in filter cakes, possibly because the K-MAC minerals are more likely to be coated with heavier preasphaltenes. Some preasphaltenes that are strongly adsorbed by these minerals are capable of undergoing hydrocracking, hydrogenolysis reactions in the dissolver, even though they are pyridine insoluble at room temperature.

As discussed in the previous section, feeding reactive insoluble organic matter apparently increases MAF conversion and also preasphaltene yield. This is discussed in the section on preasphaltene yields.

Hydrocarbon Gas Yields

The observed hydrocarbon gas yield for 30-min residence was converted to a 40-min residence time by assuming that gas production is zero order (Joshi, 1981; Skinner, 1979; Martin, 1979). Figure 2 depicts the variation of hydrocarbon gas yield with temperature. The broken line is a correlation derived from coal/solvent data without added residues for the same coal; the solvent contained ~8 wt % hydrogen (Joshi, 1981).

The high gas yields for runs 21 and 23 seem to be due to high solvent hydrogen content (~8.9 wt % H) rather than residue addition. Agreement between the broken line and the data from run 27 (solvent containing 8.1 wt % H) is good. It is also apparent from Figure 2 that the gas yields observed with K-MAC approximately equal those observed with filter cake. In short, solids seem to have little effect on the MAF yield of hydrocarbon gas.

Heteroatom Gas Yields

Figure 3 shows the yield of heteroatom gases (CO, CO₂, H₂S, and NH₃) as a function of temperature. Again, residence times were corrected whenever necessary by assuming that gas production is zero order (Joshi, 1981). The heteroatom gas yields after solids

addition agree well with coal/solvent yields without added solids (broken line) (Joshi, 1981); this indicates that solids have little effect on heteroatom gas yields.

Yield of Water

The observed yield of water is plotted against reaction temperature in Figure 4. Thirty-minute residence times were not corrected. The yield of water with added solids may be marginally higher than that without, but the difference is not substantial.

Preasphaltene Yields

Preasphaltene yields due to the coal itself were studied, rather than net preasphaltene yields. First, all residence times for the total amount of preasphaltenes in the product were corrected by assuming that the conversion of preasphaltenes to benzene solubles is first order (Joshi, 1981). It is also necessary to correct for the reactive fractions in the added residues, particularly in K-MAC. The preasphaltene yield due to coal (PA_{coal}) can be calculated as the net yield of preasphaltenes plus the yield of preasphaltenes in the added residue that were converted to benzene solubles, minus the insoluble organic matter in the added residue that was converted to preasphaltenes:

$$PA_{\text{coal}} = PA_{\text{net}} - (\text{conv} - 90) + 0.5 \text{ added PA on MAF basis}$$

On the basis of the mathematical model (Skinner, 1979; Martin 1979) and the discussion in the preceding sections, one can assume that about 50% of the preasphaltenes in the added residue were converted to benzene solubles, and that the amount of insoluble organic matter in the residue that has been converted to preasphaltenes approximately equals the increase in the apparent MAF coal conversion.

All corrected data were plotted in Figure 5. The broken line is derived from the analysis of coal/solvent data without added solids (Joshi, 1981), and the solid line correlates CPDU data with added solids data. It is apparent that the added solids reduce preasphaltene yield by roughly 7–10 wt % MAF coal, which is statistically significant at a 95% confidence level. Efforts to correlate the decrease with the ash-to-coal ratio were inconclusive. Therefore, the effect of residue concentration cannot be discerned from the data in Figure 5. One surprising conclusion, however, is that K-MAC appears to be as effective as filter cake in reducing the preasphaltene yields. There seems to be little distinction between the types of residue added.

Asphaltene Yields

For material-balance calculations, all MAF yields except asphaltene yields were examined and compared as independent quantities. The MAF yields of asphaltenes were specified and correlated after the conversion, hydrogen consumption, and MAF yields of all the other fractions were specified and correlated.

Oil Yields

To correct nominal residence time from 30 to 40 min, oil yields were increased as necessary by 4-5 wt % absolute using Skinner's (1979) and Martin's (1979) models. Also, the data from run 21 obtained by distillation I (with a heated column) were increased by 3-4 wt % absolute to conform with oil yields determined by solvent separation.

The corrected data are plotted in Figure 6 (MAF oil yield vs. temperature). The broken line was derived by analyzing coal/solvent data without any added solids, and the solid line correlates the data. The addition of solids, except for a few data points, increases the MAF yield of oils by 5-10 wt % (statistically significant at a 95% confidence level). Neither the kind of residue nor its concentration within the 5-10% range examined appears to have a discernible effect on the yield.

Total Hydrogen Consumption

According to an earlier analysis (Joshi, 1981), total hydrogen consumption (gaseous hydrogen consumed plus hydrogen donated by the solvent) appears to be independent of the nature of the process solvent. Therefore, it may be regarded as an indicator of the hydrogen gas that would be consumed in a recycle mode with an equilibrium solvent.

Total hydrogen consumed during runs 21, 23, and 27 after addition of solids is shown in Figure 7. The data from 30-min residence runs were increased by about 20% to normalize them to a 40-min residence time (Skinner, 1979; Martin, 1979). The broken line in the figure represents the total hydrogen consumed without adding solids. Adding solids raises total consumption by about 0.5% MAF coal, and the increase is seemingly independent of the kind of solids or their concentration. The solid line correlates the data.

CONCLUSIONS

The following conclusions refer specifically to the liquefaction of Kentucky #9 coal in the presence of filter cakes or K-MAC, and substantiate what has already been reported (Skinner and Givens, 1981b):

- Hydrocarbon gas, heteroatom gas, and water yields are unaffected by the addition of solids.
- The preasphaltene MAF yield attributable to coal decreases by about 7-10 wt % absolute; the decrease seems to be independent of the nature or amount of the added solids. On the other hand, the net preasphaltene yield does depend upon the nature and the concentration of added solids.
- Oil yields increase by about 5-10 wt % on a MAF basis, and the increase seems to be independent of the nature and amount of added solids.
- Total hydrogen consumption increases by about 0.5 wt % absolute on a MAF coal basis and also appears to be independent of the nature and amount of added solids.

It should be mentioned that other experiments processing Kentucky #9 coal and 10 wt % pyrite in the CPDU (Garg et al., 1980) resulted in 15 wt % decreases in preasphaltene yield and 15 wt % increases in oil yield on MAF coal.

The present analysis clearly shows that adding solids to the reactor/dissolver results in more favorable yields. We must still investigate the mechanisms by which solids aid coal dissolution, and determine whether the data on filter cake and K-MAC catalysis truly simulate the effect of dissolver solids.

At least 95% of the coal that is fed to the dissolver at Wilsonville is -200 mesh, but the solids that accumulate in the dissolver are generally 80 mesh or larger. Walker et al. (1980) reported that particles of mineral matter increase in size inside the dissolver. Particle agglomeration and growth are important factors that are responsible for the accumulation of solids. Therefore, the data on filter cake and K-MAC catalysis may not truly represent the effect of dissolver solids on coal liquefaction. It should also be pointed out that, according to a recent study (Vargese et al., 1981), the catalytic effect of dissolver solids is small.

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Table 1

Characteristics of Kentucky #9 Coal Used in Various CPDU Runs

	Range (wt %)
Carbon	69.3-70.3
Hydrogen	4.7-4.8
Nitrogen	0.9-1.5
Sulfur	3.0-3.3
Volatile matter	35.1-37.0
Ash	13.0-13.4
Moisture	1.8-1.9
Pyritic sulfur	1.6-1.8

Table 2

Residue Additives

	Weight percent for run no. and additive				
	Run 21 KM1 ^a	Run 21 FC1 ^b	Run 23 FC2 ^c	Run 27 FC3 ^c	Run 27 KM2 ^d
Carbon	50.7	21.9	34.1	38.2	62.0
Hydrogen	2.7	1.5	2.3	2.7	3.7
Sulfur	5.2	5.3	4.0	3.3	2.3
ASTM ^e ash	37.2	65.3	53.1	50.7	26.4
Iron	3.2	7.4	5.7	6.2	2.8
Oils	3.0	0	9.2	16.0	0
Asphaltenes	1.2	4.7	0.9	3.0	2.0
Preasphaltenes	24.8	4.4	4.6	5.0	45.0

^aKM1 = Kentucky #6/11 coal and Kerr-McGee ash concentrate (K-MAC).^bFC1 = Indiana V coal and filter cake.^cFC2 and FC3 = Kentucky #9 coal and filter cake.^dKM2 = Kentucky #9 coal and K-MAC.^eASTM = American Society for Testing and Materials.

Table 3

Comparison of CPDU Runs 21, 23, and 27

Run	Solvent (wt % H)	Additive ^a	Concn of additive (wt %)	Ratios		Nominal res. time (min)	Analytical method
				Coal/solvent	Ash/MAF coal		
21	WRS ^b	KM1	10	0.50	0.30	30	Distillation II
	(8.9)	FC1	10	0.50	0.41	30	Distillation II
23	WRS	FC2	5	0.46	0.27	30	Solvent separation
	(8.9)	FC2	13	0.53	0.44	30	Solvent separation
27	WRS	FC3	15	0.55	0.45	40	Solvent separation
	(8.1)	KM3	15	0.55	0.31	40	Solvent separation
	Original coal	None		0.43	0.16		

^aSee Table 2 for definition of additives.^bWRS = Wilsonville recycle solvent.

Table 4

Yield Structure with Recycle Streams (% MAF Yields)

	Coal, net	Net	Coal + 15 wt % MAF preasphaltenes	
			Due to	
			Coal	Recycle
Preasphaltenes	37.4	29.3	37.4	-8.1
Asphaltenes	33.5	39.7	33.5	6.2
Total distillates	10.1	12.0	10.1	1.9

Figure 1
Reactivity of Insoluble Organic Matter vs. Ash Content

Figure 2
Hydrocarbon Gas Yield

Figure 3
Heteroatom Gas Yield

Figure 4
Yield of Water

Figure 5
Preasphaltenes Yield

Figure 6
Yield of Oils

Figure 7
Total Hydrogen Consumption

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