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EVALUATION OF ANALYTICAL TECHNIQUES FOR SRC-I
CHARACTERIZATION, RECYCLE SOLVENT STUDIES,
AND PRODUCT FRACTIONATION STUDIES
Development of SRC-I Product Analysis

By
F. K. Schweighardt
I. S. Kingsley
F. E. Cooper
A. Z. Kamzelski
D. M. Parees

September 1983

Work Performed Under Contract No. AC05-78OR03054

International Coal Refining Company
Allentown, Pennsylvania
and
Air Products and Chemicals, Inc.
Allentown, Pennsylvania

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**DEVELOPMENT OF SRC-I PRODUCTS ANALYSIS:
VOLUME 2**

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VOLUME 2

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III. DEVELOPMENT OF SRC-I PRODUCT ANALYSIS

INTRODUCTION

ICRC conducted an experimental program to determine the most precise analytical procedures to include in the SRC-I Demonstration Plant analytical laboratory for process control and product characterization. These procedures must be well-established in order to develop a meaningful data base and to provide operational control during start-up and operation. Correlation of process and product data generated from the Wilsonville Pilot Plant and from ICRC's coal process development unit (CPDU) is essential in developing a process control model. Standardization of work-up methods therefore becomes of prime importance.

To correlate product distribution from the CPDU with that from Wilsonville, four key analytical procedures used at Wilsonville were identified: boiling point distribution by gas chromatography; cresol solubility; Soxhlet extraction; and vacuum distillation. Throughout this program, these tests were reproduced at ICRC.

The test for cresol solubility measures the amount of material in a process sample that is soluble in cresol. This gives a measure of the amount of coal converted during the SRC-I process. Previous work in duplicating the Wilsonville cresol-solubility technique indicated that the procedural reproducibility was ± 0.7 wt % (2 standard deviations representing the 95% confidence limit). In the current program, four Wilsonville process-stream samples were analyzed in triplicate. They contained from 7 to 74 wt % cresol insolubles. The results compared to within 3-5 wt % of Wilsonville's measurements, and linear regression showed a correlation coefficient of 0.997.

Numerous work-up procedures are used to characterize SRC-I products and intermediates. One approach is to separate coal-liquefaction samples into oil/distillate, asphaltene, preasphaltene, and residue fractions according to their boiling ranges or their solubility in a series of solvents. Because these methods are highly empirical, procedural variables must be defined and evaluated. As such a comparison

was made of the yields of oils and residues from SRC-I process-stream samples based on the present extraction techniques used at Wilsonville, the effect of selected independent variables on these yields was determined:

- ° Oil yields were compared by employing three commonly used nonpolar extracting solvents. We found that the oil yields from an SRC sample increased from 3 to 5.5 to 11% using n-pentane, hexanes, and n-heptane, respectively. This fluctuation can be attributed to the slight increase in polarity of the three solvents: n-pentane < hexanes < n-heptane.
- ° Oil yields were also compared by using different ratios of extracting solvent volume to sample weight. In previous analyses, this ratio was held constant based on the assumption that samples of different composition would extract in a similar fashion. Our results show that this assumption may be invalid. For example, we found that, for a blend of SRC plus heavy distillate, the critical variable is the ratio of extracting solvent volume to oil weight. The dependence of oil yield on sample composition can be explained by the effect of cosolubility. Our results indicate that cosolubility can be minimized if the oil concentration in the initial extraction step is kept below 0.02 g/mL. To ensure reliable and reproducible extraction of coal-liquefaction samples, this maximum concentration must be considered.
- ° Residue yields were compared using four polar extraction solvents: pyridine, tetrahydrofuran, cresol, and a 90:10 methylene chloride/methanol mixture. We found that the yield of insoluble residue depends on the extracting solvent used and increases from pyridine to cresol to tetrahydrofuran to methylene chloride/methanol. In addition to its dependence on the extracting solvent, the yield of insoluble residue also depends on sample composition (oils, asphaltenes, preasphaltenes, and residue). The yield using pyridine as solvent is least dependent on sample composition.

REPRODUCING WILSONVILLE'S CRESOL SOLUBILITY PROCEDURE AT ICRC

ICRC performed Wilsonville's cresol solubility test (see Appendix III-A) on Wilsonville-analyzed SRC-I process-stream samples. A schematic of this procedure is shown in Figure 1. The method determines the amount of cresol-insoluble matter in a process-stream sample. Because unconverted coal and mineral matter are defined as insoluble in cresol, this procedure provides a measure of the amount of coal converted.

Four Wilsonville process-stream samples were analyzed at ICRC, and the results were compared with those obtained at Wilsonville. Table 1 identifies the samples, lists ICRC and Wilsonville test results, and gives the arithmetic means ($\bar{x}$) and standard deviations (SD). Multiple assays from Wilsonville and ICRC were performed, as indicated. Linear regression analysis of the mean assay gave a slope of 1.07, an intercept of -2.6, and a correlation coefficient of 0.997. Figure 2 illustrates the mean assay results. The solid line represents perfect agreement between results from both laboratories. The data points are in close proximity to the solid line, showing that cresol solubility results from both facilities are comparable.

DEPENDENCE OF OIL YIELD ON EXTRACTING SOLVENT

Because different DOE contractors use different nonpolar solvents to extract SRC samples, we determined how oil yield depends on the extracting solvent. Wilsonville/ICRC, Conoco, Exxon, and Kerr-McGee use pentane, hexane, cyclohexane, and heptane, respectively, for extraction. We compared the oil yield from Soxhlet extraction of an SRC sample using the normal alkanes (n-pentane, hexanes, and n-heptane) as extracting solvents.

Procedure

A 3-g SRC sample (Wilsonville SN 67248) was ground to -100 mesh, mixed with 1.5 g of filter aid (Celite), and placed in a 250-mL cellu-

lose thimble in the Soxhlet extraction apparatus (see Figure 3). The extraction flask was filled with 300 mL of extraction solvent. Soxhlet extraction was determined complete when the thimble extract became colorless at an extraction rate of about 800 mL/hr. After the extracting solvent was removed by rotary evaporation, the extracted material was weighed. The insoluble material remaining in the thimble was also weighed to determine the material balance of the extraction procedure.

Results

Table 2 lists the weight percent of soluble oils and percent recovery for each of three extractions. Figure 4 illustrates the average oil yields obtained with each solvent. The yield of Soxhlet-extracted oils increases depending on the solvent used: n-pentane yield < hexanes yield < n-heptane yield. The differences can be related to the polarity of each solvent (see Table 2 for their polarities and boiling points). Although the respective boiling points of these solvents increase, the difference in oil yields is not due to the difference in extraction temperature. In each case, the sample is exposed to the condensed solvent at about 40°F, and not to the solvent vapors. Therefore, the Soxhlet extraction temperature is the same for each solvent, and the difference in yields can be attributed to differences in solvent strength.

DEPENDENCE OF OIL YIELD ON RATIO OF SAMPLE WEIGHT TO EXTRACTION SOLVENT VOLUME

The oil fraction in a coal-liquefaction sample can be determined by various techniques, including Soxhlet, chromatographic, pressure-filter, and beaker extraction. The latter two methods allow the operator to vary the ratio of the extraction-solvent volume to sample weight over a wide range. In this study, we determined whether varying this ratio has any effect on the oil yield of a sample. This information will aid us in developing a meaningful and reproducible standard work-up procedure.

Procedure

A 3-g sample of a blend of heavy distillate and SRC was ground to -100 mesh, mixed with various quantities of n-pentane ranging from 10 to 4,000 mL, sonicated for 10 min, stirred for an additional 20 min, and then filtered through a 5- μ m pore size Millipore filter membrane. The insoluble material was washed with additional pentane to produce a total of 5,000 mL of filtrate. The resulting residue was dried at 110°C for 4 hr and weighed. The soluble oils were stripped of the extracting solvent and weighed. Appendix III-B describes this procedure.

Results

Oil yields from extractions using varying amounts of solvents are listed in Table 3. Duplicate analyses were performed as indicated. We found that the oil yield is greater for samples that have been extracted with the lower solvent-to-sample ratio. This is due to the polar nature of the oil fraction, which causes it to act as a cosolvent with the pentane. In the first experiment when we used a 3:1 solvent-to-sample ratio, about 10% of the oils dissolved in the pentane; this changed the solvent character from nonpolar, pure pentane to a more polar oil/pentane mixture. This change in polarity allows about 3-5% of the asphaltenes that are insoluble in pure pentane to be codissolved and extracted with the oil fraction. We observed that, below a solvent-to-sample ratio of 17:1, the oil yield increases significantly. This ratio represents an oil concentration of about 0.02 g/mL for the sample we studied. Therefore, to minimize cosolubility effects, the solvent-to-sample ratio should be such that the oils concentration will not exceed 0.02 g/mL of oil in pentane in the initial dissolution step.

Our results indicate that the initial amount of nonpolar solvent used should exceed the amount of oils anticipated in the sample by a factor of 50. For example, a 10-g sample of a blend of SRC and heavy distillate, containing about 30% oils, should be suspended in a minimum of 150 mL of pentane during the initial step of the extraction procedure. However, for the dissolved coal slurry sample (V110), 10 g containing about 60% oils should be suspended in a minimum of 300 mL of pentane. It should be noted that the polarity of an oil fraction decreases significantly when the phenol and nitrogen base content of the

fraction is lowered, e.g., in samples that have been hydrotreated. In such cases, the ratio of extraction solvent to sample may be decreased without adverse effect. For 10 g of a totally unknown sample, we determined the "safe" minimum initial extractant volume to be 500 mL.

DEPENDENCE OF RESIDUE YIELD ON EXTRACTING SOLVENT

The amount of residue, or insoluble material, in coal-liquefaction samples indicates the amount of unconverted coal and minerals in a process-stream sample. The residue fraction is determined by extracting the sample with a polar solvent such as pyridine, cresol, tetrahydrofuran, or a mixture of 90 vol % methylene chloride and 10 vol % methanol. These solvents are commonly used at Kerr-McGee/ICRC, Wilsonville, Conoco, and Auburn University/Pittsburgh Energy Technology Center, respectively.

Our objective was to determine the difference in residue yields based on the type of solvent used for four Wilsonville samples. The resulting data will aid in optimizing a standard procedure for residue determination.

Samples used were dissolved coal slurry (V110), which is the feed to the distillation tower; distillation tower bottoms (T102), which is the feed to the critical solvent deashing (CSD) unit; and ash concentrate (K-MAC), which is a product stream from the CSD unit. For a description of the process streams, see Lamb and Kingsley (1981). Two different K-MAC samples and one sample of each of the other two process streams were extracted. The sampling points are labeled in the Wilsonville SRC-1 process flow sheet illustrated in Figure 5.

Procedure

Solvent (100 mL) was added to 10 g of the sample (ground to -100 mesh, where applicable); the mixture was then stirred for 30 min and filtered through a 5- μ m Millipore filter membrane in a 145-mm-diameter Buchner funnel. The insolubles were washed with an additional 500 mL of solvent, rinsed successively with equal volumes of methylene chloride and pentane, dried at 110°C for 4-6 hr, and weighed. Pyridine, tetra-

hydrofuran, and the methylene chloride/methanol mixture were used at room temperature, but cresol was heated to 110°C before and during the extraction. Pyridine at 85°C was also used, but the results were the same as pyridine results obtained at room temperature.

Results

For these process-stream samples, we found that, as solvent strength decreased (in the order pyridine < cresol < tetrahydrofuran < 90% methylene chloride/10% methanol), the yield of residue increased (see Table 4). The only exception is the T102 btm process-stream sample. In this case, cresol appears to be a stronger solvent than pyridine, possibly due to the presence of solubilized material from the T102 btm sample. Thus, this dependence on sample composition is attributable to cosolubility. The compositions of the process streams are shown in Table 5. The samples were analyzed for oils, asphaltenes, preasphaltenes, and residue content by solvent separation (see Appendix 2). We observed that the T102 btm sample has a high concentration of asphaltenes and preasphaltenes compared to the other samples. Therefore, cresol's apparent increase in strength may be due to the presence of dissolved asphaltenes and preasphaltenes in the T102 btm sample, which decrease the amount of cresol-insoluble residue. The V110 sample, which contains fewer asphaltenes and preasphaltenes, also shows this cosolubility effect when cresol is the extracting solvent, but to a lesser degree.

To aid in comparison of these solvents, we selected a ratio of two dependent variables: weight percent residue/weight percent ash for each process-stream sample analyzed. The ash-normalized residue results are listed in Table 6. We found that the residue-to-ash ratio depends on the type of polar solvent used. Plotting these ash-normalized residues as a function of solvent polarity (Figure 6) reveals some common trends. The two K-MAC samples exhibit similar relative solubility with all the solvents tested. The V110 and T102 btm samples have a solubility pattern that is different from that for the K-MAC samples. The vertical spread of data points demonstrates that residue yield depends on sample composition for a given solvent. Pyridine shows the closest cluster of

points, which indicates that its strength is not influenced as strongly by sample composition as the other solvents. This study, therefore, shows that residue determination by using pyridine is influenced least by cosolubility.

It is also interesting to compare the residue yields obtained by solvent separation (Table 5), a sequential extraction with pentane, benzene, and pyridine, with the residue yields obtained by beaker extractions (Table 4) with pyridine. Generally, the beaker extractions showed a more complete extraction, which again can be attributed to cosolubility effects.

CONCLUSIONS

- ° We were able to duplicate Wilsonville's cresol solubility procedure, which will be used to determine the amount of residue in CPDU process-stream samples. Cresol-residue yield at ICRC can now be related to Wilsonville values within 3-5 wt %.
- ° We found that oil yields of a coal-liquefaction sample depend on the extraction solvent used. Because of polarity differences of the three solvents, the oil yield of an SRC sample increased from 3 to 5.5 to 11% using n-pentane, hexanes, and n-heptane, respectively.
- ° Oil yields of coal-liquefaction samples depend on the extraction solvent-to-sample ratio in the initial extraction step. The oil yield of a blend of SRC and heavy distillate was about 10% higher when the concentration of dissolved oils in the extracting solvent pentane increased above 0.02 g/mL. This limiting concentration must be considered in order to extract coal-liquefaction samples reliably and reproducibly.
- ° Residue yields of coal-liquefaction samples depend on the type of polar solvent used. Pyridine, cresol, tetrahydrofuran, and a methylene chloride/methanol mixture all gave different results. Pyridine is the strongest solvent, resulting in the least residue. Cresol's strength increases when asphaltenes

and preasphaltenes are present. Without this cosolubility effect, cresol is a weaker solvent than pyridine. Tetrahydrofuran, a weaker solvent than pyridine and cresol, yields higher amounts of residue. Methylene chloride/methanol was the weakest solvent tested. Our results show a strong dependence of residue yield on sample composition for each extracting solvent used. Pyridine was least influenced by differing sample composition.

ACKNOWLEDGMENTS

We wish to acknowledge Shirley Dukett and Jeffrey Rabe, who carried out the Soxhlet extractions, cresol solubility tests, and beaker extractions.

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- Snyder, L. R. 1974. J. Chromatogr. 92:223.
- _____. 1978. J. Chromatogr. Sci. 16:223.

Table 1

Results from ICRC and Wilsonville
Cresol Solubility Tests (Wilsonville Method #34550-21)

Wilsonville								
X cresol Insolubles								
Sample	Sample no.	process stream no.	Wilsonville	$\bar{X}$	SD	ICRC	$\bar{X}$	SD
T102 btm	67249	30	15.8 20.7	18.3	3.5	13.4 13.6 13.5	13.5	0.1
T102 btm	64886	30	17.5	17.5	-	16.8	16.8	-
K-MAC	64889	28	71.1	71.1	-	72.9 75.2 74.8	74.3	1.2
V110	67250	3	7.6 7.4	7.5	0.1	7.8 7.9 8.2	8.0	0.2

Table 2

Oil Yields of an SRC Sample (67248) Determined
by Soxhlet Extraction Using n-Pentane, Hexanes, and n-Heptane Solvents

Solvent	p ^a	Boiling point Normalized		Average	% recovery
		(°C)	% oils		
n-Pentane	0.0	36	2.6	2.8	100.3
			2.0		99.7
			3.8		100.5
Hexanes	0.1	69	5.9	5.6	99.8
			5.9		99.9
			5.0		99.4
n-Heptane	0.2	98	10.5	10.8	101.5
			11.0		101.3

^aSolvent polarity parameter; see Snyder, 1974, 1978.

Table 3

Experimental Conditions and Results for the Determination
of Oil-Yield Dependency on Solvent-to-Sample Ratio
(Sample Size, 3 g)

Sonicate in mL of pentane	Wash insols. with mL of pentane	Ratio solvent:sample	% oils
10	5,000	3:1	30.3
			31.9
50	4,950	17:1	26.7
200	4,800	67:1	25.7
			25.7
500	4,500	167:1	28.3
1,000	4,000	333:1	27.0
4,000	1,000	1333:1	25.5
			25.5

Table 4

Comparison of Residue Yields (Weight Percent)
Using Different Extraction Solvents

Sample	Sample no.	Pyridine	Cresol	Tetrahydrofuran	Methylene chloride/ methanol
K-MAC	SN 67245	54.8	71.5	79.6	87.9
		54.7	72.0	80.6	88.1
		54.8	71.0	80.1	88.3
		55.7	71.2	81.0	88.3
K-MAC	SN 64889	59.4	72.9	81.1	88.9
			75.2		
			74.8		
T102 btm	SN67249	15.9	13.4	19.4	31.6
		15.9	13.6	19.7	31.5
		15.9	13.5	19.9	31.9
V110	SN 67250	7.4	7.8	9.0	14.0
				9.3	13.9

Table 5

Composition of Wilsonville Process Streams as Determined by
Solvent Separation^a and Ash Analysis (Weight Percent)

Sample	Sample no.	Oil	Asphaltenes	Preasphaltenes	Residues ^b	Ash
K-MAC	67245	1.8	2.3	34.3	61.6	28.5
	64889	0.9	2.1	32.2	64.9	33.5
T102 btm	67249	6.9	48.4	28.5	16.0	9.3
V110	67250	61.5	16.5	13.6	8.3	4.6

^a See Appendix 2.

^b By pyridine extraction.

Table 6

Ash-Normalized Residues
(Weight Percent Residue/Weight Percent Ash)

Sample	Sample no.	Pyridine	Cresol	Tetra- hydrofuran	Methylene chloride/ methanol
K-MAC	67245	1.92	2.51	2.81	3.09
	64889	1.77	2.22	2.42	2.65
T102 btm	67249	1.71	1.45	2.12	3.40
V110	67250	1.61	1.70	2.00	3.04

Figure 1
Cresol Solubility (Beaker Extraction)

Figure 2
Comparison of Cresol Solubility
Results at ICRC and Wilsonville

$$\% \text{CI}_{\text{ICRC}} = 1.07 \times \% \text{CI}_{\text{WV}} - 2.6$$

CORRELATION COEFFICIENT = 0.997

Figure 3
Soxhlet Extraction Apparatus

Figure 4
Yield of Oils by Soxhlet Extraction of SRC Using
Different Nonpolar Extracting Solvents

Figure 5
Wilsonville Pilot Plant Process Flow Diagram

Figure 6
Ash-Normalized Residues, Obtained by Extracting Different
Wilsonville Process Streams with Different Polar Solvents

Appendix III-A

Wilsonville's Cresol Solubility Test
(Procedure No. 34550-21)

Scope: This test is designed to measure the cresol-insoluble solids in solvent-refined coal (SRC).

Principle: The procedure is based on fractional solubility in organic solvents. Because the solvent was selected to give the maximum solubility of extract, the insoluble residue represents, primarily, unreacted coal or similar material in the product. Strict adherence to all specified conditions is essential because of the empirical nature of the test.

Apparatus: Beakers (300 mL)
Mechanical stirrer
Suction flask (100 mL)
Steam-jacketed Buchner funnel (15 cm)
Filter paper, no. 42 (15 cm)
Hot plate
Oven, $105 \pm 5^{\circ}\text{C}$
Water aspirator
Wash bottle [for cresol (hot) methanol]
Analytical balance
Powder paper (glassine, 4-3/8 X 5-3/4, Eli Lilly Co.)

Reagents: Cresol
Acetone

Procedure: 1. Place 100 mL of cresol in a beaker and heat on a hot plate until vapors are visible.

Appendix III-A (Continued)

2. Prepare sample to -20 mesh. Do not crush too finely.
3. Weigh 10-g sample on glassine paper.^a
4. Add the sample, stirring constantly, to the hot cresol; stir the mixture for 0.5 hr. The sample can be weighed in a beaker and the hot cresol added to the sample while stirring.
5. Weigh a No. 42 filter paper and prepare the steam-jacketed Buchner for filtering. Be sure the funnel is hot.
6. Filter the sample and wash several times with hot cresol or until the sample does not look tacky.^b
7. Turn off the steam and let the funnel cool. Wash the insoluble material with acetone until the sample is free of cresol.
8. Dry the filter paper in the oven at 105°C for 30 min. Residue should be free of any cresol odor. Cool in a desiccator and weigh. Subtract weight of filter paper to obtain weight of insolubles.

Calculations: $\frac{\text{Weight of insoluble material}}{\text{weight of sample}} \times 100 = \% \text{ cresol insolubles}$

^aSample size depends on the percent insolubles in the SRC. With a high percentage of insolubles present, a smaller sample can be used, and vice versa.

^bSome samples filter very slowly. When this occurs, a new smaller sample should be used, or the sample should be stirred and heated for a longer period of time.

APCI's Total Product Solvent-Separation Procedure

Scope:

This procedure is designed to separate a total product sample into the following fractions:

- Oils: pentane soluble
- Asphaltenes: pentane insoluble/benzene insoluble
- Preasphaltenes: pyridine soluble/benzene insoluble
- Residue: pyridine insoluble

This procedure is carried out at room temperature under nitrogen, using high-quality solvent [pesticide or HPLC (high-performance liquid chromatography) grade]. The sample can be liquid, solid, or a mixture thereof, with less than 1% material boiling below 300°F. The reproducibility of the solvent-separation procedure on a total product liquid is exemplified by the following data:

	<u>Mean (%)</u>	<u>Standard deviation^a (%)</u>
Oils	63.3	1.06
Asphaltenes	8.7	0.94
Preasphaltenes	9.7	1.23
Residue	18.2	0.31

^aThe result of five trials.

Equipment and Solvents Required:

Branson Model 350 Sonicator with 0.5-in. horn, or Heat Systems Model W375 Ultrasonic

Millipore 142-mm pressure filter with 1,500-mL capacity; No.'s XX42-142.35 and YY-30-142-35 with 142-mm filter, 5-μm LSWP 142-50

Glass, stainless-steel, or Teflon tubing can be used for solvent-transfer lines

Appendix III-B (Continued)

Four round-bottomed distilling flasks (1 L)

Rotary evaporator RE 120, WWR No. 27582-406

Vacuum pump and trap

Nitrogen gas (0-20 psi adjustable), pressure-filter feed

Nitrogen gas (0-20 psi adjustable), rotovapor feed

Nitrogen liquid (1-2 L), freeze sample (Dewar)

Solvents: n-pentane, benzene, pyridine, methanol, or methylene chloride. Grade of solvent depends upon ultimate use of sample subfractions. Pesticide, distilled in glass, or HPLC grade are acceptable.

Fume hood, 150-200 cfm air exchange rate

Cooling water or heat exchanger for rotary evaporator condenser

Balance to read weights to ± 0.005 g or better with maximum load of 500 g

Glass Millipore, 47 mm, Model No. xx15047-00 with 5- μ m No.

LSWG-04700

Safety Features:

Solvents must be used only under the fume hood. Workers must wear protective gloves and overalls for laboratory work. Hands can be mildly scrubbed with waterless hand cleaner, followed by a warm water wash. All normal safety precautions must be observed during the entire operation.

Sampling Handling for Total Product Liquids:

The sample chosen for this procedure must represent the process unit output. Great care must be used to isolate about 5 g of gross product. Hot samples may be taken in 8-oz glass jars.

The sample must be kept free of air (oxygen), heat, and light. Samples not ready for separation should be stored at 4°C under a blanket of nitrogen. Samples may be warmed to 65°C in the jars in an oven for 15 min and then sonicated for 15 min to induce good mixing just before a 5-g sample is procured for actual work-up.

Procedure:

The laboratory equipment is prepared in the following order:

- a. Weigh the jar containing the sample and the jar lid, record the weight, and sonicate the sample for 15 min. Mix the sample with a spatula and reweigh. Record any loss in weight as light ends. Clean off spatula and sonicator horn by placing a tared 250-mL beaker with 200 mL of CH_2Cl_2 under the sonicator for 6 min. Evaporate CH_2Cl_2 by placing the beaker on a hot plate (at setting 2 or 3) for 1 hr. Record differences in beaker weight and subtract from light ends.
- b. Put Millipore filter in place after weighing the dry filter element. Ensure that all Teflon o-rings (and viton gasket) fit well with no leaks (test with n-pentane under 10 psi). No silicone gaskets or grease should be used in filter apparatus!
- c. Prepare rotary evaporator bath temperature at 55-60°C for n-pentane; nitrogen flow rate should cause just a 0.25-0.5-in. dimple in the liquid in a 1-L flask.
- d. Temperature of cooling liquid for rotary evaporator condenser should be less than 10°C.

Step 1:

Tare a 600-mL heavy-walled Pyrex beaker and then add about 5 g (± 0.01 g) of the desired coal-derived sample. Obtain the sample as soon as possible after sonication, so that it is liquid. Slowly add about 100-150 mL of liquid nitrogen to the beaker to maintain a quiet solution. The total volume of liquid nitrogen used may exceed 300 mL.

Step 2:

With a Pyrex glass stirring rod (3/8-in. diameter), grind the frozen sample to a fine powder. This step requires 5-8 min. Fill the beaker with more liquid nitrogen to maintain a volume of at least 30 mL during grinding.

Step 3:

Allow the liquid nitrogen to evaporate to just above the solid mixture. Slowly add 100 mL of n-pentane; continue adding another 400 mL of pentane (to a total of 500 mL of pentane). Sonicate for 5 min at the 50% power level dial.

Step 4:

Prior to decanting, wipe outside of beaker to remove water condensate. Decant supernatant into filter unit, refill beaker with 500 mL of n-pentane, and sonicate again for 3-5 min. Allow decant liquid to filter into a 500-mL flask. To ensure complete recovery of oils, do not allow filter to dry from this time on.

Step 5:

Repeat step 4 five to eight times. If catch flask fills, transfer contents to rotary evaporator flask and begin to remove n-pentane under nitrogen at about 60°C. Transfer the solids from beaker with small portions (25-50 mL) of pentane onto the filter and wash sonicator probe and filter with pentane. Then wash sonicator again for 5-8 min with pure benzene. Set original sample aside for benzene extraction. (Do not discard beaker; hold for additional transfer of solvents to filter. This ensures removal of maximum amount of material and reduces loss.)

Step 6:

Filter the solids, adding nitrogen pressure (5-10 psi) if needed. (The solvents can be collected from the rotary evaporator unit during the continuous solvent removal steps.)

Step 7:

Continue solvent filtering using pentane (about 5-20 L), in a clean beaker, until the filtrate is a very light yellow. At the end of pentane extraction, switch collection flasks and add the benzene from the original sample beaker (step 5).

Step 8:

The pentane solubles from steps 6 and 7 should be held on the rotary evaporator for 2 min after the last drop of pentane has condensed in the catch flask. Remove from the rotary evaporator, clean and dry the outside of the flask, and weigh. From the difference on tare, obtain the yield of oils as x grams. Store the oils in a refrigerator at 4°C.

Step 9:

Now extract benzene, similarly to steps 6-8. Rotary evaporate in a new 500-mL tared, round-bottomed flask under vacuum (15-20 in.) at 80°C to remove benzene. Keep adding 500-mL aliquots (totaling 5-20 L) until the filtrate is a very light yellow. Remove the flask containing benzene solubles from the rotary evaporator when 5-10 mL of solution remains. Swirl flask in liquid nitrogen to evenly coat two-thirds of the inner flask and freeze the solution in place. Quickly transfer the flask to a vacuum line (1 mmHg) with trap, and allow flask to stand unheated to freeze-dry the benzene (sublime) in about 2 hr. Calculate the yield of asphaltenes as x grams. [If weight recovery is greater than 100%, ^1H NMR may be used to detect either pentane (oils), benzene (asphaltenes), or pyridine (preasphaltenes). Use CH_2Cl_2 and a 10% sample size.]

Step 10:

After the last benzene extraction, start adding pyridine (total 5-20 L) and continue extracting as in steps 6-8. Extract pyridine until the filtrate is light beige. Rotary evaporate the solvent to dryness at 100°C under 20 psi vacuum pressure. Clean rotary

evaporator and condense by placing 300-500 mL of methylene chloride in a 1-L flask and rotary evaporating; discard as waste. Place 500 mL of methanol into the flask containing the pyridine solubles and shake. Pour onto a tared 47-mm Millipore glass filter (the filter may be weighed in an aluminum dish) and continue adding methanol, while shaking and scraping the flask until most of the presphaltenes are on the filter. Wash with 100 mL of pentane to remove the methanol, which is vacuumed off. Allow filter to dry on hot plate before weighing. Reweigh rotary evaporator flask to check flask tare. Record yield of preasphaltenes as x grams.

Step 11:

Let the residue dry in place after washing with 500 mL of methanol, 500 mL of methylene chloride, and 500 mL of pentane. Dry the filter using N_2 pressure and weigh to obtain the yield of residues as x grams.

Step 12:

Oils	A
Asphaltenes	B
Preasphaltenes	C
Residue	<u>+ D</u>
Total recovered	

Original mass of sample = MS

MS - total recovered = net loss or gain

If weight gain is observed, leave solvent in oils or asphaltenes and test with NMR. If weight loss is observed, oils have too much volatile matter.

Results should not be reported unless >97% material is recovered. Repeat the analysis.

Add net loss to mass of oils (A + net loss) and calculate material recovery.

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Appendix III-B (Continued)

	<u>Recovered</u>	<u>Corrected</u>	<u>%</u>
Report: Oils	A	A + net loss	_____
Asphaltenes	B	B	_____
Preasphaltenes	C	C	_____
Residue	+ D	D	_____
	Total recovered	MS	100%

It is now possible to compare samples derived during the coal conversion process with a high degree ($\pm 1\%$) of reliability, within 10-14 hr. After the classical separation has been made, the subfractions can undergo first-level chemical characterization.

IV. ELEMENTAL ANALYSIS ROUND ROBIN

INTRODUCTION

Apparent difficulties in the determination of nitrogen, sulfur, and oxygen (by difference) at the Wilsonville Advanced Coal Liquefaction Facility laboratory prompted A. Rao of Wilsonville to suggest a cooperative investigation of nitrogen analysis. As part of program area 12.1.10, SRC Product Analysis, ICRC participated in the round robin analysis.

Six samples from the hydrotreater unit operation process streams were selected as representative of materials routinely analyzed for elemental distribution. Each laboratory involved analyzed the product streams and three chemical standards prepared at Wilsonville. The objective of the investigation was to determine the range of analytical results for elemental nitrogen determined by different instrumental procedures and different analysts.

The data show that the Wilsonville laboratory should consider reviewing their current elemental analysis sampling techniques (Perkin-Elmer 240 system). If the current instrument cannot be updated or if future samples have low nitrogen contents that cannot be detected with the present instruments, a new method should be considered as a replacement or supplement.

EXPERIMENTAL APPROACH

Sample Selection

Six hydrotreater unit process stream samples were selected as representative of typical materials used for material and elemental balances. Figure 1 illustrates the process flow diagram of the H-Oil hydrotreater system and the streams sampled are listed in Table 1.

Sampling

All samples were collected in clean, dry quart containers that were tin-plated, except for the process wastewater (V-1080), which was collected in a plastic quart container. As the material was collected by a Wilsonville staff member, each site was photographed to document sampling problems. The sampling was witnessed by R. Hickey (DOE) and F. Cooper (Wilsonville).

Sample Distribution

The original sample from each site was divided three ways by the Wilsonville staff for initial distribution to Wilsonville Analytical Laboratory, Pittsburgh Energy Technology Center (PETC), and ICRC. All materials were shipped within 5 days of sampling in washed-and-dried glass sample jars with protected inner seals. Included with each sample set, or mailed separately, were three chemical standards prepared by the Wilsonville laboratory staff for absolute elemental reference purposes.

Analysis

The samples were analyzed by Wilsonville, PETC, and ICRC and also by selected independent analytical labs (Galbraith and Huffman), known for their commercial analysis of coal-related materials. In total, seven methods were used at six laboratories to measure nitrogen in each sample:

Wilsonville	Perkin-Elmer 240A
ICRC/APCI	Perkin-Elmer 240XA
Galbraith	Perkin-Elmer 240B
	Kjeldahl
	Antek
	Carlo Erba
	Leco
Huffman	Merz oxidation, Dumas modified
PETC	Kjeldahl
Kerr-McGee	(N) Kjeldahl/(C&H) ASTM/(S) Parr bomb

DATA

Table 2 summarizes the complete elemental analysis, "as received," for each hydrotreater sample, as performed by Huffman Labs, Kerr-McGee, and Air Products Analytical Service. Table 3 lists the complete elemental analysis of the chemical standards selected by Wilsonville, performed by the same laboratories. Table 4 summarizes the nitrogen analyses for all materials, either by method or location.

Table 5 presents data from an independent statistical analysis conducted by Air Products on a single Wilsonville recycle solvent. This data set is included to provide confidence limits for the overall elemental analysis. The distillate was divided into four equal parts (CH1-CH4), 25 mL each, and submitted in duplicate to Air Products Analytical Service and Huffman Laboratories, 10 days apart, with no indication that the samples were identical. Duplicate analysis was requested for each sample.

OBSERVATIONS

The data in Table 4 from the nitrogen analyses are well scattered, if all methods and all laboratories are compared. Table 6 gives the numeric average and one standard deviation for nitrogen analysis. Results are reported with one additional significant figure to show the trend for rounding off. The Wilsonville and Carlo Erba (Galbraith) results are random, suggesting sampling and/or instrumental problems.

Overall results show that reproducible nitrogen analysis of hydrotreater samples is possible, and a number of methods can be used to acquire precise data. Air Products has compared the classical Kjeldahl method with the newest instrumental approach by Antek. Appendix IV-A summarizes these findings. These results are included to provide a comparison of samples with low nitrogen content on a second independent set of hydrotreater samples.

CONCLUSIONS

The data presented here clearly show that the Wilsonville laboratory should consider an in-depth review of their elemental analysis sampling techniques for subsequent determination of carbon, hydrogen, and nitrogen by their Perkin-Elmer 240. Air Products' laboratory has a similar Perkin-Elmer 240 system that was recently updated. In combination with instrument modification, Air Products modified its sample-handling procedures for low-boiling mixtures to standardize the entire analysis method by sample type.

Wilsonville should consider purchasing a new elemental analysis system only if the current instrument cannot be updated and/or if low nitrogen (<0.3 wt %) contents that cannot be detected on the current instrumentation are expected in future samples. A replacement system could be considered as a complement to the Perkin-Elmer 240 system (if modified) for low-level nitrogen analyses.

Table 1

Samples Selected August 30, 1982

HT code no.	Sample
1	V-1064 SRC melt tank
2	V-1074 Recycle solvent
3	V-1072 Vacuum flash overhead
4	V-1078 Flashed distillate
6	V-1082 Heavy resid
10	V-1080 Process wastewater

Table 2
Elemental Analysis^a of
Hydrotreater Sample Set, "As Received"

Element	APCI	Huffman	Kerr-McGee	APCI	Huffman	Kerr-McGee
Process wastewater (91155)			Flashed distillate (91156)			
C	0.04	0.13	0.5	88.45	87.86	88.0
H	11.39	11.09	10.5	11.46	11.42	11.1
O	86.70	86.03	86.8	0.61	0.44	0.7
N	1.22	1.35	1.41	0.11	0.56	0.19
S	1.38	0.82	0.83	<0.1	<0.10	0.02
Σ	100.73	99.42	----	100.63	100.28	----
Heavy resid (91158)			SRC melt tank (91160)			
C	89.55	89.38	89.4	87.78	87.76	87.9
H	6.93	6.89	6.95	7.83	7.92	7.95
O	1.74	1.70	1.90	2.47	2.45	2.3
N	1.44	1.53	1.38	1.23	1.23	1.06
S	0.24	0.22	0.18	0.53	0.47	0.47
Σ	99.90	99.7	----	99.84	99.83	----
Vacuum flash overhead (91157)			Recycle solvent (91159)			
C	88.78	88.65	88.6	88.64	88.45	88.7
H	10.12	10.12	10.0	10.40	10.40	10.2
O	0.65	0.40	1.0	0.62	0.65	0.7
N	0.37	0.59	0.40	0.31	0.69	0.35
S	<0.1	<0.10	0.02	<0.10	<0.10	0.05
Σ	99.92	99.76	----	99.97	100.19	----

^aDuplicate averaged, not normalized.

^bOxygen by difference.

Table 3
Analysis of Standards Prepared by
Wilsonville Analytical Laboratory

Element	APCI	Huffman	Kerr-McGee	Theory
Sample A (V7022) (2366), 10% quinoline + 90% methylnaphthalene				
C	91.76	91.62	91.5	92.0
H	6.88	6.95	6.86	6.92
O	0.12	0.31	0.5	--
N	1.16	1.46	1.11	1.08
S	<0.1	<0.1	0.03	--
	99.92	100.34		100.00
Sample B (V7023), 100% methylnaphthalene				
C	92.80	92.80	92.5	92.96
H	7.06	7.07	7.0	7.04
O	0.04	<0.1	0.4	--
N	0.08	<0.1	0.13	--
S	<0.1	<0.1	0.01	--
	99.98	100.07		100.00
Sample C (V8151) (normalized), 100% quinolinediol				
C	66.73	65.78	65.82	67.08
H	4.31	4.30	4.37	4.34
O	20.38	21.48	21.77	19.87
N	8.50	8.43	8.03	8.69
S	--	--	--	--
	100	100	100	100

Table 4

Summary of Nitrogen Analysis, by Method or Laboratory

Sample	WV	Huffman	APCI	PETC	Kerr-McGee	Galbraith				
						Leco	Kjeldahl	Antek	Perkin-Elmer	Carlo Erba
Process wastewater (91155/V-7016)	--	1.35	1.22	1.3	1.41	--	1.50	1.32	1.55	0.80
Flashed distillate (91156/V-7017)	1.44	0.56	0.11	0.2	0.19	--	0.26	0.24	0.28	0.31
Heavy resid (91158/V-7018)	1.49	1.53	1.44	1.5	1.38	1.75	1.56	1.59	1.62	1.54
SRC melt tank (91160/V-7019)	1.07	1.23	1.23	1.2	1.06	1.32	1.30	1.09	1.10	1.18
Vacuum flash overhead (91157/V-7020)	0.36	0.59	0.37	0.4	0.40	--	0.41	0.33	0.63	0.56
Recycle solvent (91159/V-7021)	0.33	0.69	0.31	0.4	0.35	--	0.42	0.47	0.33	0.54
Standard A ^a (V-7022)	2.47	1.46	1.16	1.3	1.11	--	0.93	0.90	1.15	0.53
Standard B ^b (V-7023)	1.70	<0.11	<0.08	0.2	0.13	--	0.06	0.19	0.20	0.29
Standard C ^c (V-8151)	8.25	8.43	8.50	8.2	8.03	--	8.48	8.11	8.43	--

^a10% quinoline plus 90% methylnaphthalene.^b100% methylnaphthalene.^c100% quinolinediol.

Table 5

Statistical Comparison: Elemental Analysis of
Wilsonville Recycle Solvent by Two Laboratories

	APCI				$\bar{X}$ (% abs)	2 SD (% abs)	Huffman				$\bar{X}$ (% abs)	2 SD (% abs)
	CH1		CH3				CH2		CH4			
C	87.67	87.77	87.54	87.57	87.64	0.21	87.44	87.40	87.28	87.46	87.40	0.16
H	8.27	8.24	8.26	8.28	8.26	0.03	8.20	8.25	8.17	8.22	8.21	0.07
O	2.94	2.91	3.07	2.92	2.96	0.15	2.49	2.85	3.26	3.09	2.92	0.67
N	0.79	0.82	0.67	0.63	0.73	0.18	0.96	0.87	0.78	0.87	0.87	0.15
S	0.53	0.54	0.45	0.51	0.51	0.08	0.53	0.50	0.50	0.49	0.51	0.03
Total	100.20	100.28	99.99	99.91	100.10	0.34	99.62	99.87	99.99	100.13	99.90	0.43

Table 6

Average Results and One Standard Deviation
for Nitrogen Analysis^a

HT code no.	Sample no.	Average	S
1	V-1064 SRC melt tank	1.19	0.1
2	V-1074 recycle solvent	0.44	0.13
3	V-1072 vacuum flash overhead	0.46	0.11
4	V-1078 flashed distillate	0.26	0.14
6	V-1082 heavy resid	1.55	0.11
10	V-1080 process wastewater	1.38	0.12
A	10% quinoline in methylnaphthalene	1.14	0.2
B	100% methylnaphthalene	0.16	0.08
C	100% quinolinediol ^b	8.31	0.19

^aWilsonville and Carlo Erba results are not included.

^bNormalized to remove "ash" content of 23 wt %.

Figure 1

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Appendix IV-A

Determination of Nitrogen in SRC-I Hydrotreated Naphtha and
LC-Finer Distillate Fractions

An Instrument Evaluation Report

A rapid, reliable, and sensitive analytical technique is required to determine total bound nitrogen in hydrotreated naphtha (nitrogen levels less than 1 ppm) and LC-Finer distillates (nitrogen levels less than 0.3%). The Kjeldahl method has been the preferred method for determining nitrogen in petroleum for many years. However, the somewhat hazardous procedure requires considerable time for acid digestion and distillation, and is unreliable at low nitrogen concentrations. Furthermore, tedious techniques of questionable value must be used to avoid contamination. Such techniques, apparatus, and reagents all affect the accuracy of analysis at low-ppm nitrogen levels.

Recently, a microcoulometric analysis method (Dohrmann analyzer) has been used extensively in the petroleum industry. This technique involves reductive pyrolysis of the sample in the presence of nickel catalyst and coulometric titration of the ammonia produced using a four-electrode hydrogen cell. The coulometric system, although an improvement over Kjeldahl, has its own drawbacks. The large amount of high-purity hydrogen needed, specialized analytical techniques, small dynamic range, and safety factors make this method costly and nearly as time-consuming as the Kjeldahl procedure. Also, on high-boiling aromatic oils and residual oils, the method leads to low recoveries because of incomplete vaporization or coking.

An appropriate method for determining nitrogen in SRC-I products is another recently developed technique, combustion with chemiluminescence detection of nitric oxide (Antek Digital Nitrogen Analyzer, Models 703, 705, and 707). The principle of analysis involves pyrolysis of the sample in a pure oxygen atmosphere at approximately 1,000°C, converting all chemically bound nitrogen to nitric oxide:

The nitric oxide is then reacted with ozone to produce metastable nitrogen dioxide. Almost instantaneously, the excited nitrogen dioxide molecule, as it relaxes to its ground state, emits a photon of light (ϵ):

This emission is measured quantitatively in the 650-900-nm range, providing an interference-free detection of nitric oxide.

The procedure is totally specific for nitrogen-bearing compounds in the sample. Atmospheric, diatomic nitrogen does not enter into the reactions; therefore, no interfering substances affect the end results.

The commercially available Antek System is sensitive enough to enable accurate and reproducible analysis of from 0.1 ppm to 3.0% or more nitrogen in any type of liquid or solid sample. The technique offers several advantages over the microcoulometric method. Analysis time is shorter because the response peak is sharp and does not exhibit the "tail" caused by adsorption on the nickel catalyst of the microcoulometric system. The tedious cleaning and filling of the complex microcoulometric cell is eliminated, and the time required to condition and calibrate the system is reduced. Also, the chemiluminescent method provides a much wider dynamic range.

The microcoulometric method uses 50- μ L samples; this requires a sample injection time of about 6 min to prevent oxygen and/or ozone starving. A voltage level (peak height) is used for quantitation. This technique severely limits the linear dynamic range. In fact, any concentration above 200 ppm requires dilution in the microcoulometric method. Also, when high-boiling residual fuels are analyzed by microcoulometry, catalytic hydrogenolysis occurs, which leads to low recoveries because of incomplete vaporization or coking; in contrast, complete combustion occurs with a boat inlet Antek combustion system.

Table A-1 compares the Antek results with those from Kjeldahl analysis of hydrotreated coal liquids.

An Antek instrumental technique is recommended for precise and rapid analysis of total chemically bound nitrogen. This method, based on oxidative pyrolysis followed by chemiluminescence measurement, is free from the hazards and time-consuming features of some of the older, traditional chemical techniques.

Table A-1
Comparison of Antek and Kjeldahl Techniques for
Measuring Nitrogen in Coal Liquids

Sample no.	Antek average response	% nitrogen (w/w)	
		Antek (using FS as reference) ^a	Kjeldahl
FS	1,638 counts/mg		0.915
HT ₁	626 counts/ μ L	0.443	0.452
HT ₂	217 counts/ μ L	0.153	0.147
HT ₃	121 counts/ μ L	0.086	0.075

^a Assuming specific gravity to be 0.90 g/mL for each of the hydrotreated samples.

V. RECYCLE SOLVENT STUDIES

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1. RECYCLE SOLVENT CHARACTERIZATION

SUMMARY

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.

In the work covered by this report, the physical and chemical properties of six recycle solvents were compared and it was 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, solvent F (Wilsonville recycle solvent generated from Dotiki Mine Kentucky #9 coal) was selected 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. High-resolution mass spectrometry was also attempted for compound identification, with moder-

ate success; it was found that this technique consolidates all the isomers and provides a better overview of compound classes.

The results also 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 Plant); solvent B is a hydro-treated 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 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 bituminous 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.

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.

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 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 μL , 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. $\text{C}_{16}\text{H}_{10}$ is pyrene and fluoranthene and $\text{C}_{14}\text{H}_{10}$ 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 subroutines.

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 C_1 - C_4 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 C_1 - and C_2 -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 C_1 - C_5 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 (C_1 - C_2 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:

quinoline

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 (CH_3) 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 available from processing bituminous coal. ~420°F naphthalene would be produced as a nonsubstituted 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

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.

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 _a by NMR	30.1	30.7	30.9	31.9	35.5	29.5
Wt % H _a	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 _u	30.7	31.4	28.2	24.8	28.6
H _B	32.0	35.7	31.5	38.2	35.9

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 _a	2.5	2.9	2.4	2.0	2.2
H _B	1.6	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	x 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	MW = 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-Ethylnaphthalene	
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 methyl ethyl naphthalene? MW = 170
847	F = 945	1-tert-Butyl naphthalene	Plus MW = 200?
AA2	821/928	5H-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 ₃ -alkyl naphthalene?
947	F = 980	A C ₂ -alkylbiphenyl	
961		An alkane	
970	769/954	1,1'-(1,2-Ethenediyl)biphenylene	
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	Benzo[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-Ethynaphthalene	MW = 156
645	810/990	A dimethylnaphthalene	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 -alkylidene)

Table 18 (continued)

can no.	Library search result ^b	Compound	Comments
96.	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-Phenylnaphthalene	MW = 204, this is distinguishable from a dihydrofluoranthene or -pyrene
1291	F = 960	An ethylphenanthrene	9- or 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	715/980	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 =
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 methylnaphthal 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 M
641		See 624	
650		See 624	
658		See 624	
667		An ethenylisoquinoline?	Plus an ethylmethylquinoline (?), MW = 171
671		Unknown	MW = 155; C ₃ -alkylbenzene; plus MW = 157
685		See 624	MW = 171 and 175
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 = F = 902
722		An isopropylnaphthalene	
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 is 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 MW = 182; plus MW = 185
854	F = 951	4-Methyldibenzofuran	There are no compounds in this class in the computer library; plus MW = 185
857		A methylnaphthalenamine?	
868	902/966	4-Methyldibenzofuran	See scan 854. One is presumably an isomer. Plus M

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-fluoren-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[n]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 alkene	
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 dihydrodropyrene)
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-fj]isoquinoline?	(Azafuoranthene); MW = 203
1341	965/994	Pyrene	MW = 204
1352	904/970	1-Phenylanthralene	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	025/915	A methylpyrene	MW = 216; or a 11H-benzofluorene
1444		A methylindeno[1,2,3-fj]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-fj]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 benzofluoranthene	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 benzofluoranthenes, 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 indenoisoquinolines 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
	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.

^b n = 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	Percentage of ion total	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 ₈ 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	
					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	
		Oxygen		8.8	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	
					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	
40,000	10.5	Hydro	767-792K	19	C ₁₀ H ₁₀ S	489	
					C ₇₈ H ₃₂ S ₂	300	
					C ₁₂ H ₈ S	129	
					C ₂₀ H ₂₆ S	128	
		Oxygen		6.9			
		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 I-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 I-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										
Accumulated total	0.4	5.0	23.9	16.6	15.1	16.2	9.8	6.0	4.0	3.0
Calculated boiling point (°F)										
	393	454	541	574	634	695	755	815	875	936

Scan ^a	Library search result ^b	Compound ^c	Comments
26			Small alkane
30			Small alkane
43	937/995	Benzene	
49	910/965	A dimethylcyclopentane	
53	965/990	Heptane	
62	930/990	Methylcyclohexane	
70			Unsat. alkyl
89	879/994	Toluene	Largest component
94	835/933	Dimethylcyclohexane	
105	934/990	Ethylmethylcyclopentane	
109	964/951	6 dimethylcyclohexane	
117	904/905	Octane	
123			C ₉ cyclic alkyl, MW = 112 (isopropylcyclopentane) (801/956)
135	911/905	An ethylmethylcyclopentane	
141	856/976	A dimethylcyclohexane (1,2-cis)	
149		Propylcyclopentane?	1137, 2,6-dimethylheptane, 902/963, MW = 120
150			C ₉ -alkane?
163			C ₉ -ketone, C ₉ -cycloalkane
172			Ol real C ₉ -C ₁₁ -cycloalkane
180			C ₉ -C ₁₁ -cycloalkane
193	930/999	Ethylbenzene	
196			C ₈ -C ₁₀ -bicyclo or diene
196	822/990	A dimethylbenzene	
211			C ₃ -C ₁₀ branched alkane
216		Propylcyclohexane	
219	907/969	A dimethylbenzene	But 3-ethoxy-3-methylcyclopentane (912/980)
227	920/990	Nonane	
236	822/972	1-Propenylcyclohexane	Probably not exactly correct
240	902/997	Propylcyclohexane	
254	800/942	Nonanol	May not be exactly correct, a branched C ₉ 812/995, butylcyclopentane also, MW = 126
259	908/994	2,6-Dimethylcane	MW = 142
263	902/983	3-Ethyl-2-methylheptane	MW = 142
274			F = 975 for octa-10-iodene and 935 for 1,9-nonadiol P = 700
278	936/990	Propylbenzene	
283			Alkane
290	888/996	An ethylmethylbenzene	
299		A trimethylbenzene	Plus an alkane
304	803/940	2-(Methylbutyl)cyclopentane	Or similar
309	941/971	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	886/998	A trimethylbenzene	
341	F = 956	Phenol	
345			C ₁₀ -Alkene, MW = 140, 97/11/69/56
356	956/999	Decane	MW = 142
361			Aromatic trace C ₆ -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	2,7-Dimethylnonane	
420	757/971	1-Methyl-4-(2-methylethenyl)-trans-cyclohexane	477 counts
427	885/995	A methylpropylbenzene	
433		2-Methylpropylbenzene	
438	858/994	A dimethylstyrene	
446		A C ₉ -alkylbenzene	Methylpropylphenol, etc., F = 973 plus 122 + 87/100
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	1 large 132/148 and 152 at 530 (F = 949 for 3,5,5-trimethylbicyclo[4.1.0]heptan-2-one) Or a dimethyldecane, etc.
537	739/945	A methylundecane	
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 ₉ -alkylbenzene	Plus 1 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 148/119?
601	F = 917	4-Methylundecane	Plus 1 105
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
339	001/995	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	061/993	2-Methylnaphthalene	
808	908/971	1-Methylnaphthalene	
884		Tridecane	
883	025/970	1,2,3,4-Tetrahydrodimethylnaphthalene	
885	F = 897	2,3-Dihydro-1,1,5-trimethyl-1H-indene	Mixture
884	772/928	6-Ethyl-1,2,3,4-tetrahydronaphthalene	Perhaps it is an isomer of this compound
890		See 844	Plus a component with predominant ions at 82/83
896			
866	002/990	An ethyl-1,2,3,4-tetrahydronaphthalene	
875			Mixture
884	F = 931	1,2,3,4,5-Hexahydronaphthalene	Mixture
896	032/991	1,1'-Biphenyl	
906		An alkane	
911	F = 985	2-Ethylmethylphenol	Plus a tetrahydrodimethylnaphthalene
924	020/926	A dimethylnaphthalene	
933	019/984	Biphenyl ether	
939	074/968	Tetradecane	
943	984/995	A dimethylnaphthalene	
947	F = 978	A dimethylnaphthalene	Mixture
954		A tetrahydrotetramethylnaphthalene?	Mixture; trace
965	718/992	A tetrahydrodimethylnaphthalene	
977		Alkane	Mixture
988	003/974	2-Isopropylmethylphenol	
998		Alkane	Mixture
1003	F = 850	A dihydrotetramethylnaphthalene	Mixture
1016	F = 987	1,2-Dihydronaphthalene	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 isopropylmethylphenol	
1056	097/996	Benzofuran	
1062		Pentadecane	
1071	F = 949	A trimethylnaphthalene	
1076		An isopropylmethylphenol	Possibly a trimethylnaphthalene
1084	747/937	A dihydrotetramethylnaphthalene	
1090	F = 980	An n-butyl- or isobutylnaphthalene	
1098	053/971	A trimethylnaphthalene	Perhaps 2,3,6- or 1,6,7-
1113			Mixture: 178/155; 188; 185; 32/83

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	
1178		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		Eicosane	

^aBecause 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.

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

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

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
19		Dichloromethane	
21		Benzene	
25		Toluene	Added solvent
120		Mesitylene	1,3,5-Trimethylbenzene, added internal standard
270	005/990	2,3-Dihydro-methyl-1H-indene	
290	036/007	See 270	A methylpropenylbenzene is also possible
363	007/052	1,2,3,4-Tetrahydronaphthalene	(tetralin)
327	959/099	Naphthalene	
330	F = 97%	2,3-Dihydrodimethyl-1H-indene	Plus something else, ion at 130
342	703/005	A tetrahydromethylnaphthalene?	Major ions at 117/131/146 do not match ratios of standards
340	906/900	2,3-Dihydrodimethyl-1H-indene	
362		Alkane	
367	009/997	1,2,3,4-Tetrahydro-2-methylnaphthalene	
370	096/993	1,2,3,4-Tetrahydro-1-methylnaphthalene	
304	008/929	A butenyldimethylbenzene?	
392		Possibly another isomer of 367	
399	750/903	o-Isopropyl-m-methylstyrene	A tetrahydro-methylnaphthalene is also possible
410	047/937	2,3-Dihydro-1,3-dimethyl-1H-indene	Or another isomer
425	077/925	1,2,3,4-Tetrahydro-5-methylnaphthalene	Possibly the 6-methyl isomer
445		A tetrahydro-C ₂ -alkylnaphthalene?	Ions at 160/145 (100)/131/113
450		See 445	Ions at 160/145/131 (100)/113
463	049/900	2-Methylnaphthalene	Plus a tetrahydromethylnaphthalene
469	709/943	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	099/976	1-Methylnaphthalene	
489		An alkane	
495	704/941	1,2,3,4-Tetrahydro-2,6-dimethylnaphthalene	Major ion at 117 does not fit
511		An alkane	Mixture, PAM, 6 components
533		Heptylcyclohexane?	Ions at 182 (4%), 145 (6%), 111 (4%), 83 (100), 62 (7%), 67 (15%), 55 (57%)
539	775/941	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	
626		An alkane	

^a Because 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 24 and 35. Comparisons with Table 32 can be made.

^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 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
4-Hydroxymethylbenzene	202	Presently in use
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	

^aAldrich 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	
N-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), all 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 ₉ -alkylphenol.
An ethylmethyl- or isopropylphenol	860/980	410	
A C ₉ -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 = 258-258°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
78	869/945	Benzenamine	(Aniline). Ion at 187 (68) also present.
145	945/960	A dimethylpyridine	
151	800/800	A trimethylpyridine	
169	890/905	A trimethylpyridine	Or an ethylmethylpyridine
174	885/918	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	941/981	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 -ethylpyridine 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 (64%), 131 (67), 130 (12), 118 (100), 117 (36).
303	864/986	N-Ethylbenzenamine	
315		A trimethylpyridine	Possibly a mixture with an ethylmethylpyridine (838/907).
321		A dimethylaniline	
324		A dimethyl- or ethylaniline	
327		A C ₃ -alkylpyrazine?	122 (76%), 212 (10), 120 (12), 107 (100). Some C ₂ -alkylphenols produce similar spectra. Naphthalene is also present (about 25%).
335		See 327	
351		A C ₃ -ethylpyridine?	Also ions at 146 and 160.
354		See 327	122 (35%), 121 (100), 120 (46), 107 (30), 106 (64) plus a dimethyl-2,3-dihydro-1H-indole: 147 (7%), 146 (8), 142 (12).
358		Unknown. M _r = 1197	119 (17%), 118 (36), 117 (100), 116 (6.6), 98 (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	861/952	3-Methyl-5-propylpyridine	
414	867/961	N-Ethyl-2-methylaniline	Plus 3-ethyl-5-methylphenol (872/936).
472	745/842	N-Ethyl-2-methylbenzenamine	Or similar.

Table 31 (Continued)

Scan no.	Library search result ^a	Compound	Comments
429	F = 565	1,2,3,4-Tetrahydro-5(or 6)-methylnaphthalene	Plus something producing large ion at 120.
438		Unknown	136 (64%), 121 (6%), 108 (31), 107 (100), 106 (12), 91 (9.4), 77 (26). A methylpropylpyrazine? See 414.
461	961/975	1-Methylnaphthalene	
471	931/990	3H-Indole	
481		2-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 = 891	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	

^a Because 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.

^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. Small peaks containing multiple components were ignored in many cases for this listing.

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) Methyl ethylphenol (b) Tetrahydroquinoline (?) $C_9H_{11}N$ (c) Quinoline	231.40
2	Methyl ethylphenol	23.02
3	(a) Isoquinoline, 108 (b) p-N-Propylphenol	470.37
4	Trimethylphenol	
5	Methyl-n-propyl or n-butylphenol	
6	Methyl ethylphenol	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	943/950	A trimethylpyridine	
203	916/930	A trimethylpyridine	
210	885/990	A methylaniline	(Methylbenzenamine). Not N-substituted.
216	978/985	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.
261		A methyl-2,3-dihydro-1H-indole	135 (55%), 132 (71), 130 (17), 118 (130), 117 (35). Note the high reproducibility between this background subtracted spectrum and the one in Table 31.
235		A C ₄ -alkylpyridine?	
237		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.
311		An ethylmethylpyridine and a trimethylpyridine	Large ions at both M - 1 and M - 15 indicate a probable mixture. Perhaps there is a single isomer or one of 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.
324	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 (35%) 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 vinyllaniline 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	957/1080	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 ₃ -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-butylnaphthalene.
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	350/990	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-Butylnaphthalene	
859		N-Hexadecane	
868	F = 391	4-Methyldibenzofuran	Plus N-phenylbenzenamine (F = 910).
914		An alkane	
931		An alkane	
972		N-Heptadecane	
978		An alkane	
1020	865/512	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 Saturated/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
786	714/874	A dimethyl-biphenyl	Ions at 182, 178, 167, and 165
793	810/988	2-Ethyl-1,1'-biphenyl	Plus a 1-methylbutyl or methylbutylnaphthalene, MW = 198, loss of C ₂ H ₄ produced the base ion
798		3-Pentylnaphthylene	Plus another component
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		Anthracene	
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 = 312	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 = 220 and 230 components
1057	793/552	A methylphenanthrene	Plus MW = 224 trace, ion at 204
1062	F = 879	A methylphenanthrene	Plus MW = 224 trace, ions at 210 and 204
1080	860/379	Nonacene	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/E3
1135		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	

^a Because 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.

^b See Table 1E, 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.

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 13
Total Ion Chromatogram of Nitrogen Bases

GC Chromatogram of Pheno's

Figure 15
GC Chromatogram of Nitrogen Bases

Figure 16
Functional Group Distribution

Figure 17
GC/MS Total Ion Chromatogram of the Organic Fraction
of a Condensate

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 28
GC/MS Total Ion Chromatogram of Saturated/Aromatic
Fraction of 560-650°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)

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2. DEVELOPMENT OF METHODS TO CHARACTERIZE SOLVENTS

SUMMARY

ICRC has analyzed a series of five recycle solvents from the Wilsonville Pilot Plant in order to develop a relationship between Wilsonville's microautoclave solvent-quality test and the molecular composition of the solvent. Slurry solvents were collected at Wilsonville at material-balance periods, analyzed for solvent quality, flushed with nitrogen, and shipped to ICRC laboratories.

A comprehensive analytical protocol, which included elemental analysis, near-infrared analysis, simulated distillation, gas chromatography, mass spectrometry, and proton and carbon magnetic resonance, was used to define the chemical composition of each solvent. Results for the limited samples tested indicate that gas chromatographic determination of the total content of two-, three-, and four-ring polynuclear aromatic compounds, which can be transformed rapidly into hydroaromatics under liquefaction conditions, correlates best with the Wilsonville solvent-quality test.

To expand the data base, a set of 12 slurry solvents recently analyzed by Conoco Coal Development Company was also compared. Conoco conducted their own microautoclave test and proton magnetic resonance analysis on each sample. It was determined that the "standard coal" used by Wilsonville for microautoclave testing differs significantly from the "standard coal" used by Conoco. The Wilsonville coal sample contained substantially more sulfate sulfur and 50% less pyrite sulfur (0.77 vs. 1.5%) than the Conoco sample. Conoco's microautoclave results, on identical solvent samples, are 8-12% (absolute) higher than Wilsonville's.

Correlating the Conoco and Wilsonville results showed that the microautoclave tests have lower limits of sensitivity. For example, the Wilsonville test appears to be nonresponsive to any data correlation when the amount of tetrahydrofuran solubles (microautoclave test results) is less than 68%. Conoco data show a similar nonresponsive-

ness, but below a value of 78. It is believed that the difference is due, in part, to the use of a more active (less oxidized) coal by Conoco.

The data from this work suggest that hydrogen is transferred in several ways during the microautoclave tests. Some hydrogen from the solvent is immediately available in the proper form for transfer (possibly as α -hydrogen on hydroaromatic compounds). Additionally, the two-, three-, and four-ring aromatic compounds in the solvent are able to shuttle labile hydrogen from portions of the coal structure to free-radical sites. Although hydrogen is not present during the microautoclave test, in an actual SRC-I dissolver the interconversion from aromatics to hydroaromatics can be continued if the partial pressure of hydrogen is sufficient ($>1,500$ psi). Conoco's NMR data and the subject gas chromatography data on Wilsonville samples independently show a relationship between the aromatic content of the solvent and the microautoclave test results, above the sensitivity level.

The analytical data and the solvent-quality results were correlated to the process conditions of Wilsonville runs 225-235. Major changes in solvent composition of sample 8, for example, which had the highest aromatic content, could be related to the addition of anthracene oil and light solvent-refined coal (LSRC) and lower operating temperatures prior to sampling the solvent.

ANALYSIS OF FIVE RECYCLE SOLVENTS FROM WILSONVILLE

This program is planned to determine if there is a meaningful relationship between the composition of slurry recycle solvent and the analytical results generated by the short microautoclave test (Appendix V-A) used at Wilsonville Pilot Plant to measure solvent quality. The objective of the program is to characterize in detail the chemical compounds in the process solvents and then to correlate the molecular composition with the solvent-quality test. The resulting data base also will be used to relate the solvent-quality test to pilot-plant process conditions.

ICRC has been examining slurry solvents collected during material-balance periods at Wilsonville. Each 100-mL sample was collected from vessel V131A (process solvent product), flushed with dry nitrogen, and shipped to ICRC for analysis. Samples were then subjected to elemental analysis (C, H, O, N, S), near-infrared analysis (OH/NH/NH₂), simulated distillation by the Wilsonville method, gas chromatography/mass spectrometry, and proton (¹H) and carbon (¹³C) magnetic resonance. Details of these analytical procedures are provided in the Experimental Section.

The first set of five slurry solvents from runs 232, 233, and 234 was selected to represent a range of solvent qualities (64-75) that spanned process changes observed from July to September 1981. Figures 1-3 plot the daily solvent-quality results from runs 232, 233, and 234, respectively. The solid line represents the average value of the solvent quality for each run. Experimental error in each measurement is ± 2 units, based on duplicate analysis of random samples. Figure 4 combines all data points, showing the variation in solvent quality over three months from a single coal (Kentucky Fies #9) processed under nearly the same conditions.

Experimental Section

Solvent quality was measured at Wilsonville by the short microautoclave test (see Appendix V-A). Air Products and Chemicals, Inc. performed the remaining analyses.

Elemental Analysis. Air Products used the following instruments: a Perkin-Elmer 240 automated analyzer for carbon, hydrogen, and nitrogen; a LECO SC-132 analyzer with an infrared detector for sulfur; and a Coulometrics, Inc. oxygen analyzer for organic oxygen.

Near Infrared. A Beckman 5270 spectrophotometer was used to determine OH/NH/NH₂ absorption bands. Weight percent measurements were based upon comparison to the standard absorption of β -naphthol, carbazole, and naphthalamine.

Simulated Distillation by Gas Chromatography. The Wilsonville method of simulated distillation by gas chromatography (GC) was used to determine boiling-point distribution. This method, which uses aromatic compounds to calibrate boiling point with retention time and response

factors to quantify the weight-percent distribution, was used to analyze each sample. The initial and final boiling points were measured at 0.5 and 99.5 wt %, respectively. Calculations for simulated distillation are based on a program that was derived by Kingsley and Schweighardt (1981) to duplicate Wilsonville results of weight percent vs. degrees Fahrenheit. Laboratory-determined retention times were used to assign distillate fractions (e.g., 550-650°F) and response factors were used to relate area percent to weight percent.

GC profiles of molecular composition were obtained with a Perkin-Elmer 3920 gas chromatograph under the following conditions: 15-m SE-52 column; flame ionization detector (FID); He carrier gas at flow rate of 2.2 cm³/min; 250°C injector temperature; 275°C detector temperature; detector range, X1; 30-cm³/min makeup gas flow rate; column temperature raised from 50 to 250°C at 4°C/min.

Capillary Gas Chromatography. Capillary GC was used to separate three major compound types: naphthalenes, phenanthrenes, and pyrenes. Each includes as many alkyl (C₁, C₂, etc.) substituents as could be identified. The total area counts for each compound type were summed without regard to GC response factors. A relative measure of the two-, three-, and four-ring aromatic compounds is valid with an error of ±0.5% for the sum of the compounds. From the resulting chromatogram, 20-50 compounds were identified by matching retention time and/or mass spectrometry fragmentation patterns, with a Finnigan 4000 gas chromatograph/mass spectrometer. Major compounds identified are listed in Table 1.

Nuclear Magnetic Resonance. A Bruker WP-200 superconducting nuclear magnetic resonance (NMR) spectrometer was used to determine proton (¹H) and carbon (¹³C) distribution. To quantify the ratio of condensed aromatic hydrogens (those on naphthalene and phenanthrene) to noncondensed hydrogens (on benzene rings), we used a modification of F. Burke's method (Conoco) (Burke and Winschel, 1982).

The ¹H NMR spectrum was divided into seven sections, as proposed by Burke. The ratio of aromatic hydrogens between 6 and 7.15 ppm (defined as noncondensed aromatics, one-ring) to aromatic hydrogens between 7.15 and 10.5 ppm (defined as condensed aromatics, e.g., phenanthrene-like) is given in Table 2. Conoco uses the ratio of condensed to noncondensed hydrogens to measure solvent quality.

The proton chemical-shift region from 2 to 3.5 ppm is assigned to the benzylic hydrogens, those aliphatic hydrogens on carbon atoms attached directly to aromatic rings. Benzylic hydrogens are the hydroaromatic protons believed to be hydrogen donors in coal liquefaction. This chemical-shift region also contains protons that may not donate, such as bridgehead hydrogens in acenaphthene, or methyl protons from substituted aromatics. Because these nondonor protons are difficult to distinguish, they are combined with the hydroaromatic protons. However, we have included an accounting of these benzylic hydrogens as an additional guide for following the hydrogen distribution of recycle solvents, not as an independent measure of solvent activity. The absolute weight percents of benzylic hydrogens for each recycle solvent are listed in Table 2.

The ^{13}C NMR spectrum was obtained by adding ~1% Cr(AcAc) to aid the spin/spin (T_1) relaxation process, allowing data to be collected in 12 rather than 60 hr. The total aromatic and aliphatic ^{13}C envelopes were integrated to quantify the percent of aromatic carbons, f_a . The f_a value represents the absolute percent of carbon atoms in aromatic rings with a precision of $\pm 1\%$.

Results and Discussion

Analytical results for the five Wilsonville recycle solvents are provided in Table 2. Wilsonville generated the solvent-quality data on the identical sample lot received by ICRC. Data are presented under the assumption that the Wilsonville solvent-quality values do rank each solvent (± 2) and, therefore, provide the base line for comparison in this report.

Elemental Analysis. Elemental analysis did not reveal any relationship between solvent quality and hydrogen or heteroatom (oxygen, nitrogen, and sulfur) content. In Table 2 the entry for oxygen as hydroxyl represents the weight percent of oxygen that can be considered as hydroxyl in the original sample. For example, in Wilsonville run 232A, 54% of the total oxygen (3.38 wt %) was determined by near-infrared analysis to be hydroxyl. The remaining 46% oxygen is in ether (-O-) linkages such as those in dibenzofuran. With these few data

points, a trend that relates hydroxyl content to solvent quality is not apparent.

Nuclear Magnetic Resonance. Nuclear magnetic resonance data on hydrogen distribution are scattered and do not confirm previous observations that the amount of hydrogens α to aromatic rings (benzylic hydrogens) correlate to Wilsonville solvent quality. Figure 5 shows the ^1H NMR spectra of the "best" (WV-232A) and "worst" (WV-234C) solvents in the set of five samples. The value of the ratio of condensed/noncondensed aromatic protons, used by Conoco as a measure of solvent quality, does not appear to correlate with Wilsonville solvent quality over the range of values studied here. Independently relating the NMR data for the recycle solvents to process conditions is still under consideration.

Figure 6 graphs the ^{13}C NMR spectra for the same solvents (WV-232A and WV-234C). We found a difference in the percent of aromatic carbons: 61 vs. 57. Solvent 232A has more multi-ring (chemical shift > 140 ppm) components than solvent 234C. The range of aromatic carbon for all five samples is not very great, considering an experimental error of $\pm 1.0\%$.

In the SRC-I process at Wilsonville, solvents are hydrogenated in situ. Thus, hydroaromatic sites (benzylic, α -hydrogen) may be depleted (by shuttling of active hydrogen) by the time the solvent either reaches the holding tank (V131A) or is mixed with more aromatic material (such as LSRC) in tank V131B before blending with the feed coal. This is an important factor, because Wilsonville uses the slurry solvent from either V131A or V131B to evaluate solvent quality.

The SRC-I process slurry solvent should be highly aromatic, not hydroaromatic. As the solvent enters the process with coal, pyrite, and hydrogen, the active aromatic sites take on hydrogen, become hydroaromatics, and quickly shuttle active hydrogen to thermally generated free-radical sites. Depending upon process conditions, coal composition, and other still undefined variables, the solvent may be able to generate some new hydroaromatic sites before being distilled out to the V131A and V131B tanks. However, the most active hydrogens are being depleted to yield an aromatic-based solvent. Consequently, we are now looking for the largest population of "potential hydroaromatics," rather than the absolute quantity of hydroaromatics. Such potential hydro-

aromatics may or may not need gaseous hydrogen as a source of transferable hydrogen in order to be transformed into hydroaromatics. It seems reasonable that gaseous hydrogen will foster this transfer at the "proper" hydrogen concentration. Neavel (1976) has pointed out that bituminous coal contains enough active hydrogen to liquefy the entire coal; however, the hydrogen is not distributed properly.

Gas Chromatography/Mass Spectrometry. The preceding observation led us to investigate the molecular distribution of each solvent by capillary gas chromatography and to identify unknown components by mass spectrometry. Figure 7 illustrates the capillary chromatogram of the "best" and "worst" solvents identified by the Wilsonville microautoclave test. At first inspection, we observed differences between the relative peak heights of the 20 components identified. Peak 6, 2-methylnaphthalene, was assigned the same amplitude in each profile. From the chromatograms, we selected three major compound classes--two-ring (naphthalene), three-ring (phenanthrenes), and four-ring (pyrenes) aromatics--and as many alkyl substituents as could be identified.

The total gas chromatographic area counts for each compound class were summed to provide the distribution found in Table 2. The relative percentage of the individual compound classes and the sum of all classes can be related to the Wilsonville solvent-quality value. The error in the total area measurement is $\pm 0.5\%$. Although each value for the sum of components is just outside that of the reported error limits (95% confidence), a consistent trend, which is reproducible for duplicate analyses, is observed. The "best" solvent has the most aromatics (19.2%), and the "worst" solvent has the least aromatics (17.3%).

Of all the analytical procedures tested, the GC analysis that measures the total content of the specifically selected aromatic compounds, which have the potential to become hydroaromatics, provides the best correlation with Wilsonville's solvent-quality results.

ANALYSIS OF WILSONVILLE SLURRY SOLVENTS BY CONOCO

Comparison of Microautoclave Test Results

Recently, F. P. Burke and R. A. Winschel of Conoco Coal Development Company analyzed a series of Wilsonville recycle solvents that were

generated between January 15 and September 9, 1981 (see Burke and Winschel, 1982). Wilsonville's short microautoclave test results and process-unit performance revealed that the solvent degraded during this period. Therefore, Conoco applied NMR techniques and their own version of both short (kinetic) and long (equilibrium) microautoclave tests to relate chemical composition of the slurry and process variables to the apparent decrease in solvent quality.

To supplement our data base, we examined Conoco's results on 12 slurry solvents (Table 3). Table 4 lists the Wilsonville process conditions at the time the samples were obtained.

First, we compared Conoco's short (kinetic) microautoclave test results with those obtained by Wilsonville (Figure 8). Sample bomb preparation, reaction conditions, and work-up methods in both tests are nearly identical. However, we did note one major difference--the coals that were used. Conoco uses a fresh batch of "standard" Indiana V coal, Old Ben #1 Mine, whereas Wilsonville uses coal that is more than 3 years old, which was packed in ~1-lb lots in plastic bags and stored in a drum. Our proximate and ultimate analyses of the coals used (Table 5) revealed that Wilsonville's "standard" coal has 50% less pyritic sulfur, substantially more sulfate sulfur (which indicates aging), 50% more oxygen, and a lower Btu value than Conoco's coal.

Figure 8 reveals that Wilsonville's microautoclave results (percent of tetrahydrofuran solubles) are 6-12% (on an absolute basis) lower than Conoco's results. The results do not show a 1:1 relationship, but the data points do inflect upward, above 78 for Conoco and above 69 for Wilsonville. This change in slope may indicate the range of sensitivity of the short microautoclave test.

A comparison of Conoco's short (kinetic) and long (equilibrium) microautoclave tests, which are both carried out in the absence of gaseous hydrogen, provides only a scatter of data points without any quantitative relationship (Figure 9).

Next we attempted to correlate Conoco's NMR data on aromatic content with the kinetic (short) microautoclave test results (Figure 10). We found a trend that suggests the weight percent of total aromatics does affect the microautoclave test results: solvent quality increases as weight percent aromatics increases. These data tentatively confirm

the relationship between microautoclave results and type of aromatic compounds determined by gas chromatography, which we discussed earlier in this report.

We speculate that the weight percent of pyritic sulfur in the feed coal may affect the ultimate composition of the solvent and, hence, the solvent quality. After plotting the weight percent aromatics in the solvent against the pyritic sulfur content of the coal (Figure 11), we observed a curve that sloped positively with increasing pyrite content. Sample point #2 is off the curve, which is attributable to process conditions (see following section). Plotting pyrite concentration directly with the kinetic solvent quality (Figure 12) reveals that, above a Conoco kinetic test value of 78, the "solvent quality" appears to increase as pyrite content increases.

Process Description of Wilsonville Runs

The preceding results are not based on a detailed examination of the process conditions at Wilsonville from January to September 1981. The pilot-plant runs from which the samples were obtained are described below.

Run 225, from January 11, 1981 to February 17, 1981, evaluated hydrogenated anthracene oil as a start-up solvent under demonstration-plant conditions. Interruptions occurred on January 16, January 17-20, and January 26.

Run 227, from March 21 to May 18, tested the new V-103 high-pressure separator at demonstration-plant conditions. Interruptions included: March 22, ~500 lb of solvent lost; March 21-22, leaks were repaired; May 2, temperature in vacuum column T-102 deviated. From May 8 to 18, the temperature of the high-pressure separator was increased from 740-780 to 780-815°F.

During run 228, May 18 to June 1, the dissolver temperature was decreased from ~840 to ~825°F. To build up solvent inventory, 136 lb/hr of LSRC from the critical solvent deashing unit was added to the coal slurry from May 20 to 26, after which the LSRC addition rate was decreased back to the usual 60 lb/hr.

During run 229, June 1-20, the dissolver was operated at a higher pressure (2,300 instead of 2,100 psig). Interruptions occurred from June 1 to 19.

During August 14 to September 12, the plant was operated at low-severity conditions, namely, 35-lb/hr-ft³ space velocity, 750°F dissolver outlet temperature, 690°F V-103 temperature. One interruption occurred on August 19.

From the description of the Wilsonville runs, sample 64294 (#8) and 64044 (#6) from run 225 were generated from hydrotreated anthracene oil. Sample #6 (with Fies #9 coal) had 32 days on-stream; sample #8, which was on-stream less than 4 days, should be considered a nonrepresentative slurry solvent. Sample 68077 (#11), run 227, was obtained when a short increase in vacuum column (T-102) distillation temperature caused a greater than normal bottoms (>650°F) content to be recycled. Conoco's NMR data showed that sample #11 had the highest ratio of cyclic to alkyl protons. However, comparison of sample #11 with the other solvents indicates that the added bottoms content did not significantly affect the test results. The only other sample that affected test results is 68765 (#2) from run 228. During this run, dissolver temperature decreased from -840 to 825°F, and twice the normal amount of LSRC (136 lb/hr) was added to the coal slurry. All of our data confirm that sample #2 was adversely affected by process conditions.

CONCLUSIONS

A comprehensive analysis of a series of five recycle solvents from Wilsonville runs 232-234 indicates that the total content (identified by GC) of two-, three-, and four-ring polynuclear aromatic compounds, which can rapidly become hydroaromatics under liquefaction conditions, best correlates with the Wilsonville microautoclave result for the limited samples tested.

A comparison of 12 slurry solvents recently analyzed by Conoco Coal Development Company revealed that the "standard coal" used by Wilsonville for the short microautoclave test differs significantly from the

"standard coal" used by Conoco for the same test. Wilsonville's coal contained substantially more sulfate sulfur and one-half the pyrite sulfur (0.77 vs. 1.5). Conoco's microautoclave results are 8-12% (absolute) higher than Wilsonville's for identical solvent samples. Correlating the Conoco and Wilsonville results showed that both tests had lower limits of sensitivity. The Wilsonville test appears to be nonresponsive to any data correlation when the tetrahydrofuran solubles (microautoclave test results) are less than 68; Conoco data show a similar nonresponsiveness, but below a value of 78. We believe the difference is due, in part, to the more active (less oxidized) coal used by Conoco for the microautoclave test.

The data suggest that hydrogen is transferred in several ways during the microautoclave tests. Some hydrogen from the solvent is immediately available in the proper form for transfer (possibly as α -hydrogen on hydroaromatic compounds). Additionally, the two-, three-, and four-ring aromatic compounds in the solvent are able to shuttle labile hydrogen from portions of the coal structures to free-radical sites. Although hydrogen is not present during the microautoclave test, in an actual SRC-I dissolver the interconversion from aromatics to hydroaromatics can be continued if the partial pressure of hydrogen is sufficient (>1,500 psi). Conoco's NMR data and our gas chromatographic data on Wilsonville samples independently show a relationship between the aromatic content of the solvent and the microautoclave test results, above the sensitivity level.

When the analytical data and the solvent-quality results were correlated to the process conditions of runs 225-235, it was found that major changes in solvent composition (e.g., sample 8 had the highest aromatic content) could be related to the addition of anthracene oil and LSRC and to lower operating temperatures prior to sampling.

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- Neavel, R. C. 1976. Fuel 55:237.

Table 1

Compounds Identified by
Gas Chromatography/Mass Spectrometry

Cresols	Dibenzofuran
Tetralin	Fluorozene
Naphthalene	9,10-Dihydrophenanthrene
A methyltetralin	Dibenzothiophene
An ethylmethylphenol	Phenanthrene
2-Methylnaphthalene	Anthracene
1-Methylnaphthalene	Methylphenanthrenes
Dimethylnaphthalenes	Fluoranthene
Acenaphthene	Pyrene
A propylnaphthalene	n-Pentacosane

Table 2

Wilsonville Recycle Solvents
Analytical Data^a

WV run no.	232A	234A	233B	234D	234C
WV sample no.	71322	73283	72147	74267	74237
APCI no.	82-0229	82-0231	82-0230	82-0233	82-0232
WV solvent quality	71	70	67	63	63
Elemental analysis (wt %, as received ± 0.1)					
C	87.4	86.7	86.7	86.7	86.6
H	8.7	9.1	8.9	9.1	9.1
O	3.4	3.4	3.5	3.4	3.4
N	0.7	0.7	0.7	0.5	0.6
S	0.6	0.7	0.6	0.7	0.6
H/C	1.199	1.256	1.237	1.264	1.260
O as OH (% ± 2)	54	51	55	58	58
NMR data					
¹ H aro., cond./uncond., ± 0.2	1.8	2.5	1.7	1.9	1.3
Wt % H α to aro. ring	2.6	2.9	2.8	2.9	2.9
¹³ C f _a , % ± 1.0	61	67	58	57	57
Gas chromatography					
IBP ($^{\circ}$ F at 0.5%)	360	372	356	383	390
FBP ($^{\circ}$ F at 99.5%)	928	850	938	928	915
<550 $^{\circ}$ F (wt %, ± 1.0)	30.9	49.23	34.3	46.3	33.4
550-750 $^{\circ}$ F (wt %, ± 1.0)	41.8	42.5	42.42	42.7	44.4
750-850 $^{\circ}$ F (wt %, ± 1.0)	17.8	8.25	18.7	8.9	19.6
>850 $^{\circ}$ F (wt %, ± 1.0)	9.42	0	4.35	2.1	2.70
% naphthalene, C ₁ + C ₂	11.9	11.2	11.2	10.8	10.8
% phenanthrene, C ₁	6.6	5.8	5.9	5.9	5.8
% pyrene	0.7	0.6	0.7	0.6	0.6
Σ of all components, ± 0.5	19.2	17.6	17.8	17.3	17.2

^aAbbreviations: WV, Wilsonville; APCI, Air Products and Chemicals, Inc.; IBP and FBP, initial and final boiling points.

Table 3

Summary of Sample Codes and Wilsonville Run Numbers

Sample code	Wilsonville sample no.	Wilsonville run no.	1981 run date
1	70476	229	June 18
2	69765	228	May 30
3	74037	234	Sept 9
4	72308	234	Aug 16
5	69000	227	May 18
6	66044	225	Feb 15
7	67454	227	April 19
8	64294	225	Jan 15
9	66362	227	Mar 27
10	67913	227	April 29
11	68077	227	May 2
12	67755	227	April 26

Table 4
Process Conditions during Wilsonville Runs

	Sample no.							
	64294	66044	67454	69000	69765	70476	72308	74057
Run (Fies #9 coal)	225	225	327	227	228	229	234	234
Period	Start	End	Middle	End	End	End	Start	End
Date	Jan 15	Feb 15	April 19	May 18	May 30	June 18	Aug 16	Sept 9
Cumulative days on recycle	4	32	59	86	99	115	153	176
Pressure (psig)	2,100	2,100	2,100	2,100	2,100	2,300	2,100	2,100
Temperature (°F)	840	840	840	840	825	825	785	785
High-pressure sep vessel	Old	Old	New	New	New	New	New	New
Coal pyritic S (%)	1.37	1.25	-	1.20	1.48	1.03	0.72	0.72
LSRC recycle (lb/hr)	60	60	60	60	60	60	252	252
Solvent activity (%) (microautoclave test)	80.5	75.6	76.3	76.1	67.6	63.5	73.5	69.2

Table 5

Analysis of Standard Coal
Old Ben #1 Mine, Indiana V Coal

	Wilsonville coal (% MF ^a coal) ^b	Conoco coal (% MF coal) ^c	Conco at ICRC (% MF coal) ^b	
C	68.62	70.80	70.98	71.11
H	4.68	4.95	4.91	4.88
O	12.61	8.58	9.62	9.72
N	1.45	1.49	1.47	1.50
S	4.10	3.64	3.89	3.87
Ash	10.39	10.54	10.84	10.36
SO ₄ -S/Pyr-S	1.06/0.77	0.02/1.45	0.14/1.45	0.14/1.52
	% as received	% as received	% as received	
Moisture	4.20	2.34	2.98	3.05
Volatile matter	35.09	40.59	36.25	35.42
Fixed carbon	50.76	46.78	50.25	51.49
Ash	9.95	10.29	10.52	10.04

^aMF, moisture-free.

^bAnalyzed at ICRC.

^cAnalyzed at Conoco.

Figure 1
Wilsonville Daily Solvent-Quality
(Short Test) Results
Run 232 Fies #9 Coal

Figure 2
 Wilsonville Daily Solvent-Quality
 (Short Test) Results
 Run 233 Fies #9 Coal

Figure 3
Wilsonville Daily Solvent-Quality
(Short Test) Results
Run 234 Fies #9 Coal

Figure 4
Wilsonville Daily Solvent-Quality
(Short Test) Results

Figure 5
 ^1H NMR Spectra of "Best" and
"Worst" Solvents Analyzed

Figure 6
 ^{13}C NMR Spectra of "Best" and
"Worst" Solvents Analyzed

WV-232A

WV-234C

Figure 7
Capillary Chromatograms of "Best"
and "Worst" Solvents

Figure 8
Comparison of Conoco and Wilsonville
Short Solvent-Quality Test Results

Figure 9
Analysis of Wilsonville Recycle Solvents
by Conoco (Short vs. Long Microautoclave Test Results)

Figure 10
Analysis of Wilsonville Recycle Solvents
by Conoco (Short Microautoclave Test Results vs. Aromatic Content)

Figure 11
Analysis of Wilsonville Recycle Solvents by Conoco
(Aromatics Content vs. Pyritic Sulfur Content of Coal)

Figure 12
Analysis of Wilsonville Recycle Solvents by Conoco
(Short Microautoclave Test Results vs. Pyritic Sulfur Content of Coal)

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Appendix V-A

Determination of Solvent or Coal Quality by Microautoclave

SCOPE: This method applies to raw coal and hydrogenated recycle solvent for SRC conversion.

PRINCIPLE: The conversion potential of raw coal or hydrogenated solvent is determined by using a microautoclave under specified conditions.

PROCEDURE:

- A. Weigh (to 0.1 mg) 5 g of a standard coal of known moisture and ash content.
- B. Weigh 10 g of the solvent to be tested into a previously tared autoclave containing a stainless-steel ball bearing.
- C. Transfer coal to autoclave and then seal autoclave.
- D. Attach one end of type-K thermocouple wire to thermowell of autoclave, and the other end of the wire to a potentiometer.
- E. Attach autoclave to drive mechanism.
- F. Turn on the oil to drive mechanism; check operation.
- G. Turn on autoclave; lower autoclave into preheated fluidized sandbath.
- H. By adjusting sandbath, control temperature of autoclave so that $750 \pm 5^\circ\text{F}$ is attained within 90 sec.
- I. Control temperature at $750 \pm 5^\circ\text{F}$ for 30 min.
- J. Remove autoclave from sandbath; immerse immediately in reservoir of cold water to stop reaction and cool microautoclave to room temperature as quickly as possible.
- K. Remove contents of autoclave by washing with tetrahydrofuran (THF) (~600 mL) until THF is clear.
- L. Stir sample and THF washings for 30 min to allow maximum mixing with THF.
- M. Weigh filter paper, record weight, and place paper in steam-jacketed Buchner funnel.
- N. Pour sample into the steam-jacketed Buchner funnel under vacuum and wash with THF until THF washes clear.
- O. Transfer filter paper to heated vacuum desiccator and dry for 1 hr at 110°C .
- P. Allow sample to cool in desiccator for 1 hr.
- Q. Remove filter paper from desiccator, weigh to 0.1 mg, and record weight.
- R. Calculate conversion by using the formula in the calculations section of this procedure.

REAGENTS: Tetrahydrofuran
Desiccant for desiccator
Standard coal of known moisture and ash
1-Methylnaphthalene
1,2,3,4-Tetrahydronaphthalene (tetralin)

Appendix V-A (Continued)

EQUIPMENT:

Microautoclave
 Driving mechanism for microautoclave adjusted to 1,000 rpm and a
 1.5-in. stroke
 Type K thermocouple wire
 Potentiometer
 Fluidized sandbath (Tecam fluidized bath SBL-2)
 Nitrogen source
 Heated vacuum desiccator
 Desiccator
 Steam-jacketed Buchner funnel
 1,000-ml side-arm Erlenmeyer flask
 Rubber vacuum tubing
 3/8-in.-diameter stainless-steel ball bearing
 11-cm quantitative filter paper

CALCULATIONS:

- A. Coal sample size x percent H₂O in coal sample = grams of H₂O
 B. Coal sample size x percent ash in coal sample = grams of ash
 C. Filter paper weight + insolubles - filter paper weight =
 insolubles
 D. Original sample weight - grams of H₂O - grams of ash = grams of
 moisture- and ash-free coal
 E. Percent conversion =

$$\frac{\text{grams of moisture-free coal} - \text{insolubles}}{\text{grams of moisture- and ash-free coal in std.}} \times 100$$

REMARKS:

The procedure outlined above is for use in a long run on the autoclave. A short run consists of using an 8:1 solvent-to-coal ratio. The weight of solvent for a short run is 12 g, and the weight of coal is 1.5 g weighed to 0.1 mg. Raw coals may be tested using this procedure if percent moisture and ash are known. Conversions using this procedure are compared to a curve using concentrations of 0, 5, 10, 25, and 50% tetralin in 1-methylnaphthalene and Indiana V coal standard.

^aStainless-steel ball bearings (3/8-in. diameter) are placed in each of the two autoclaves for mixing. If ball bearings are not placed in the autoclave, mixing will not be sufficient; as a result, the conversion may be lower than normal.

^bTemperatures for the sandbath before the autoclaves are introduced may vary; however, under normal conditions, this temperature should be between 810 and 830°F. Such a temperature range should allow for heat transfer from the sandbath to the autoclave and give the necessary 750 ± 5°F within 90 sec.

3. SOLVENT CHARACTERIZATION METHOD DEVELOPMENT

SUMMARY

A data analysis was performed to determine the relationship between the Wilsonville Solvent Quality test result and SRC liquefaction process parameters. The data base studied covers the years 1979 to 1982, Wilsonville runs 133 to 234. Only process-defined material balance data sets were included to best represent steady-state operation. Each material balance period provided 48 variables from which common process conditions were selected by imposing a range of acceptable deviations from a norm, e.g., a reactor hydrogen pressure of $2,100 \pm 100$ psi.

Data for all variables vs. solvent quality were plotted, and in some cases variables were compared with each other to determine common trends, e.g. gas production vs. hydrogen consumption.

The plotted data produced no discernible trends. Separating the data by coal type (mine location) and identifying common process conditions with coal types still provided no absolute correlations with solvent quality. However, the effect of the weight percent pyrite present in the feed coal produced a consistent trend. A coal containing more than 1.2% pyrite and less than 0.1% sulfate sulfur yielded results in which any one correlation would cluster about a central point. It was observed that, on average, Kentucky Fies and Pyro mine coal and Indiana V coal clustered together, while Kentucky Lafayette and Dotiki mine coals clustered together. These data point clusters for the variables tested were nearly independent of reactor pressure, space rate, and temperature.

One unusual observation of all the data points, independent of process conditions, was that at each change of feed coal, the sum of hydrocarbon and heteroatom gas production was greatest for the first 30 days, after which gas production reached a steady state dependent on process conditions, primarily temperature. It is postulated that this occurrence is related to the fact that on changing feed coals, the solvent of the previous coal was required to slurry the new coal until a

complete solvent composition change occurred, which required about 30 days. Therefore, in this correlation, no data point taken within the first 30 days of a change in feed coal or during the addition of anthracene oil to make up solvent loss was used.

As a consequence of this study, a new solvent quality measurement has been proposed that incorporates the use of the daily solvent and the coal forming the new feed slurry.

INTRODUCTION

"Solvent quality" is a contrived property of solvents used in coal liquefaction, and is important as a guide in expressing the degree of confidence in the conversion of coal to products soluble in strong organic solvents such as tetrahydrofuran or pyridine. For the purposes of this report, solvent quality is defined as the result of the solvent quality microautoclave test (described in Appendix V-B). Solvent quality properties have not been fully quantified. Can total solvent quality be measured, and if so, can it can be controlled by selected changes in process parameters or feedstocks? Over the past 40-50 years, much has been written about the solvents used to prepare coal slurries. This report addresses the relationship between solvent quality and solvent-refined coal (SRC) liquefaction process conditions.

Solvent quality has been used at the Advanced Coal Liquefaction Facility in Wilsonville, Alabama to express confidence in the daily liquefaction processing of coal to make SRC. Originally developed by Conoco Coal Development Company, a microautoclave test has been used to quantify solvent quality at Wilsonville since 1978. This method (Appendix I) defines solvent quality as the weight percent tetrahydrofuran solubles based on weight percent moisture- and ash-free (MAF) coal. Traditionally, the lower range of the solvent quality (<65) warned of potential preheater coking problems. More recently, solvent quality has been used to document the effect of the addition of LSRC to the solvent stream to enhance coal liquefaction and maintain solvent balance.

Over the past 3 years, the Wilsonville plant operation has increased in efficiency, has standardized many of its analytical pro-

cedures, and has installed process control/monitoring devices that permit a more precise material balance. Sufficient operating time on five different coal types under a variety of processing conditions now allows solvent quality to be examined from a new perspective. This study attempts to determine the important independent and dependent variables associated with the solvent refining of coal by relating plant operation to coal feedstock and product slate and correlating the impact to changes in the microautoclave solvent quality test result.

Properties and Characteristics of Coal Liquefaction Solvents

In SRC coal liquefaction, an effective process solvent must be coal-derived to permit continuous plant operation; must be a distillate with a nominal boiling range of 450-850°F; must be able to sustain a 20-40 wt % coal slurry through feed pumps; must rapidly accept coal dissolution products in solution or suspension; must act as a hydrogen donor or shuttling agent for hydrogen transfer under a predominantly free radical mechanism; and must carry the liquefaction product stream through solid/liquid separation processes and ultimately be recycled to continue the process.

The chemical properties of recycle solvents have been well-documented by Whitehurst et al. (1977), Burke et al. (1980), and Neavel (1982). A recycle solvent generated under SRC-I process conditions exhibits a unique molecular composition. The solvent is composed of a highly complex mixture of alkyl (C_1 - C_4)-substituted polynuclear hetero- and hydroaromatic compounds. Gas chromatography-mass spectrometry (GC-MS) data have revealed that almost 60 wt % of the solvent comprises about 40 individual components. A representative list of solvent components is given in Appendix V-C. The remaining 40 wt % may represent hundreds to thousands of individual compounds. The major molecular species (10-25%) are two-ring aromatics or naphthalenes. In the SRC-I process, 0-30 wt % new solvent material is generated on a MAF feed coal basis per pass of the solvent/coal mixture through the reactor. Therefore, the molecular composition would be expected to constantly change, shifting the physical and chemical properties in response to processing conditions and feed slurry composition. At Wilsonville, the virgin

distillate solvent exits the process at vacuum tower T102, trays 3 and 8. The solvent is then held briefly in a small holding tank (V178) from which daily samples are taken for solvent quality testing. More recently, the solvent in V178 (originally V131A) is mixed with LSRC or other product streams in V131B just before recycling back into the process at V101A as a new coal slurry; (see Figure 1 for process flow scheme). The addition of LSRC, a product stream from the critical solvent deasher, to the distillate solvent to generate a process solvent has been made for several reasons. Most important to the overall process is that LSRC will enhance solvent quality by adding high-boiling compounds (Whitehurst et al., 1977), and thereby promote distillate yield to maintain solvent balance. Because the addition of LSRC to the distillate solvent has not been continuous for all coal types, solvent quality values from V131B are not included.

The holding time for the recycle solvent in each of the storage or mixing tanks under normal operation is short. The recycled solvent represents an average 8-hr-period blend before new coal and additives are mixed in, thus normalizing minor process excursions.

Anthracene oil is sometimes added to the system at V178 to maintain solvent balance. Anthracene addition affects the solvent quality result by increasing the value to near 76 from values below 70. If anthracene oil is added to the system, an apparent initial drop in solvent quality (SQ) (~ 5 SQ units) occurs. This decline in activity may be a result of the molecular composition of anthracene oil. Fresh anthracene oil is highly aromatic with minimal alkyl substitution; its principal component is phenanthrene. In the presence of bituminous coal at SRC process conditions, anthracene oil is rapidly hydrogenated (1-10 days). Solvent quality increases if a large volume (>20 vol %) is added to the solvent stream and the original solvent quality is less than 70 ± 2 . If solvent quality is $>77 \pm 2$, the effect is either too slight an increase to be observed or it is dependent on the coal feedstock.

The Role of Solvent in SRC-I Liquefaction

The present understanding is that at temperatures of 200-250°F, bituminous coal, when mixed with solvent, begins to dissolve, but the

larger portion of the coal matrix is still like a particle in suspension. The primary dissolution products are believed to be the small molecules already present and trapped within the coal (Vahrman, 1970). Depending on coal type and rank, these compounds may represent 5-20% of the coal. At Wilsonville, the feed slurry is held at 150-250°F (depending on the percent LSRC added) for 8-12 hr without hydrogen before entering the preheater (B102) under a hydrogen partial pressure. Under these solvent soaking conditions, the recycle solvent must exhibit good dissolving power within the V101A and V101B holding tanks. The recycle solvent can then extract and exchange with the small trapped molecules in coal and fill other voids created by loss of water and swelling. Thermal reactions involving the breaking of scissile bonds to initiate actual coal matrix liquefaction do not occur until ~600°F. Such temperatures are first reached in the preheater (B102) under ~2,000 psi hydrogen pressure. At liquefaction temperatures, it is believed that the nascent free radicals first rapidly combine with labile hydrogen from the feed coal (1-5 min) to form a cresol- (or pyridine-) soluble product (Neavel, 1976). Hydrogenation reactions are exothermic and cause the coal slurry temperature to rise 25-60°F. In the preheater at temperatures of 780°F, the recycle solvent appears to rapidly solvate the primary liquefaction product. As the process slurry stream enters the reactor, the exothermic reaction drives the temperature to near 840°F during a residence time of 30-60 min. Here the original recycle solvent and the new coal product components shuttle hydrogen to free radical sites generated from splitting and cracking reactions at reaction temperature (840°F).

The solvent, which is now modified in molecular composition by the addition of 0-30 wt % MAF-coal cracking and splitting products, can itself be rehydrogenated. This newly available hydrogen can be shuttled to the recently generated active sites formed in reactor R101 to further stabilize the system. The activation energy first proposed by Curran et al. (1967) for the rapid dissolution of coal to form asphaltenes was about 30 kcal/mol, and the activation energy for the slowest liquefaction step (now considered to be asphaltene to oil) was estimated to be ~45 kcal/mol. In comparison, covalent bond dissociation of model 3- and

4-ring polynuclear aromatic carbon-to-carbon bonds may be as low as 65-85 kcal/mole. It was concluded from these apparent activation energies that coal liquefaction is a free radical process. No substantial information to the contrary has yet been published.

The solvent property that is active in shuttling hydrogen to free radical sites has been associated with hydroaromatic content. Other hydrogen transfer species have been documented to be active when hydroaromatic species were absent or depleted, and include the aromatic hydroxyl (e.g., beta-naphthol) and alkyl (methyl) side chains such as those found on 2-methylnaphthalene. Curran et al. (1967) concluded that the liquefaction solvent needs sufficient donatable hydrogen to promote greater distillate yield and reduce coking, and that the hydrogen can come from many sources.

METHODS

Correlation of Solvent Quality to Process Operation

A review of past operating reports from Wilsonville and interviews with Wilsonville staff resulted in a assemblage of 48 primary input parameters that define a pilot plant run under the SRC-I first-stage regime. Appendix V-D lists these variables, defines their abbreviations, and provides the units used in this report. The 57 data points analyzed for these 48 variables span from 1978 (run 133) to 1982 (run 234). Over this period, five major coal types were processed for 3-58 days on stream, per run. Usually one to three data points per run were selected to represent a material balance at nominal steady-state conditions. These material balance points form the data base of this report.

In analyzing these data, it was assumed that each coal type may be viewed independently, and data for each coal type averaged. The reason for this assumption was that the variability in coal reactivity changes the demand on the operating conditions, generates a coal-specific recycle solvent after line out, and promotes a unique product distribution. All coals or similar coal types are combined only when deemed necessary for general comparison purposes. The objective of this study is to relate the microautoclave solvent quality test result to process

factors that cause or are affected by a change in the solvent's role in SRC-I liquefaction.

SRC-I First-Stage Liquefaction Objectives

Understanding the first stage of the SRC-I process has lead to the definition of limits for process operational variables, slurry feed composition, and product stream distribution. A priority listing of these variables has been deduced from a study of the data correlation presented here.

The five objectives of first-stage SRC-I liquefaction are:

1. Maximize conversion of coal to cresol (or pyridine) solubles.
2. Minimum hydrogen consumption based on MAF coal conversion.
3. Maintenance of process solvent in solvent balance and insignificant change in its physical or chemical properties.
4. Minimum hydrocarbon and maximum heteroatom gas production.
5. Minimum preasphaltene content in the vacuum tower (T102) bottoms.

Solvent Quality and Process Data Correlation

Absolute comparisons between solvent quality and process variables are difficult to make because the entire data set (Appendix III) contains only a limited number of material balance periods in which all process variables were maintained constant and only coal type was varied, or in which only a single process variable was changed and coal type and the run line-out period were maintained constant. Judgements are presented in the text concerning the exclusion or inclusion of individual data points in a data subset. The major process variables considered are coal type, dissolver (R101) temperature and pressure, and coal space rate at R101.

Reaction severity, i.e., the degree of coal conversion to distillate and gas, can be assessed in various ways. Yield structure information, such as hydrocarbon and heteroatom gas production (total gas less H_2O) and net hydrogen consumption (measured by both the elemental balance and process methods), provide measures of reaction severity. An

operational goal would be to maximize distillate yield while minimizing gas production and hydrogen consumption and maintaining full plant operation.

Although total gas production may not appear to relate to the physical or chemical properties of the recycle solvent, it is presumed to be affected by "solvent quality." Solvent quality refers to the solvent's ability to shuttle hydrogen to those coal species that have split into large components and prevent hydrocarbon cracking that forms C_1 - C_4 gases. We will only analyze data that share a single dissolver temperature (e.g., 825°F), the same coal type, and have been lined out for long (>20-day) periods so as to best approach steady-state conditions.

The benzene solubles (SRC oils and asphaltenes) of the vacuum tower bottoms (T102) and the total SRC of this same stream may be the best analyzed samples to quantify product (less distillate) distribution. This T102 bottoms stream is process-normalized in that minor process excursions are averaged by the volume and throughput of the tower. Sample site V110 is the most sensitive to process changes, but past sampling problems and the fact that this sample site was abandoned after run 217 makes data correlation difficult.

Process solvent is not yet a measured quantity, but is determined by difference when calculating a material balance from distillation and subsequent gas chromatography results. Process solvent yield is therefore the least accurate parameter and will not be considered for this correlation. The light oils (C_5 -450°), which are streams quantified by gas chromatography data, provide a third measure of liquefaction severity and solvent breakdown independent of total gas production.

Table 1 gives a typical common process parameter listing with the range of values accepted as constant.

These process conditions were used in the following material balances: Pyro coal (160 B-C, 161C, 163A); Lafayette coal (166A-B, 166A-C, 201 ABC); Dotiki coal (202A, 203DE); Fies coal (211B, 212AB); and Indiana V coal (143, 138).

The V131A (V178) solvent quality for the past 4 years as defined in Appendix V-B is compiled and plotted as a function of time and coal type

in Figure 2. Day-to-day variation can be as great as 10 units on the solvent quality scale. As an analytical test, solvent quality may be considered to have a precision of ± 2 .

RESULTS

Total Gas Production

Figure 3 presents the entire data set for total hydrocarbon and heteroatom gas production (MAF coal) vs. solvent quality for all coals. The distribution is clustered at $8 \pm 2\%$ total gas and 75 ± 6 solvent quality. If the data are divided by coal type for Kentucky #9 coals only, the four distributions show individual clusters with a few outlying data points. In Figure 4, the data points are coded to define common dissolver conditions. Only in the Fies Mine coal case is there an apparent shift to greater gas production with higher temperature and pressure. Figure 5 provides a different perspective by presenting the total gas production data set as a function of days on stream. Because all data points are presented, process conditions at times varied more than the accepted limits for any one common preheater/reactor condition. Note that high gas production cycles with each new coal type. This trend is apparently independent of reactor pressure, coal space rate, and nearly independent of temperature (825-840°F).

The trends in gas production are presented as a function of total elemental hydrogen consumption in Figure 6; all data points are presented. If a total gas production range of 5-10% and a hydrogen consumption of 1.5-3% on MAF coal are arbitrarily set as lower and upper limits, the points outside these limits are mainly those from the material balance periods taken within 30 days after a change in coal type for SRC-I processing.

Figure 7 displays trends derived by averaging all gas production data points for each coal type, except those from the first 30 days of each run.

Coal-Type Correlations to Solvent Quality

Average data points for solvent quality and hydrogen consumption are provided in Figure 8 as a function of coal type. The trends of

solvent quality (Figure 8) and gas production (Figure 7) are similar. Feed coal type in the first-stage SRC-I Wilsonville Advanced Coal Liquefaction Facility is an important factor in light of the relationships displayed in Figures 7 and 8. In order to present the remaining data in a meaningful and objective manner we have chosen to relate the solvent quality result at the selected material balance periods to their respective product distribution by coal type. Process operational variables such as preheater temperature, reactor pressure, temperature, and volume will be considered in the discussion.

Dotiki Kentucky #9 Coal. In the processing of Dotiki coal, the major differences in process conditions occurred between Runs 202/203 and 204/206/208. The first set of runs was made at a lower dissolver temperature (825 vs. 840°F) and the coal pyrite content in runs 206B and 208 was less than 1.1%, while in run 203 it was 1.3%.

Figure 9 (a-d) gives the set of solvent quality vs. specific product component plots. The plot of pyrite content vs. solvent quality identifies each point by run/material balance number and may be used as a guide to identify the equivalent run in each of the other figures.

Solvent quality does not appear to affect product yield. The percent pyrite in the feed coal may affect solvent quality: that is, if the percent pyrite is below 1.1 wt %, the solvent quality value deviates from the major distribution cluster. The operating conditions during runs 206 and 207 were upset due to failure of the high-pressure separator. Nearly 70 vol % of the unit was filled with cresol-insoluble material. Run 208 was short-lived and had the highest solvent quality (~70) with lowest (<1.1%) pyrite content. This solvent quality value is unusually high; however, its cause is unknown and only one material balance (MB) sample was taken for this run. Daily solvent quality samples before and after the 208AB MB were between 64 and 66.

Lafayette Kentucky #9 Coal. Runs 163 to 201 were conducted with Lafayette coal. Runs 163, 166, and 201 were at 75% dissolver volume at conditions of 1,700 psi and 825°F; dissolver pressure in runs 167, 168, 171, and 172 increased to 2,100 psi with only 50 vol % of the dissolver in use; and run 190 was performed at 2,100 psi, 825°F, and 75% dissolver volume. The largest volumes of anthracene oil were added to the system between runs 170 and 182. Solvent quality increased from 65 to 75, but

fell to 68 after run 182 and remained there until the next coal type (Dotiki) was used. Figure 10 (a-d) gives the solvent quality relationships for Lafayette coal. (The light oil vs. solvent quality figure provides the run number identification.) Note that most Lafayette feed coals had a pyrite content of less than 1.2 wt %.

Pyro Kentucky #9 Coal. Pyro mine coal was run under dissolver conditions of 1,700 psi and 825°F for runs 151, 159, 160, and 161, and at 2,100 psi and 825°F for run 162. These process conditions are the most constant of the coals tested. Because run 151 was made from Indiana V coal derived solvent and processed 3 months before run 159, it can be eliminated from each solvent quality correlation. Figure 11 (a-d), which gives the relationships between Pyro coal solvent quality and product distribution, shows a range of product yield ($\pm 8\%$), but only a small change in solvent quality (± 2). The range of product distribution is no less than other coal types that experienced solvent quality changes of more than ± 10 from the average.

Fies Kentucky #9 Coal. Fies mine coal was processed under the most varied conditions of all coal types; refer to Appendix III for the exact conditions for any one material balance. Most Fies mine coal was run at a dissolver pressure of 2,100 psi, 840°F temperature, and 75 vol %. All but three feed coals (229A, 229B, 210AB) had a pyrite content below 1.1%. Anthracene oil was added only once, after run 210. Solvent quality was 75 and was not greatly affected. The reason for this is not clear, but the optimum activity of hydrogenated anthracene oil may be $\sim 75 \pm 2$ as measured by the solvent quality test. Solvent quality and product distribution for Fies mine coal are compared in Figure 12 (a-d). In general, only total gas production depicted earlier in Figure 4 shows any apparent correlation between solvent quality and dissolver temperature: lower dissolver temperature and higher solvent quality yield the lowest gas production.

DISCUSSION

Coal-Type Relationship to Solvent Quality

From the analysis of 57 material balance periods over 4 years using five different coal types, one observation repeats itself. Once a coal

type has lined out (30 days on stream) with minimal change to process conditions in the preheater and dissolver, the average solvent quality reaches an apparent steady-state condition, i.e., solvent quality does not change (± 4). Figure 13 plots all daily solvent quality (SQ) results from Figure 2 as a function of coal type with and without LSRC addition. The circle indicates the number average SQ result and the bar represents the range of data points. Figure 14 plots pyrite content against averaged SQ points; extreme data points have been eliminated due to documented process problems. The average pyrite content of Dotiki and Lafayette coals is below 1.2%, while Pyro, Fies, and Indiana V are above 1.2%. Average solvent quality for the coal types falls into two groups: coals with more than 1.2 wt % pyrite have a solvent quality of 72 or greater, while coals with pyrite contents less than 1.2% have a solvent quality of 68 or less.

At this time, it is important to make a comparison between SRC-I liquefaction and other coal liquefaction processes. The SRC-I process apparently has the unique advantage of not changing the nature of solvent, such as in the Exxon Donor Solvent process in which the solvent is catalytically hydrotreated before recycle; in addition, the SRC-I process does not add a catalyst to increase the kinetic rate within the liquefaction process reactor, such as in the H-Coal process, nor does it severely treat recycled distillation tower bottoms to enhance distillate recovery, as in the SRC-II process. From a purely scientific point of view, the SRC-I process demonstrates the effect of coal type, pyrite content, and coal composition on direct liquefaction.

Effect of Solvent Quality on the Attainment of Liquefaction Objectives

As used at Wilsonville, the solvent quality test does not appear to provide an absolute or relative measure of liquefaction behavior, although the test is sensitive to coal type and pyrite content (Schweighardt and Kamzelski, 1982). The solvent is a primary product of the feed coal, and as such, its composition is first controlled by the coal's structure, second by processing conditions, and third by external material addition (LSRC) or control of distillate boiling point distribution.

Once a new steady-state condition is reached and the solvent lined out, it may be the solvent's new properties that allow a different yield distribution to be maintained. Certain generalizations can be made concerning what affects the previously stated five objectives in first-stage SRC-I liquefaction:

1. High Conversion of Coal to Cresol (or Pyridine) Solubles. The selection of specific coal types with low concentrations of nonreactive organic components (2-5%) and 6-10 wt % of well-dispersed mineral matter high in pyrite (1.1-1.5%) appears to contribute most in maintaining the liquefaction product distribution under a set of process conditions.

2. Minimum (1.5-2.5 wt %) Hydrogen Consumption Based on MAF Coal Conversion. Hydrogen consumption is apparently dependent on feed coal type and process severity. Less hydrogen is necessary from the solvent and gas phase when the hydrogen in the feed coal is more labile for free radical capping.

3. Maintenance of Process Solvent in Solvent Balance and Insignificant Change in its Physical or Chemical Properties. The recycle solvent is dependent on the feed coal for its properties and composition. By design, processing conditions affect product yield and to some degree the relative distribution and molecular composition of the solvent. Addition of LSRC, anthracene oil, and coal distillates may be made to maintain solvent balance, but the effect on yield distribution has yet to be proven, particularly if LSRC materials are considered inert additives.

4. Minimum Hydrocarbon and Maximum Heteroatom Gas Production. Gas distribution may also be coal-type dependent. Hydrocarbon gas production can result from cracking reactions of coal fragments from alkyl side chains (C_1 - C_4) generated early in the coal dissolution phase (preheater B102). Higher gas production (>10%) was observed when a new coal type was introduced with the solvent of the previous coal type, independent of its quality, but relative to the reactivity of the new coal type. Heteroatom gas from the organic coal matrix, specifically H_2S , is a desired product if reduction in the total sulfur content of the solid or distillate product is desired. The relative merits of oxygen and nitrogen compound removal in the first stage are not apparent

if solvent recycle retains these compounds to enhance solvent polarity, or if the distillate is to be catalytically hydrotreated.

5. Minimum Preasphaltene Content in the Vacuum Tower (T102)

Bottoms. Data analysis of Wilsonville operations by J. R. O'Leary and C. F. Harris (Air Products, personal communication) indicate that inorganic solids separation within the Critical Solvent Deasher (CSD) is more efficient if the preasphaltene content of the CSD feed is less than ~20%. This condition apparently exists when the feed coal has a pyrite content of ~1.2% or greater and the solvent is at line-out 30 days after a change in coal type.

Based on these statements, a logical approach to defining coal-derived recycle solvent quality is to react samples of the solvent from V178 (T102 trays 3 and 8) or the modified solvent of holding tank V131B (usually containing 0-30 wt % LSRC) in the microautoclave test with the daily tote bin coal. This solvent quality test would involve a daily comparison of the product distribution, residue, preasphaltenes, and total benzene solubles with the product distribution derived from a well-maintained standard coal of identical coal type presently under SRC liquefaction. The primary liquefaction activity of the solvent would be determined under hydrogen-starved, solvent-rich conditions to mimic the slurry tanks V101A/V101B and the rapid coal dissolution process in the preheater B102 at $750 \pm 2^\circ\text{F}$. The secondary liquefaction activity of the solvent would be determined from a similar product distribution under hydrogen-rich conditions (2,000 psi) to quantify the sustaining hydrogen transfer reactions in reactor R101.

These two tests would be made within the same sand bath and at the same time a third test microautoclave is run. In this third bomb, the standard process coal type would be reacted with a standard model solvent mixture. Together, all three results would provide internal checks on the reliability of the test (standard coal vs. standard solvent); optimum continued dissolution of process coal (tote bin coal vs. recycle solvent/no H_2); and optimum continued conversion to the desired product slate (tote bin coal vs. recycle solvent/ H_2). Figure 15 summarizes the proposed solvent quality test matrix.

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Table 1
Typical Wilsonville
Run Conditions

Dissolver pressure	$1,700 \pm 100$ psig
Dissolver temperature	$825 \pm 10^{\circ}\text{F}$
Dissolver volume in use	75%
Coal space rate	38 ± 3 lb/hr-ft ³
H ₂ partial pressure (heater inlet)	$1,470 \pm 75$ psi

Figure 1
Wilsonville Pilot Plant Process Flow Diagram

FIGURE 2
WILSONVILLE SOLVENT QUALITY (SQ)
VS.
COAL TYPE

FIGURE 2 (Continued)
WILSONVILLE SOLVENT QUALITY (SQ)
VS.
COAL TYPE

FIGURE 2 (Continued)
WILSONVILLE SOLVENT QUALITY (SQ)
VS.
COAL TYPE

FIGURE 2 (Continued)
WILSONVILLE SOLVENT QUALITY (SQ)
VS.
COAL TYPE

FIGURE 3
TOTAL GASES VS. SOLVENT QUALITY
ALL DATA POINTS

FIGURE 4
SOLVENT QUALITY VS. TOTAL GAS (WT % MAF COAL)

	●	■	◈	△	○	▲
DISSOLVER	1700	2100	2100	1800	2100	2000
TEMP.	825	825	825	840	840	825
VOLUME USED	75	50	75	75	75	75

FIGURE 5
TOTAL GAS (HYDROCARBON + HETEROATOM)
AS A FUNCTION OF TIME

FIGURE 6
HYDROGEN CONSUMPTION VS.
TOTAL GAS PRODUCTION
ALL DATA POINTS

FIGURE 7
TOTAL GAS PRODUCTION VS. HYDROGEN CONSUMPTION
BY COAL TYPE

FIGURE 8
SOLVENT QUALITY VS. HYDROGEN CONSUMPTION
BY COAL-TYPE

FIGURE 9
SOLVENT QUALITY VS.
PRODUCT YIELDS FOR DOTIKI COAL

FIGURE 9 (Continued)

FIGURE 10
SOLVENT QUALITY VS.
PRODUCT YIELDS FOR LAFAYETTE COAL

FIGURE 10 (Continued)

FIGURE 11
SOLVENT QUALITY VS.
PRODUCT YIELDS FOR PYRO COAL

FIGURE 11 (Continued)

FIGURE 12
SOLVENT QUALITY VS.
PRODUCT YIELDS FOR FIES COAL

FIGURE 12 (Continued)

FIGURE 13
WILSONVILLE SOLVENT QUALITY (SQ)
VS. COAL TYPE

FIGURE 14
COAL PYRITE VS. SOLVENT QUALITY
BY COAL TYPE

**FIGURE 15
PROPOSED
SRC-I SOLVENT QUALITY TEST**

COAL SOLVENT	STD PROCESS COAL-TYPE (1)	DAILY TOTE-BIN NO H ₂ (1)	DAILY TOTE-BIN H ₂ (2)
	QUALITY ASSURANCE TEST		
STD SOLVENT TET/MN			
DAILY RECYCLE SOLVENT		PRIMARY COAL DISSOLUTION	SECONDARY PRODUCT DISTRIBUTION
DAILY RECYCLE SOLVENT & ADDITIVE		PRIMARY COAL DISSOLUTION	SECONDARY PRODUCT DISTRIBUTION

- (1) MICROAUTOCLAVE S/C (8/1); 10 MINUTES AT 750°F
DETERMINE: RESIDUE (THR) – PREASPHALTENES – BENZENE SOLUBLES
- (2) TEST CONDITIONS TO BE DETERMINED

Appendix V-B

Determination of Solvent or Coal Quality by Microautoclave

Project no. 43080

Method no. 43080-60

Submitted by: Chuck Roberts and David Hall
Analytical Department
Wilsonville Advanced Coal Liquefaction Facility
Southern Company Services, Inc.
Catalytic, Inc.

Revised by: F. E. Cooper

Reference: Consolidated Coal Co.
Research Division

September 1982

I. Scope

This method applies to raw coal and hydrogenated recycle solvent for solvent-refined coal conversion.

II. Principle

The microautoclave test evaluates the conversion potential of process solvents relative to a standard coal, or of raw coals relative to a standard solvent. When used for solvent evaluation, the test can be run in either a short or long mode. The methods differ not only in the time during which the microautoclave is held at temperature (10 and 30 min at 750°F for the short and long tests, respectively), but also in the solvent-to-coal ratio (8:1 and 2:1 for short and long tests, respectively). The microautoclave test sequence is diagrammed and described in Figure B-1.

Appendix V-B (Continued)

[III. Procedure

A. Long Test (for coal and solvent evaluation)

- (1) Weigh 5 g of coal (to the nearest 0.1 mg) of known moisture and ash content. For solvent evaluation, weigh 5 g of standard coal.
- (2) Weigh 10 g of standard solvent (25% tetralin and 75% 1-methylnaphthalene) for coal evaluation into a previously tared autoclave containing a stainless-steel ball. For solvent evaluation, weigh 10 g of solvent to be tested into the autoclave. (See Note 1.)
- (3) Transfer coal to autoclave and seal with high-pressure grease on sealing threads.
- (4) Attach type K thermocouple wire to thermowell of autoclave and the other end of the wire to potentiometer.
- (5) Attach autoclave to drive mechanism.
- (6) Turn on oil to drive mechanism and check to see that it is operating correctly.
- (7) Turn on shaker mechanism of autoclave and lower autoclave into preheated fluidized sand bath. (See Note 2.)
- (8) Control temperature of autoclave by adjusting sand bath so that autoclave reaches a temperature of $750 \pm 10^{\circ}\text{F}$ within 90 sec.
- (9) Control temperature @ $750 \pm 10^{\circ}\text{F}$ for 30 min.
- (10) Remove autoclave from sand bath and immerse immediately in reservoir of cold water to stop reaction and bring microautoclave to room temperature as quickly as possible.
- (11) Remove contents of autoclave by washing with tetrahydrofuran (THF) into a 1,000-mL beaker until THF wash is clear (about 600 mL).
- (12) Stir sample and THF washings for 30 min to allow maximum mixing with THF.
- (13) Weigh filter paper, record, and place in a Buchner funnel by melting the paper with water.
- (14) Pour sample into Buchner funnel under vacuum and wash with THF until THF wash is clear (about 1,000 mL).

Appendix V-B (Continued)

- (15) Transfer filter paper to heated vacuum desiccator and dry for 1 hr @ 110°C.
- (16) Allow sample to cool in desiccator for 1 hr.
- (17) Remove filter paper from desiccator, weigh to 0.1 mg, and record.
- (18) Calculate conversion by formula in calculations section of this procedure.

B. Short Test

- (1) Weigh 5 g of coal to be tested or standard coal for solvent quality.
- (2) Weigh 12 g of standard solvent (25% tetralin and 75% 1-methylnaphthalene) for coal evaluation or solvent to be tested into a previously tared autoclave containing a stainless-steel rod.
- (3) Control temperature at $750 \pm 10^\circ\text{F}$ for 10 min.
- (4) Pour sample into a steam-jacketed Buchner funnel under vacuum and wash with THF until THF wash is clear (about 400 mL).

Remark: Conversions using this procedure are compared to a curve using concentrations of 0, 5, 10, 25, and 50% tetralin in 1-methylnaphthalene and Indiana V coal standard. The curve is shown in Figure 2.

IV. Reagents

- (1) Tetrahydrofuran (THF)
- (2) Desiccant for desiccator
- (3) Standard coal of known moisture and ash
- (4) 1-methylnaphthalene
- (5) 1, 2, 3, 4-tetrahydronaphthalene (tetralin)

Equipment

- (1) Microautoclave
- (2) Driving mechanism for microautoclave adjusted to 1,000 rpm and a $1\frac{1}{2}$ -in. stroke
- (3) Type K thermocouple wire
- (4) Potentiometer

Appendix V-B (Continued)

- (5) Fluidized sand bath (Tecam fluidized bath SBL-2)
- (6) Nitrogen source
- (7) Heated vacuum desiccator
- (8) Desiccator
- (9) Steam-jacketed Buchner funnel
- (10) 1,000-mL side arm Erlenmeyer flask
- (11) Rubber vacuum tubing
- (12) 3/8-in. diam stainless-steel ball bearing
- (13) 11-cm quantitative filter paper

V. Calculations

- (1) Coal sample size x % H₂O in coal sample = grams of H₂O.
- (2) Coal sample size x % ash in coal sample = grams of ash.
- (3) Filter paper wt + insolubles - filter paper wt = insolubles.
- (4) Original coal sample weight - grams of H₂O = grams of moisture-free coal.
- (5) Original coal sample wt - grams of H₂O - grams of ash = grams of moisture- and ash-free coal.
- (6) % conversion = $\frac{\text{grams moisture-free coal} - \text{THF insolubles}}{\text{grams moisture- and ash-free coal}} \times 100.$

VI. Notes

- (1) A 3/8-in.-diam stainless-steel rod is placed in each of the two autoclaves for mixing. If the rods are not placed in the autoclave, maximum mixing will not occur, and as a result, the operator may experience a lower conversion than normal.
- (2) Temperature for the sand bath before autoclaves are introduced may vary; however, under normal conditions, this temperature should be between 810-830°F. This should allow for heat transfer from the sand bath to the autoclave and give the necessary 750 ± 10°F within 90 sec.
- (3) During normal operation and material balance periods, two of three composite solvent samples and one to three coal samples are tested per day. With the present system, a run of two samples requires about 3-5 hr. Therefore, the percent conversion numbers are generally single analyses of one composite sample.

Appendix V-B.(Continued)

Obtaining a consistent temperature profile in the sand bath, and thus in the microautoclave, is the most critical and most operator-dependent aspect of the test. Once thermal equilibrium at 750°F is reached, the heat capacity of the aluminum oxide in the sand bath is sufficient to maintain $750 \pm 10^\circ\text{F}$ without much difficulty. However, attaining 750°F in 90 sec without significant over- or undershooting requires considerable operator skill and experience.

Figure B-1
Schematic of the Microautoclave Test

Step 1: 12 g (10 g)* of solvent is weighed to the nearest 0.1 g into a previously tared microautoclave containing a 3/8-in.-diameter stainless-steel ball bearing.

Step 2: 1.5 g (5 g) of coal is weighed to the nearest 0.1 mg and transferred to the microautoclave containing the solvent and ball bearing.

Step 3: The microautoclave is capped, fitted with a thermocouple, and attached to the shaker. The shaker is turned on, 1,000 strokes/minute, with a 1.5-in. stroke length.

Step 4: The shaking microautoclaves are lowered into a fluidized sand bath, previously heated to 810-830°F. The time of contact of microautoclaves with the sand is set as zero time. The temperature of the sand bath is regulated by manual addition of cold sand such that the microautoclave reaches 750 ± 5°F in 90 sec. The temperature of the microautoclave is maintained at 750 ± 5°F for the duration of the 10-min (30-min) test.

Step 5: After a total of 10 min (30 min) at 750 ± 5°F has elapsed, the shaking microautoclaves are hydraulically lifted from the sand bath and immersed immediately in a room-temperature water bath. This stops the reaction and brings the microautoclaves to room temperature.

Step 6: The microautoclaves are opened and the contents removed and transferred to a stainless-steel beaker by washing with tetrahydrofuran (THF) until the THF rinse is colorless (approximately 600 mL). The THF suspension is stirred at room temperature for 30 min.

Step 7: The THF-insoluble residue is collected on a predried, preweighed, water-wetted filter paper by vacuum filtration with a steam-jacketed Buchner funnel. The filter paper plus residue is washed with THF until the filtrate is clear. The residue and filter paper are dried at 110°C for 1 hr without vacuum, cooled for 1 hr, and weighed to the nearest 0.1 mg. The percent conversion to THF solubles is calculated according to:

$$\% \text{ conversion} = \frac{\text{grams of moisture-free coal} - \text{grams of residue}}{\text{grams of moisture- and ash-free coal}} \times 100$$

*Values in parentheses refer to the long test method.

Figure B-2
Microautoclave Calibration Curves

RUN	TEMP (°F)	SOLVENT TO COAL RATIO	REACTION TIME* (MIN)
SHORT	750	8:1	10
LONG	750	2:1	30

*INCLUDES HEAT-UP PERIOD.

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Appendix V-C

COMPOUND TYPES FOUND IN
LIQUEFACTION DISTILLATES

<u>NAME</u>	<u>MW</u>	<u>BP (°F)</u>	<u>STRUCTURE</u>
1. Pentane	72	97	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$
2. Hexanes	86	156	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
3. Cyclohexane	84	178
4. Benzene	78	176
5. Heptane	100	209	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$
6. Toluene	92	232
7. Octane	114	258	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
8. Xylenes	106	280-284
9. Phenol	94	328
10. Methylphenol	108	348-366
11. Dimethylphenols	122	412

Appendix V-C (Continued)

<u>NAME</u>	<u>MW</u>	<u>BP (°F)</u>	<u>STRUCTURE</u>
12. Tetralin	132	405
13. Naphthalene	128	424
14. Dodecane	170	421	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$
15. Methyltetralin	146	—
16. Quinoline	129	460
17. 2-Methylnaphthalene	142	466
18. 1-Methylnaphthalene	142	472
19. Biphenyl	154	493
20. Tetradecane	198	488	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$
21. Dimethylnaphthalenes	156	504-516
22. Acenaphthene	154	534
23. Methylbiphenyl	168	~514

Appendix V-C (Continued)

<u>NAME</u>	<u>MW</u>	<u>BP (°F)</u>	<u>STRUCTURE</u>
24. Dibenzofuran	168	549
25. Pentadecane	212	519	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_3$
26. Fluorene	166	561
27. Hexadecane	226	548	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$
28. Xanthene	182	594
29. 9,10-Dihydrophenanthrene	180	551
30. Methylfluorenes	180	—
31. Heptadecane	240	576	$\text{CH}_3(\text{CH}_2)_{15}\text{CH}_3$
32. Dibenzothiophene	184	600
33. Phenanthrene	178	644
34. Anthracene	178	644
35. Octadecane	254	602	$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$

Appendix V-C (Continued)

<u>NAME</u>	<u>MW</u>	<u>BP (°F)</u>	<u>STRUCTURE</u>
36. Carbazole	167	641
37. Methylphenanthrenes	192	676
38. Nonadecane	268	627	$\text{CH}_3(\text{CH}_2)_{17}\text{CH}_3$
39. Eicosane	283	641	$\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$
40. Fluoranthene	202	707
41. Pyrene	202	739
42. Heneicosane	297	674	$\text{CH}_3(\text{CH}_2)_{19}\text{CH}_3$
43. Docosane	311	696	$\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$
44. Methylpyrenes	216	—
45. Tricosane	325	716	$\text{CH}_3(\text{CH}_2)_{21}\text{CH}_3$
46. Tetracosane	339	736	$\text{CH}_3(\text{CH}_2)_{22}\text{CH}_3$
47. Benzo(ghi)fluoroanthene	226	—

Appendix V-C (Continued)

<u>NAME</u>	<u>MW</u>	<u>BP (°F)</u>	<u>STRUCTURE</u>
48. Chrysene	228	838
and/or			
Triphenylene	228	838
49. Pentacosane	353	755	$\text{CH}_2(\text{CH}_2)_{23}\text{CH}_3$
50. Hexacosane	367	774	$\text{CH}_3(\text{CH}_2)_{24}\text{CH}_3$
51. Heptacosane	381	792	$\text{CH}_3(\text{CH}_2)_{25}\text{CH}_3$
52. Octocosane	395	809	$\text{CH}_3(\text{CH}_2)_{26}\text{CH}_3$
53. Nonocosane	409	825	$\text{CH}_3(\text{CH}_2)_{27}\text{CH}_3$
54. Triacontane	413	841	$\text{CH}_3(\text{CH}_2)_{28}\text{CH}_3$

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Appendix V-D
Wilsonville Data Base

No.	Code	Description
1	RUN	Run
2	MBDT	MB Date
3	RS DT	Run Starting Date
4	TRDA	Total Run Days
5	COAL	Coal
6	CLFM	MF Coal Feed (lb/hr)
7	CLASH	Coal Ash (wt %)
8	CLFMA	MAF Coal Feed (lb/hr)
9	CLSL	Slurry Concentration (MF %)
10	PERH	H ₂ Purity (mol %)
11	TOTGF	Total Gas Feed (SCFH)
12	LSRC	LSRC in Process Solvent (% slurry feed)
13	MACO3	NA ₂ CO ₃ Addition (lb/hr)
14	PHIPR	B102 Inlet Pressure (psig)
15	DVOL	R101 Volume (ft ³)
16	DOT	R101 Outlet Temperature (°F)
17	DOPR	R101 Outlet Pressure (psig)
18	DSRT	R101 Space Rate (MF lb/ft ³ -hr)
19	CSRT	Cumulative Space Rate (MF lb/ft ³ -hr)
20	SLDWD	Solids Withdrawal (% slurry feed)
21	SEPT	V103 Temperature (°F)
22	VACBT	T102 Bottom Temperature (°F)
23	CONV	Conversion (% MAF)
24	SQS	Solvent Quality (short)
25	SQL	Solvent Quality (long)
26	HCONS	H ₂ Consumption (% MAF)
27	TOTG	Total Gases (% MAF)
28	HETA	Heteroatoms (% MAF)
29	HYC	Hydrocarbons (% MAF)
30	W	Water (% MAF)
31	LOIL	Light Oils (% MAF)
32	SOLP	Process Solvent, Process Method (% MAF)
33	SOLV	Process Solvent, V110 Method (% MAF)

Appendix V-D (Continued)

No.	Code	Description
34	SRCP	SRC, Process Method (% MAF)
35	OILP	SRC 011, Process Method (% MAF)
36	ASP	Asphaltenes, Process Method (% MAF)
37	PAP	Preasphaltenes, Process Method (% MAF)
38	SRCV	SRC, V110 Method (% MAF)
39	OILV	SRC 011, V110 Method (% MAF)
40	ASV	Asphaltenes, V110 Method (% MAF)
41	PAV	Preasphaltenes, V110 Method (% MAF)
42	ION	Insoluble Organic Matter (% MAF)
43	SLOASH	% Ash in Solids Withdrawal
44	KSRCF	% Kerr-McGee SRC Recovery, Forced Ash Method
45	KSRCN	% Kerr-McGee SRC Recovery, Normal
46	SKSRC	% S in SRC (Kerr-McGee)
47	SVSRC	% S in SRC, V110 Method
48	ASHBAL	% Ash Balance

Appendix V-D (Continued)

RUN	MBDT	MSDT	TRDA	COAL	CLFM	CLASH	CLFMA	CLSL	PERH	TOTGF	LSRC
133	2/8-9	1/5	33	IVOB1	422	10.4	378	37.8	82	8479	0.0
134	3/16-17	2/18	38	IVOB1	448	10.5	402	39.9	83	8479	0.0
135	4/8-10	3.27	16	IVOB1	431	10.7	385	37.5	83	9400	0.0
136	5/3-5	4/10	26	IVOB1	460	10.5	412	39.2	85	10260	0.0
137	5/31-2	5/9	25	IVOB1	481	10.3	431	39.2	85	10260	0.0
138	6/10-12	6/3	9	IVOB1	455	10.2	409	37.2	63	10360	0.0
140A	6/23-24	6/18	17	IVOB1	456	10.3	409	37.4	83	9860	0.0
140B	7/1-3	6/18	17	IVOB1	436	10.4	391	36.5	83	9890	0.6
143	8/20-21	7/30	25	IVOB1	468	11.4	415	38.2	88	10025	0.0
147	9/7-8	9/5	4	IVOB1	447	10.6	400	38.0	85	10132	0.0
151	11/4-5	10/27	18	PyKy9	428	9.4	388	37.6	86	10260	1.6
159BC	3/9-11	2/22	19	PyKy9	440	12.1	387	37.0	82	9980	3.1
160BC	3/25-26	3/14	13	PyKy9	488	10.5	347	38.2	81	7800	1.2
161C	4/9-10	3/29	15	PyKy9	498	12.6	435	38.5	82	9920	4.1
162A	4/26-27	4/12	20	PyKy9	494	13.4	428	38.4	84	10225	7.2
163A	5/11-12	5/1	31	LfKy9	498	12.9	434	38.7	81	10360	6.3
164A	6/4-5	6/2	4	LfKy9	241	8.8	220	35.3	85	1770	31.1
166AB	7/21	6/21	44	LfKy9	523	8.6	478	40.1	85	10690	2.8
166AC	8/2-3	6/21	44	LfKy9	536	8.5	490	37.5	84	10140	2.6
167C	9/7	8/19	22	LfKy9	473	8.8	431	37.8	79	9180	3.9
168A	9/12	9/9	5	LfKy9	489	8.9	446	37.2	81	9450	3.4
171A	9/28	9/22	9	LfKy9	442	8.7	404	36.1	85	9945	2.8
172A	10/1	9/30	3	LfKy9	458	8.8	418	36.2	84	9910	2.7
190AB	12/12-14	12/8	7	LfKy9	478	9.5	433	37.1	85	10190	0.0
201ABC	2/19-21	2/11	16	LfKy9	518	9.4	469	37.3	85	10520	0.0

Appendix V-D (Continued)

RUM	MBDT	RSDT	TADA	COAL	CLFM	CLASH	CLFMA	CLSL	PERH	TOTGF	LSRC
202A	3/6	2/26	11	DoKy9	525	9.0	470	37.9	83	10035	3.0
203DE	3/14-16	3/7	10	DoKy9	505	9.3	450	36.9	81	9659	3.1
204C	3/31	3/16	17	DoKy9	537	9.1	480	37.4	83	10126	2.9
206B	4/26-27	4/17	11	DoKy9	522	9.5	437	38.1	85	10401	0.0
206A	4/25	4/17	11	DoKy9	535	10.1	481	37.9	83	9978	0.0
208AB	5/7-8	5/4	6	DoKy9	556	9.1	505	39.6	84	10570	5.1
209AB	6/4-5	5/25	13	FsKy9	520	7.2	483	37.7	80	9761	5.0
210AB	6/13-15	6/7	10	FsKy9	535	8.4	490	39.1	82	10276	5.2
211B	7/13-14	6/20	25	FsKy9	543	8.1	498	39.5	86	9122	5.2
212AB	7/26-28	7/14	16	FsKy9	527	8.2	484	38.8	83	8325	5.3
217AB	9/19-20	9/17	12	FsKy9	313	8.9	285	33.4	93	5208	29.4
217CD	9/26-27	9/17	12	FsKy9	304	8.6	278	33.0	94	5285	29.4
219AB	10/20-21	10/11	13	FsKy9	535	8.7	189	36.2	85	7535	3.4
220AB	10/28-29	10/23	17	FsKy9	544	8.5	498	36.5	85	7488	4.3
220LE	11/7-9	10/23	17	FsKy9	540	8.7	493	36.5	85	7800	4.3
221B	12/20	12/9	20	FsKy9	311	8.7	284	30.6	89	3510	30.6
221G	12/27	12/5	20	FsKy9	333	8.6	305	30.1	89	3000	30.6
221H	12/28	12/9	20	FsKy9	324	9.3	294	30.2	89	3404	30.6
222ABC	1/1-4	12/29	7	FsKy9	333	8.3	305	29.8	86	3157	17.8
225BC	1/30-31	1/11	38	FsKy9	566	8.3	519	36.4	85	7498	3.8
225F	2/11-12	1/11	38	FsKy9	551	8.2	505	35.7	78	6781	3.8
225G	2/12-13	1/11	38	FsKy9	559	8.5	511	37.3	83	7236	3.9
225I	2/15	1/11	38	FsKy9	558	8.6	510	37.6	85	7272	4.0
227CD	4/15-17	3/21	58	FsKy9	565	8.4	518	39.0	83	7565	4.8
227G	5/7	3/21	58	FsKy9	566	7.9	521	39.0	85	7753	4.4
227E	5/3-4	3/21	58	FsKy9	575	8.1	528	39.5	85	7790	4.4

Appendix V-D (Continued)

RUN	MDDT	RSDT	TRDA	COAL	CLFM	CLASH	CLFMA	CLSL	PERH	TOTGF	LSRC
228AB	5/30-31	5/18	25	FsKy9	576	8.3	528	39.0	88	8128	4.1
229A	6/16	6/1	21	FsKy9	554	8.1	509	39.0	84	7808	4.3
229B	6/17-18	6/1	21	FsKy9	562	8.7	513	39.1	85	7771	4.1
232A	7/20-21			FsKy9	479	8.2	449	33.6	84	5979	

Appendix V-D (Continued)

RUN	NACOB	DHPR	BVOL	DOT	DORR	DSRT	CSRT	SLOWD	SEPT	VACBT	CONV	SQS	
133	0.0	2420	18.1	844	2400	23.3	19.9		655	601	95.0		
134	0.0	2410	18.1	844	2390	24.7	21.1		620	598	93.8	77.6	W/O ^a
135	0.0	2435	18.1	845	2400	46.9	35.1		630	607	93.6	76.0	W/O
136	0.0	2243	18.1	824	2200	50.0	37.4		625	601	93.9	77.4	W/O
137	0.0	1744	18.1	845	1700	52.3	39.1		655	604	93.0	71.9	W/O
138	0.0	1744	18.1	825	1700	49.5	37.0		625	593	93.7	73.0	W/O
140A	0.0	2443	18.1	845	2400	49.6	37.1		630	600	93.9	75.2	W/O
140B	0.0	2445	18.0	845	2400	47.4	35.5		625	596	93.9	77.9	W/O
143	0.0	1796	18.1	823	1750	26.0	22.1		620	595	94.4	77.0	W/O
147	0.0	1789	18.1	825	1450	24.0	21.1		600	595	92.2	74.6	W/O
151	0.0	2190	9.1	825	2160	46.5	34.0			578	93.5	63.9	
159BC	0.0	1709	9.1	825	1700	47.0	35.0			580	93.6	74.0	
160BC	0.0	1728	9.1	825	1066	35.9	29.2		610	580	94.2	73.6	
161C	0.0	1782	9.1	825	1037	36.6	29.0	7	610	575	93.4	71.9	
162A	0.0	2150	9.1	825	1412	36.3	29.6	6	633	550	94.0	72.9	
163A	0.0	1735	9.1	826	967	36.6	29.0	7	630	555	93.3	67.9	
164A	0.0	2396	0.0			0.0	61.0		643	567	90.9	66.4	
166AB	0.0	1751	13.6	825	1700	38.5	31.4	10	725	559	92.2	66.7	
166AC	0.0	1758	13.6	825	1700	39.5	32.1		625	553	91.9	67.0	
167C	5.3	2175	9.1	825	2100	51.4	38.5		625	557	92.7	66.4	
168A	5.4	2175	9.1	825	2100	53.2	39.8		655	532	92.4	68.9	
171A	4.9	2185	9.1	824	2175	40.1	33.7			561	92.0	71.7	
172A	5.1	2184	9.1	823	2184	49.0	35.0	6		497		72.6	

^aWithout LSNC.

Appendix V-D (Continued)

RUN	NACOB	PHIPR	DVOL	DOT	DOPR	DSRT	CSRT	SLOWD	SEPT	VACBT	CONV	SQS	
190AB	1.3	2132	13.6	823	2132	35.2	27.4	6		595	93.6	65.2	W/O ^a
201ABC	5.8	1731	13.6	824	1700	38.2	31.1	6		830	92.5	65.7	W/O
202A	0.0	1740	13.6	826	1700	38.7	31.5	6	645	628	93.8	64.2	
203DE	5.6	1742	13.6	826	1700	37.2	30.3	6	645	723	93.0	69.0	
204C	6.0	1860	13.6	841	1800	39.5	32.2	6	645	553	93.6	65.7	
206A	6.0	1840	13.6	840	1800	39.4	32.1	6	800		92.8	60.3	W/O
206B	5.8	1840	13.6	840	1800	38.5	31.4	6	800	589	92.3	60.3	W/O
208AB	6.2	1850	13.6	843	1800	40.9	33.3	6	800	600	92.4	69.6	
209AB	0.0	2140	13.6	839	2100	38.3	31.2	6	710	559	93.8	71.5	
210AB	0.0	2150	13.6	833	2100	39.4	32.1	6	740	588	94.7	69.1	
211B	0.0	1750	13.6	826	1700	40.0	32.5	6	680	576	94.2	77.4	
212AB	0.0	1750	13.6	826	1700	38.8	31.6	6	680	567	94.3	70.6	
217AB	2.2	2050	9.1	786	2000	34.0	25.5	6	600	546	93.0	81.7	
217CD	2.1	2056	9.1	784	2000	33.1	24.7	6	550	546	93.2	82.3	
219AB	3.7	2190	13.6	841	2100	39.4	32.1	6	710	598	92.5	76.0	
220AB	3.7	2210	13.6	840	2100	40.1	32.6	6	700	591	93.6	78.1	
220DE	3.7	2210	13.6	840	2100	39.8	32.4	6	690	597	93.5	81.1	
221B	2.2	2043	18.1	765	2000	16.9	14.5	6	642	594	92.8	85.8	
221G	2.3	2043	18.1	770	2000	18.1	15.5	6	654	593	93.7	75.1	W/O
221H	2.3	2043	18.1	770	2000	18.1	15.5	6	654	593	92.4	76.1	W/O
222ABC	1.4	2038	18.4	755	2000	18.0		6		597	91.6	94.8	W/O
225BC	2.3	2188	13.8	840	2100	41.0		6		609	93.8	82.2	W/O
225F	2.3	2170	13.8	841	2100	41.0		6		598	93.5	78.5	W/O

^aWithout LSRC.

Appendix V-D (Continued)

RUN	NACOB	PH1PR	DVOL	DOT	DOPR	DSRT	CSRT	SLOWD	SEPT	VACBT	CONY	SQS
225G	2.3	2193	13.8	841	2100	41.0		6		608	93.2	84.2 W/O ^a
225I	2.3	2177	13.8	842	2100	41.0		6		605	93.7	75.6 W/O
227CB	2.4	2145	13.8	840	2100	41.4		7		582	93.8	73.6 W/O
227E	2.4	2145	13.8	840	2100	41.0		7		584	93.4	78.9 W/O
227G	2.4	2140	13.8	839	2100	41.0		7		585	94.8	80.1 W/O
228AB	2.9	2137	13.8	825	2100	41.5		6		593	94.3	69.4 W/O
229A	2.5	2326	13.8	823	2300	42.1		6		597	94.7	69.4 W/O
229B	2.5	2328	13.8	825	2300	42.1		6		597	92.8	67.6 W/O
232A											93.4	

^aWithout LSAC.

Appendix V-D (Continued)

RUN	SQL	HCONS	TOTG	HEIA	MYC	W	LOIL	SOLP	SOLV	SRCP	OILP	ASP
133		4.1	13.4	5.1	8.3	8.1	13.3	18.1		46.6	6.4	35.7
134	78.0	4.2	10.9	5.1	5.6	7.6	13.7	15.5		50.1	2.0	38.3
135	76.0	3.0	9.5	3.9	5.6	8.5	9.4	10.0	10.9	58.9	10.7	32.1
136	73.9	2.3	9.0	4.4	4.7	8.3	7.0	4.9	2.6	67.0	10.2	33.7
137	66.9	3.1	8.3	4.4	3.9	7.6	11.9	5.8	5.8	63.0	13.7	28.5
138	66.9	3.1	5.9			8.2	10.1		2.2			
140A	72.0	3.0	9.1	4.9	4.2	8.7	10.4	14.5	0.3	54.5	7.6	26.6
140B	71.2	3.3	8.8	4.2	4.5	9.2	6.8	20.6	5.8	50.2	9.8	21.7
143	74.1	2.7	9.5	3.9	5.6	6.0	8.3	21.0	17.9	53.5	13.9	25.3
147	74.4	3.0	9.6	4.1	5.5	8.6	9.1	15.5	12.3	53.6	13.5	20.1
151	62.9	2.4	9.3	4.9	4.5	4.7	4.2	9.0	18.4	68.4	14.2	36.8
159BC	66.1	1.6	6.1	3.4	6.0	9.6	7.3	14.0	8.1	58.8	17.6	20.3
160BC	71.8	2.8	8.0	3.8	4.3	3.1	5.7	19.6	17.3	62.2	16.2	26.5
161C	69.0	2.7	8.1	3.9	4.2	5.7	9.5	7.3	7.1	65.1	15.4	27.8
162A	71.1	2.9	10.5	4.1	6.4	4.1	5.7	18.0	14.7	59.5	17.5	34.2
163A	63.5	3.0	11.3	3.6	7.6	5.6	7.7	15.3	14.8	57.7	12.5	27.2
164A	63.0	1.4	13.2	6.6	6.6	10.1	-9.0	16.2	25.0	61.8	6.9	23.5
166AB	60.6	2.0	4.8	4.8	3.1	2.4	3.3	34.9	6.7	49.8	6.7	23.5
166AC	62.4	1.9	5.0	5.1	2.9	5.1	4.2	28.1	10.5	52.3	7.5	26.0
167C	60.5	1.7	6.8	2.0	4.9	5.5	4.3	20.2	6.4	58.0	11.8	22.4
168A	62.4	1.8	7.8	3.2	4.7	2.9	3.8	25.8	6.7	54.3	7.3	26.2
171A	68.3	1.9	5.9	2.7	3.2	1.8	3.5	24.6	-2.1	58.3	10.7	28.2
172A	67.6	2.0	6.5	3.6	6.6	1.1	6.6	16.1	-6.9	63.0	8.8	32.9
190AB	63.5	2.3	8.4	3.4	4.9	4.7	7.6	21.3	-6.0	56.7	6.6	26.0
201ABC	78.2	2.5	6.8	2.2	4.6	3.1	6.9	10.1	0.7	69.7	16.1	30.2

Appendix V-D (Continued)

RUN	SQL	HCONS	TOTG	HETA	HYC	W	LOIL	SOLP	SOLV	SRCP	OILP	ASP
202A	60.4	2.1	6.9	1.9	5.0	5.3	5.0	22.9	3.6	55.9	13.3	19.0
203DE	64.2	2.0	7.9	2.7	5.2	5.1	8.9	14.7	4.9	59.6	9.1	37.0
204C	62.2	2.7	8.4	2.0	5.6	3.0	7.5	23.1	3.2	55.5	12.0	28.3
206A	66.7	2.7	7.0	1.7	5.3	5.1	12.0	16.5	-9.3	56.2	13.7	19.6
206B	66.7	2.5	7.5	2.2	5.3	2.1	11.5	21.2	-5.1	54.0	16.5	18.5
208AB	61.4	2.4	7.7	2.5	5.2	2.7	10.33	15.6	0.7	59.1	9.0	27.4
209AB	65.0	2.9	9.7	2.5	7.2	5.9	8.7	17.4	4.5	54.0	9.9	29.1
210AB	64.0	2.9	10.0	3.3	6.7	9.5	10.1	17.1	5.6	51.5	5.3	22.4
211B	67.3	1.8	5.6	2.7	2.9	5.7	4.4	20.0	7.4	60.2	11.0	24.1
212AB	64.7	2.1	7.1	2.0	5.1	2.6	5.5	23.0	5.7	57.9	7.3	29.5
217AB	61.5	2.6	6.0	4.0	2.8	4.6	4.7	24.2	-2.9	57.1	7.3	24.5
217CD	65.3	2.9	6.0	3.6	2.4	4.7	8.2	18.4		60.2	9.4	30.1
219AB	67.6	2.5	7.0	3.7	4.1	2.5	10.0	17.4		50.6	14.9	32.5
220AB	65.9	2.5	7.3	2.8	4.5	4.3	10.0	22.0		53.6	14.4	28.6
220DE	66.6	2.3	8.1	3.5	4.6	4.1	8.0	21.0		54.3	16.2	26.4
221B	66.8	1.9	4.4	2.4	2.0	3.3	5.0	23.4		59.6	4.5	31.1
221G	64.1	2.0	6.2	3.9	2.3	4.9	8.6	12.6		64.0	24.0	20.3
221H	68.6	2.2	6.0	4.3	1.7	5.0	8.5	2.9		72.9	19.5	30.0
222ABC	69.7	1.4	5.9	3.6	2.3	4.3	5.1	15.5		63.7	13.3	24.8
225BC	65.0	2.1	7.2	3.0	4.2	3.9	8.7	21.7		55.3	16.4	25.6
225F	65.5	2.4	8.1	3.6	4.5	3.3	11.4	17.4		55.8	14.4	27.2
225G	64.9	2.6	8.3	3.6	4.7	3.0	9.6	19.0		56.5	13.9	26.0
225I	61.5	2.5	8.9	3.4	5.5	3.5	8.0	17.1		58.5	20.5	23.5
227CD	62.7	2.9	8.7	3.2	5.5	2.2	6.8	21.1		52.5	12.7	22.2
227E	67.6	3.0	8.5	3.9	4.6	4.2	13.2	12.5		57.2	15.0	24.4
227G	66.8	3.0	8.6	3.6	5.0	1.1	13.9	18.3		54.0	15.3	22.2

Appendix V-D (Continued)

RUN	SQL	HCONS	TOTG	HETA	HYC	W	LOIL	SOLP	SOLV	SRCP	OILP	ASP
228AB	62.7	2.0	6.0	2.7	4.1	5.7	10.3	14.5		50.9	9.7	27.5
229A	63.3	2.4	7.2	3.1	4.1	4.0	9.7	15.1		60.4	8.2	36.5
229B	61.4	2.5	7.4	3.4	4.0	3.4	9.3	17.9		57.1	7.7	32.4
232A		1.6	5.9	2.8	3.1	3.5	6.2	10.4		67.6	15.9	28.2

Appendix V-D (Continued)

RUM	PAP	SRV	OILV	ASV	PAV	LOM	SLDASH	NSRCF	NSRCM	SKSRC	SVSBC	ASHBAL
133	4.5				5.0							
134	9.8				6.6							
135	16.1	59.8	16.9	25.1	16.8	6.8						
136	23.1	68.5	17.4	31.6	19.5	6.5						
137	20.8	62.5	13.2	21.2	28.1	7.0						
138		70.9	18.4	25.9	26.6	6.3						
140A	20.3	69.5	19.4	36.2	13.9	3.3						
140B	18.7	76.7	18.4	28.9	19.4	3.0						
143	14.3	55.3	16.1	25.0	14.2	5.4		83.5				
147	20.0	56.2	13.7	29.1	13.4	7.0		72.5				
151	17.4	58.4	10.7	28.2	19.5	6.5		76.8				
159BC	21.0	67.2	16.7	30.0	20.5	6.5		72.8	73.0	0.9		87.1
160BC	19.4	63.5	17.2	22.5	23.8	5.8		82.3	81.2	0.8		93.5
161C	24.0	66.1	16.0	24.5	25.6	6.6		75.9	76.3	0.9	0.90	103.5
162A	7.9	62.1	20.3	31.4	10.4	6.0		80.6	82.5	0.9	0.86	99.1
163A	18.1	54.9	17.3	23.0	14.6	6.7		78.9	80.1	0.8	0.77	98.7
164A	31.5	53.8	1.1	16.8	35.9	9.1		77.6	74.3	1.1	0.86	93.7
166AB	19.5	76.1	14.1	26.5	35.5	7.9		75.3	75.1	0.9	0.91	90.3
166AC	18.8	68.3	14.0	22.3	32.0	5.0		72.5	69.3	0.9	0.94	91.7
167C	23.8	71.8	14.0	32.1	28.0	7.3		81.2	73.9	1.0	1.03	109.7
168A	20.8	72.1	16.2	25.1	30.8	7.6		78.5	76.6	1.0	1.00	110.1
171A	19.4	83.8	25.6	34.5	25.3	8.0		78.5	79.0	1.1		111.9
172A	21.3	84.9	21.0	36.2	27.7	7.7		82.4	80.7	1.1		124.8
190AB	24.2	80.1	25.2	36.3	19.2	4.9				1.0	0.96	90.6
201ABC	23.4	76.5	19.2	29.1	28.1	7.5	10.2				0.9	96.4

Appendix V-D (Continued)

RUN	PAP	SRCV	DILV	ASV	PAV	ICM	SLDASH	KSRCF	KSRCM	SKSRC	SVSRC	ASHBAL
202A	22.8	72.6	15.0	31.8	25.8	6.2	9.2	77.7	78.0	0.8	1.0	90.3
203DE	12.6	68.1	13.1	33.6	21.4	7.0	9.8	81.4	83.1	0.9	0.9	102.2
204C	14.4	72.6	16.1	42.2	14.3	6.4	10.3	78.9	80.8	0.8	1.0	102.5
206A	22.7	77.3	22.5	27.4	27.4	7.3	8.7	68.7	72.2	1.0	0.9	94.1
206B	19.9	75.6	18.5	27.4	29.7	7.7	9.4	72.1	70.2	0.9	0.9	91.0
208AB	22.7	71.7	13.8	32.8	25.1	7.6	8.8					105.0
209AB	15.8	65.4	17.5	24.0	23.9	6.2	8.5	79.0	79.3	0.9	0.8	102.7
210AB	23.8	61.7	12.6	27.1	22.0	8.3	10.1	79.1	79.6	0.8	0.8	94.5
211B	25.1	71.9	17.0	24.2	30.7	9.8	7.2	79.6	76.2	1.0	1.0	93.3
212AB	21.6	74.2	17.9	31.0	25.3	9.7	7.3	78.6	80.0	1.0	1.0	95.5
217AB	25.3	84.8	29.3	25.0	30.5	6.6	4.0	90.2	88.9	1.0	1.0	95.6
217CD	20.7					6.9	3.9	89.8	88.2	0.9	1.0	94.9
219AB	17.2					6.4	7.4	85.1	84.7	0.9	0.8	100.7
220AB	18.5					5.6	8.1	84.4	84.6	1.0	0.9	97.4
220DE	17.8					6.4	8.0	86.5	85.9	1.0	0.9	98.2
221B	24.0					7.2	4.2					104.0
221G	19.7	64.0				6.3	4.6					101.0
221H	21.4	72.9				6.9	4.0					109.0
222ABC	25.6					7.6						98.3
225BC	13.3					6.3						96.5
225F	14.2					7.3						96.0
225G	15.8					6.9						98.0
225I	14.5					7.3						98.0
227CD	18.8					6.5						99.0
227E	17.8					8.1						98.0
227G	17.3					7.5						93.4

Appendix V-D (Continued)

RUN	PAP	SRCV	OILV	ASV	PAV	IOM	SLDASH	KSRCF	KSRCN	SKSRC	SVSRC	ASHBAL
228AB	21.7					7.7						96.0
229A	15.7					6.3						102.0
229H	17.0					8.1						96.1
232A	23.5					7.7						

Appendix V-D (Continued)

SQ vs. Coal Data Analysis^a

Run no.	Coal type	Pyritic S (wt %)	Proximate ash content (wt %)	Fe (in wt % coal) ^b	H/C (atomic)	O/C (atomic)	Volatile matter (wt %)
133	Ind V/Old Ben #1	1.45	10.35	2.030	0.068	0.160	29.18
134	Ind V/Old Ben #1	0.95	10.05	1.463	0.063	0.177	25.05
135	Ind V/Old Ben #1	1.09	9.64	1.514	0.068	0.199	38.65
136	Ind V/Old Ben #1	1.02	9.89	1.457	0.072	0.150	33.60
137	Ind V/Old Ben #1	1.14	8.86	1.255	0.072	0.179	42.58
138	Ind V/Old Ben #1	1.15	9.44	1.477	0.069	0.176	34.52
140A	Ind V/Old Ben #1	1.23	9.93	1.477	0.068	0.185	32.11
140B	Ind V/Old Ben #1	0.85	10.16	1.417	0.064	0.195	33.10
143	Ind V/Old Ben #1	1.75	11.65	2.061	0.067	0.158	36.03
147	Ind V/Old Ben #1	1.39	10.85	1.449	0.064	0.192	34.71
151	Ky 9/Pyro	1.12	9.24	1.168	0.072	0.118	34.20
159BC	Ky 9/Pyro	1.32	11.18	1.480	0.066	0.092	31.00
160BC	Ky 9/Pyro	1.11	10.40	0.965	0.071	0.104	29.74
161C	Ky 9/Pyro	1.30	12.60	1.555	0.067	0.108	27.83
162A	Ky 9/Pyro	1.17	13.44	1.762	0.066	0.122	29.56
163A	Ky 9/Laf	1.59	12.90	1.640	0.069	0.118	28.11
164A	Ky 9/Laf	1.11	8.77	1.108	0.068	0.132	27.33
166AB	Ky 9/Laf	0.85	8.50	0.894	0.065	0.147	32.27
166AC	Ky 9/Laf	0.76	8.38	0.994	0.066	0.129	32.79

^aThe values for the coal data analysis were obtained from the "Feed Coal Analyses" found in the Wilsonville, Alabama Quarterly Reports.

^b $\text{FeO}_3 \text{ (wt \%)} \times 0.006994 \times \text{ash (wt \%)} = \text{Fe (wt \%)} \text{ in coal.}$

Appendix V-D (Continued)

Run no.	Coal type	Pyritic S (wt %)	Proximate ash content (wt %)	Fe (in wt % coal) ^b	H/C (atomic)	O/C (atomic)	Volatile matter (wt %)
167C	Ky 9/Laf	0.75	8.65	1.035	0.066	0.123	31.92
168A	Ky 9/Laf	1.15	8.84	1.138	0.065	0.118	30.40
171A	Ky 9/Laf	1.09	8.61	1.150	0.065	0.124	30.53
172A	Ky 9/Laf	1.03	8.69	1.175	0.066	0.128	30.36
190AB	Ky 9/Laf	0.75	9.33	0.927	0.063	0.123	31.51
201ABC	Ky 9/Laf	0.66	9.33	0.852	0.060	0.140	31.36
202A	Ky 9/Dot	1.18	8.95	1.305	0.060	0.175	30.15
203DE	Ky 9/Dot	1.34	9.17	1.291	0.065	0.103	33.68
204C	K6 9/Dot	1.20	8.99	1.188	0.067	0.100	35.13
206A	Ky 9/Dot	1.14	10.02	1.327	0.068	0.102	33.42
206B	Ky 9/Dot	1.03	9.46	1.262	0.065	0.122	33.92
208AB	Ky 9/Dot	1.08	8.97	1.181	0.069	0.107	31.89
209AB	Ky 9/Fies	1.18	6.99	1.171	0.067	0.171	31.61
210AB	Ky 9/Fies	1.14	8.24	1.271	0.070	0.145	34.16
211B	Ky 9/Fies	1.11	7.96	1.276	0.067	0.131	31.49
212AB	Ky 9/Fies	1.11	8.07	1.332	0.068	0.164	31.45
217AB	Ky 9/Fies	1.42	8.70	1.438	0.069	0.122	33.32
217CD	Ky 9/Fies	1.42	8.56	1.389	0.071	0.147	34.94
219AB	Ky 9/Fies	1.35	8.68	1.451	0.065	0.150	27.79
220AB	Ky 9/Fies	1.41	8.66	1.424	0.069	0.173	35.84
220DE	Ky 9/Fies	1.18	8.70	1.410	0.071	0.147	32.47
221II	Ky 9/Fies	-	-	-	-	-	-
221G	Ky 9/Fies	-	-	-	-	-	-

^b $\text{FeO}_3 \text{ (wt \%)} \times 0.006994 \times \text{ash (wt \%)} = \text{Fe (wt \%)} \text{ in coal.}$

Appendix V-D (Continued)

Run no.	Coal type	Pyritic S (wt %)	Proximate ash content (wt %)	Fe (in wt % coal) ^b	H/C (atomic)	O/C (atomic)	Volatile matter (wt %)
221B	Ky 9/Fies	1.07	8.26	1.222	0.066	0.141	32.82
222ABC	Ky 9/Fies	1.10	8.29	1.220	0.067	0.162	31.12
225I	Ky 9/Fies	1.10	8.63	1.158	0.067	0.150	30.45
225G	Ky 9/Fies	1.10	8.45	1.131	0.067	0.128	35.31
225F	Ky 9/Fies	1.11	8.22	1.203	0.066	0.107	31.44
225BC	Ky 9/Fies	1.37	8.33	1.201	0.068	0.123	33.68
227A	Ky 9/Fies	1.14	7.71	1.119	0.068	0.164	34.53
227CD	Ky 9/Fies	1.22	7.86	1.140	0.063	0.136	34.85
227E	Ky 9/Fies	1.17	8.12	1.172	0.065	0.159	36.14
227G	Ky 9/Fies	1.27	7.86	1.138	0.064	0.153	34.51
228AB	Ky 9/Fies	1.48 ^c	8.34	1.347	0.067	0.135	35.03
229A	Ky 9/Fies	1.01	7.75	1.229	0.066	0.141	34.82
229B	Ky 9/Fies	1.06	7.81	1.252	0.069	0.149	34.09

^b FeO_3 (wt %) = $0.006994 \times \text{ash (wt \%)} = \text{Fe (wt \%)} \text{ in coal.}$
^c Questionable data.

VI. PRODUCT FRACTIONATION STUDIES

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1. ROUND-ROBIN STUDY OF METHODS USED TO
CHARACTERIZE SRC-I PRODUCTS

INTRODUCTION

ICRC conducted an experimental program to determine the most precise analytical procedures to include in the SRC-I Demonstration Plant analytical laboratory for process control and product characterization. Both the complexity and thermal instability of SRC-I process-stream samples warrant the need for standardized work-up methods that are used for their characterization.

As part of the program to develop a standard work-up procedure, ICRC conducted a round-robin study among five laboratories to compare and contrast distillation and solvent-extraction procedures that are used to quantify the distribution of fractions such as distillate, oils, asphaltenes, preasphaltenes, and residue. Each laboratory used its own work-up methods to characterize a set of samples from seven process streams at the Wilsonville SRC-I Pilot Plant.

EXPERIMENTAL METHODS

Sample Selection

Samples from seven process streams from the SRC-I Pilot Plant in Wilsonville, Alabama were collected during run no. 220B (material-balance period; see Table 1). The sampling sites are illustrated in Figure 1, a schematic of the SRC-I process. Samples were divided, shipped to five laboratories participating in this study, and stored in air-tight containers under nitrogen at refrigerated temperatures until analysis.

The selection of these specific samples allowed two material-balance calculations: one for the 30/70 sample and one for the critical solvent deashing (CSD) feed sample (T102 bottoms).

1. The 30/70 sample was a laboratory-prepared mixture of 30 wt % light solvent-refined coal (LSRC) and 70 wt % process solvent

(V131A). Therefore, a material balance of each fraction (ϕ)¹ could be calculated as:

$$\phi_{30/70} = 0.7\phi_{V131A} + 0.3\phi_{LSRC}$$

2. Relative yields of LSRC, SRC, and Kerr-McGee ash concentrate (KMAC) from the CSD feed sample (T102 bottoms) were determined to be 14.9, 53.2, and 31.9 wt %, respectively, for run 220B. Therefore, the material balance of each fraction (ϕ) could be calculated as:

$$\phi_{T102 \text{ btm}} = 0.149\phi_{LSRC} + 0.532\phi_{SRC} + 0.319\phi_{KMAC}$$

Analytical Scheme

The five laboratories participating in this round-robin study separated samples into five fractions (distillate, oils, asphaltenes, preasphaltenes, and residue) by vacuum distillation and/or extraction (see Table 2). The weight percent yield of each fraction from each process-stream sample was measured to allow direct comparison of both weight percent yields and material balances. Analytical procedures used by each laboratory are described in the following sections. Table 3 summarizes how each laboratory defines the fractions according to the separation procedures used.

Wilsonville. The laboratory at Wilsonville Pilot Plant routinely uses two analytical schemes to characterize products: one is for the V110 sample (dissolved coal slurry) (Figure 2) and the other is for all other samples (Figure 3). Three analytical procedures are used to determine distribution of the five fractions:

1. Vacuum distillation (see Appendix VI-A) determines the amount of distillate in each sample, and is also used to obtain the SRC

¹Weight percent of distillate, oils, asphaltenes, preasphaltenes, or residue.

fraction ($>850^{\circ}\text{F}$) in the V110 sample before Soxhlet extraction.

2. Cresol solubility (see Appendix VI-B) determines the amount of residue (cresol-insoluble material) by beaker extraction.
3. Soxhlet extraction (see Appendix VI-C) is used to determine the amount of benzene insolubles, from which the weight percent of preasphaltenes is calculated by subtracting the amount of cresol insolubles. Material that is soluble in benzene is then separated further into oils and asphaltenes by precipitating the asphaltenes in pentane.

Air Products and Chemicals, Inc. (APCI). APCI uses vacuum distillation to determine the amount of distillate in each sample (see Appendix VI-D).

ICRC. Sequential solvent extraction (Appendix VI-E) is used by ICRC to determine the weight percent of oils, asphaltenes, preasphaltenes, and residue in each sample (see Figure 4).

Kerr-McGee. Two analytical procedures are used (see Figure 5):

1. Vacuum distillation (Appendix VI-F) determines the amount of distillate in each sample.
2. Beaker extractions (Appendix VI-G) separate oils, asphaltenes, preasphaltenes (indirectly), and residue: the sample is extracted with pyridine to obtain the yield of residue; a separate sample is extracted with toluene to determine the toluene insolubles; subtracting the weight percent of residue from that of toluene insolubles provides the amount of preasphaltenes; the toluene solubles are extracted with heptane into oils (soluble) and asphaltenes (insoluble).

Conoco. Conoco uses three analytical procedures to separate the five fractions (see Figure 6):

1. Vacuum distillation (see Appendix V-H) determines the amount of distillate.

2. Beaker extraction with tetrahydrofuran (THF) (see Appendix VI-I) determines the amount of residue (THF insolubles) in each sample and generates the THF-soluble fraction necessary for liquid column fractionation (LCF).
3. LCF (see Burke et al., 1979)² determines the yield of oils, asphaltenes, and preasphaltenes in each sample by sequentially eluting the respective fractions with hexanes, benzene, and pyridine. Samples expected to contain >50 wt % distillate (V110 and 30/70) were distilled before THF extraction and LCF (path 1 in Figure 6). The amount of distillate was then added to the amount of oils obtained by fractionation. Other samples (T102 btm, LSRC, SRC, and KMAC) were extracted directly with THF (path 2 in Figure 6).

RESULTS

Table 4 summarizes weight percent yields received from the participants for each of the distillates and solvent-extracted fractions generated from all seven Wilsonville SRC-I samples.

Distillate

Vacuum distillation was performed on all seven samples by three of the participants: Wilsonville, APCI, and Kerr-McGee. Conoco distilled only the V110 and 30/70 samples. For each sample, Kerr-McGee's distillate yields were the highest; Wilsonville's distillate yields were the lowest. However, closer examination of the differences between the vacuum distillation procedures used (Table 5) indicates that the definition of distillate varies significantly from one participant to another; therefore, that the results vary is not surprising.

Oils and Asphaltenes

Comparison of the cut points for oils and asphaltenes (Table 4) shows that differences in the procedures used significantly affect the

²Preparative LCF was performed on either the THF-soluble resid or the whole sample, if it was assumed to be a THF-soluble nondistillate. Sample size was ca. 0.15 g.

yields of these two fractions. Conoco-generated oils yields are consistently higher than those obtained by the other participants. Non-polar solvents such as n-pentane, hexanes, or n-heptane are used to extract the oils fraction. However, during the first step of Conoco's LCF procedure, the sample that is introduced into the hexanes medium is dissolved in THF, which thus simultaneously introduces a small amount of highly polar solvent (THF). The THF increases the solvent strength of the hexanes, thus allowing some components to solubilize that would have been insoluble in the hexanes. Therefore, these components are carried from the hexanes-insoluble fraction (asphaltenes) to the fraction soluble in hexanes (oils). This is especially noticeable in the T102 bottom, LSRC, and SRC samples.

The ICRC and Kerr-McGee results are very similar, indicating that beaker extractions with heptane (Kerr-McGee) and sequential solvent extraction with pentane (ICRC) give comparable cut points between oils and asphaltenes. The only results that do not agree are for the LSRC sample, for which we have no explanation.

Adding the yields of oils and asphaltenes (the toluene- or benzene-soluble fractions) generally produces similar results regardless of the extraction technique used. However, the V110 sample results are inconsistent; Wilsonville found a smaller benzene-soluble fraction than did the other laboratories, which can be explained by differences in the work-up procedures (see Figure 2). Wilsonville's benzene extraction of the V110 sample is carried out after the cresol-soluble portion of the V110 sample is distilled. Conceivably, some benzene-soluble material (oils and asphaltenes) was converted to benzene-insoluble material (preasphaltenes and residue) during this distillation step, which would decrease the benzene-soluble yield and increase the preasphaltenes yield.³

Preasphaltenes and Residue

The residue yields for each of the samples analyzed by Wilsonville, ICRC, and Kerr-McGee were similar, whereas the Conoco residue yields

³The benzene-insoluble residue fraction is determined before distillation by cresol extraction and is, therefore, unaffected by this step.

were consistently higher. This indicates that using cresol or pyridine as the extracting solvent gives similar and lower residue yields than using THF. This result confirms our earlier findings (Kingsley and Schweighardt, 1982), which means that the cut point between preasphaltenes and residue is significantly different if THF is used as solvent rather than cresol or pyridine. This effect is especially noticeable in the preasphaltenes analysis of KMAC. The amount of THF-insoluble but pyridine- or cresol-soluble preasphaltenes was found to be about 25 wt % of the sample. On the other hand, the SRC sample contains preasphaltenes that are completely soluble in THF and pyridine. These variations in THF and pyridine solubility indicate that different types of preasphaltenes are present in the KMAC and SRC samples.

Adding the yields of preasphaltenes and residue, which is defined as the benzene- or toluene-insoluble portion (see last column of Table 4), shows that the results from each participant for all samples are similar, except for the V110 sample. V110 variability is due to the sample distillation prior to benzene extraction in Wilsonville's procedure, as discussed in the section on oils and asphaltenes. Distillation almost doubles the amount of benzene insolubles in the V110 sample (from 21 to 38 wt %). However, good agreement between results for all other benzene and toluene insolubles indicates that this cut point is the same for a given sample, regardless of the extraction procedure used. Sequential solvent extraction (ICRC) and beaker extraction (Kerr-McGee) and combinations of beaker extraction and LCF (Conoco) or beaker extraction and Soxhlet extraction (Wilsonville) with benzene or toluene all define this fraction similarly!

MATERIAL BALANCE OF RESULTS

As indicated previously, a material balance can be calculated for each fraction on two sets of the samples analyzed:

$$70 \text{ wt \% V131A} + 30 \text{ wt \% LSRC} = 100 \text{ wt \% 30/70}$$

$$0.7\phi_{\text{V131A}} + 0.3\phi_{\text{LSRC}} = \phi_{\text{30/70}} \quad (1)$$

$$14.9 \text{ wt \% LSRC} + 53.2 \text{ wt \% SRC} + 31.9 \text{ wt \% KMAC} = 100 \text{ wt \% T102 btm}$$

$$0.149\phi_{\text{LSRC}} + 0.532\phi_{\text{SRC}} + 0.319\phi_{\text{KMAC}} = \phi_{\text{T102 btm}} \quad (2)$$

The material-balance data are tabulated for each fraction (Tables 6-14). The weight percent yields were derived from Table 4, weight percent contributions were determined by substituting the weight percent yields into either equation 1 or 2, and the sums of all contributing fractions were divided by the weight percent of the initial sample (30/70 or T102 bottoms) to obtain the percent recovery.

Distillates

Material balances of distillates for the 30/70 and T102 bottoms samples are listed in Tables 6 and 7, respectively. The recovery for each laboratory is about $100 \pm 10\%$; the Kerr-McGee results show the best material balance (98 and 99% recovery).

Oils

Tables 8 and 9 summarize material-balance data for oils for the 30/70 and T102 bottoms samples, respectively. The oils balance varied between 88% (Wilsonville T102 btm) and 180% (ICRC T102 btm), which indicates that the respective oils analyses employed are unreliable. We do see, however, that Conoco's oils balance is 100-108%, although Conoco did not use extraction techniques exclusively to generate all the oils fractions. Conoco's procedure requires vacuum distillation of samples containing >50 wt % distillate; therefore, the 30/70 result is a sum of distillate and extracted oils from the distillate bottoms. This applies only to the 30/70 material balance, because Conoco did not distill any CSD samples. Therefore, Conoco's oils balance of 108% (Table 9) is the best of all the participants. This indicates that the LCF procedure can be applied to the CSD samples directly.

Asphaltenes

Material-balance data for asphaltenes for the 30/70 and T102 bottoms samples are listed in Tables 10 and 11, respectively. Conoco's LCF

procedure gave a balance of 94-101%, comparable to the results for oils. Wilsonville's techniques showed a good material balance for the CSD samples (104% recovery), but it was only fair for the 30/70 samples (133% recovery).

Toluene and Benzene Solubles

Adding the weight percents of oils and asphaltenes gives the fraction of a process stream that is benzene or toluene soluble. Table 12 lists the material balances for this combined fraction for the T102 bottoms; all laboratories obtained recoveries of $100 \pm 5\%$. This indicates that, regardless of the extraction technique applied, the benzene/toluene solubles do not depend on sample composition. Therefore, these fractions can be used to determine the material balance for the T102 bottoms samples.

Preasphaltenes

The T102 bottoms material balance of preasphaltenes is summarized in Table 13. Pyridine extraction (Kerr-McGee and ICRC) yields $100 \pm 5\%$ recoveries, whereas Wilsonville and Conoco recoveries (cresol and THF extraction) are low. This indicates that pyridine extracts a comparable group of compounds independent of both the sample composition and the extraction technique used; cresol (Wilsonville) and THF (Conoco) extract some components from the CSD feed (T102 bottoms) that are not extracted out of the CSD products (LSRC, SRC, and KMAC). This dependency of cresol and THF extraction on sample composition was also shown in an earlier report (Kingsley and Schweighardt, 1982). In contrast, pyridine extraction is not as strongly dependent on sample composition.

Residue

Table 14 provides the material balance of residue for the T102 bottoms; only the residue from the KMAC fraction contributes to this balance. None of the participants achieved $100 \pm 10\%$ recovery; the recoveries $>100\%$ show that the T102 btm sample is more extractable than the KMAC sample. This can be attributed to cosolubility effects (Kingsley and Schweighardt, 1982), and could also possibly indicate that residue is formed in the CSD unit.

CONCLUSION

During this round-robin study, seven different SRC-I process-stream samples were characterized at five laboratories using different work-up techniques. Results can be summarized as follows:

Distillate

- Distillate yields are dependent on the type of vacuum distillation procedure employed. Both the experimental setup and operating conditions affect distillate yields.

Oils and Asphaltenes

- Oils yields increase significantly when the extracting solvent contains small amounts of THF.
- The combined yield of oils and asphaltenes is independent of the extracting solvent used (benzene or toluene).
- Combined yields of oils and asphaltenes are unaffected by the extraction technique employed. Soxhlet extraction (Wilsonville), beaker extraction (Kerr-McGee), sequential solvent extraction (ICRC), and LCF analysis of beaker-extracted THF solubles (Conoco) resulted in comparable weight percent yields.
- Combined yields of oils and asphaltenes are reduced if the sample is distilled before extraction, because the asphaltenes are converted to preasphaltenes (Wilsonville V110 sample).

Preasphaltenes

- The yields of preasphaltenes are nearly identical when either pyridine or cresol is used as the extracting solvent.
- Preasphaltenes yields are lower if THF is used as extracting solvent.
- Preasphaltenes yields are not affected by the extraction technique used (beaker extraction vs. sequential solvent extraction).

- ° Distillation of a process-stream sample before solvent extraction (Wilsonville V110 sample) can convert benzene-soluble material into preasphaltenes or residue.

Residue

- ° Residue yields are unaffected by the extraction technique employed: beaker extractions (Wilsonville and Kerr-McGee) vs. sequential solvent extraction (ICRC).
- ° Residue yields are not significantly different if pyridine is used as the extracting solvent instead of cresol.
- ° Residue yields are significantly higher if THF is used as the extracting solvent.

NOTE

The results of this study were presented at a joint meeting in Atlanta, Georgia on December 11, 1981 with the following participants present: Fran Cooper and Ashok Rao, Catalytic Inc.; Gary Styles, Southern Company Services, Inc.; Richard A. Winschel and Frank P. Burke, Conoco Coal Development Company; John Carver and Don Rhodes, Kerr-McGee Corporation; Doug Moyer and Terry Slager, APCI; James O'Leary, Frank K. Schweighardt, and Ilse S. Kingsley, ICRC.

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Table 1
Wilsonville Process Streams Analyzed
in the Round-Robin Study

Sample description	Stream no. ^a	WV lab. no.
30/70 ^b	-	SN 67244
KMAC	28	SN 67245
V131A (process solvent)	29	SN 67246
LSRC	26	SN 67247
SRC	27	SN 67248
CSD feed (T102 btm)	30	SN 67249
V110 (feed to T102)	3	SN 67250

^aRefer to Figure 1.

^bLaboratory-prepared mixture of 30 wt % LSRC and 70 wt % V131A.

Table 2

Participants and Analyses Performed

Participant	Procedure	Wt % results				
		Dist.	Oils	Asph.	Preasph.	Residue
Catalytic, Inc. Wilsonville, Ala.	Vacuum distillation	✓				
	Soxhlet extraction		✓	✓	✓	
	Cresol solubility					✓
APCI Linwood, Pa.	Vacuum distillation	✓				
ICRC Trexlerstown, Pa.	Sequential solvent extraction		✓	✓	✓	✓
Kerr-McGee Crescent, Okla.	Vacuum distillation	✓				
	Beaker extractions			✓	✓	✓
Conoco Library, Pa.	Vacuum distillation			(✓)		
	THF ^a solubility					✓
	LCF ^b		✓	✓	✓	

^aTetrahydrofuran.^bLiquid column fractionation.

Table 3

Definitions of the Solvent-Extracted Fractions
(Listed by Participants and Procedure)

Lab.	Fraction (procedure)			
	Oils	Asphaltenes	Preasphaltenes	Residue
Wilsonville	Benzene soluble Pentane soluble (Soxhlet/beaker extraction)	Benzene soluble Pentane insoluble (Soxhlet/beaker extraction)	Cresol soluble Benzene insoluble (Calculated)	Cresol insoluble (Beaker extraction)
ICRC	Pentane soluble (Sequential solvent extraction)	Benzene soluble Pentane insoluble (Sequential solvent extraction)	Pyridine soluble Benzene insoluble (Sequential solvent extraction)	Pyridine insoluble (Sequential solvent extraction)
Kerr-McGee	Heptane soluble (Beaker extraction)	Toluene soluble Heptane insoluble (Beaker extraction)	Pyridine soluble Toluene insoluble (Calculated)	Pyridine insoluble (Beaker extraction)
Conoco	Hexanes soluble (LCF)	Benzene soluble Hexanes insoluble (LCF)	THF soluble Benzene insoluble (LCF)	THF insoluble (Beaker extraction)

Table 4

Weight Percent Yields of Distillates
and Solvent-Extracted Fractions from Wilsonville
Process-Stream Samples as Analyzed by the Participants

	Lab.	Dist.	Oils	Asph.	Preasph.	Residue	TI/BI ^a
T102 btm	WV	11.4	19.4	39.3	25.5	15.8	41.3
	ICRC/APCI	15.5	6.9	48.4	28.5	16.0	44.5
	KMG	25.3	7.4	47.8	29.2	15.6	44.8
	Conoco	-	31.4	22.7	24.3	21.6	45.9
LSRC ^d	WV	38.5	39.4	60.3	0.3	0	0.3
	ICRC/APCI	35.3	47.4	47.2	4.1	0	4.1
	KMG	62.2	31.5	65.4	3.1	0	3.1
	Conoco	-	71.9	22.1	6.0	0	6.0
SRC	WV	11.4	20.2	58.8	20.5	0.5	21.0
	ICRC/APCI	17.9	8.9	62.2	28.9	0	28.9
	KMG	24.6	8.6	60.7	30.7	0	30.7
	Conoco	-	41.0	33.9	25.1	0	25.1
KMAC	WV	2.8	1.5	1.2	30.3	67.0	97.3
	ICRC/APCI	1.9	1.8	2.3	34.3	61.6	95.9
	KMG	3.4	1.5	4.8	39.3	54.4	93.7
	Conoco	-	4.2	4.9	10.6	80.6	91.2
V110	WV	56.7	63.5	17.2	11.9	7.4	19.3
	ICRC/APCI	54.4	61.5	16.5	13.6	8.3	21.9
	KMG	64.7	59.4 ^b	21.5	13.8	5.3	19.1
	Conoco	53.0	67.8 ^b	10.5	11.0	10.7	21.7
30/70	WV	75.1	85.1 ^b	13.8	0.9	0.2	1.1
	ICRC/APCI	81.4	88.1	10.6	1.3	0	1.3
	KMG	89.0	87.2 ^b	12.8	0	0	0
	Conoco	75.2	91.2 ^b	7.0	1.8	0	1.8
V131A	WV	98.7	99.7 ^b	0.3	0	0	0
	ICRC/APCI	98.6	98.1	1.6	0.3	0	0.3
	KMG	99.6	99.6	0.4	0	0	0
	Conoco	-	100.0 ^c	0	0	0	0

^aToluene or benzene insolubles; sum of preasphaltenes and residue.

^bSum of distillate and oils after distillation of sample.

^cAssumed.

^dData on all LSRC fractions except distillate is proprietary to Kerr-McGee.

Table 5

Definitions of Distillate (Listed
by Participant and Distillation Condition)

	Pressure (mm)	Location of temp control	Max temp (°F)	Time at max temp (min)
WV	-1	Pot	600°F	5
APCI	-1 ^a	Head and pot	600°F	10
Kerr-McGee	0.1	Pot	600°F	60
Conoco	1	Head and pot	554°F	5

^aPot temperature and pressure are regulated to equal 1,000°F at ambient pressure.

Table 6

Material Balance of Distillate
for the 30/70 Samples

Participant	Sample	Wt % distillate	Wt % contribution	% recovery
WV	30/70	75.1		
	LSRC	38.5	11.6	
	V131A	98.7	<u>69.1</u>	
	Σ		80.7	107
Kerr-McGee	30/70	89.0		
	LSRC	62.2	18.7	
	V131A	99.6	<u>69.7</u>	
	Σ		88.4	99
APCI/ICRC	30/70	81.4		
	LSRC	35.3	10.6	
	V131A	98.6	<u>69.0</u>	
	Σ		79.6	98

Table 7

Material Balance of Distillate
for the T102 Bottoms Samples

Participant	Sample	Wt % distillate	Wt % contribution	% recovery
WV	T102 btm	11.4		
	LSRC	38.5	5.7	
	SRC	11.4	6.1	
	KMAC	2.8	<u>0.9</u>	
	Σ		12.7	111
Kerr-McGee	T102 btm	25.3		
	LSRC	62.2	9.3	
	SRC	24.6	13.1	
	KMAC	3.4	<u>1.1</u>	
	Σ		23.5	93
APCI/ICRC	T102 btm	15.5		
	LSRC	35.3	5.3	
	SRC	17.9	9.5	
	KMAC	1.9	<u>0.6</u>	
	Σ		15.4	99

Table 8

Material Balance of Oils
for the 30/70 Samples

Participant	Sample	Wt % oils	Wt % contribution	% recovery
WV	30/70	85.1		
	LSRC	39.4	11.8	
	V131A	99.7	<u>69.8</u>	
	Σ		81.6	96
ICRC	30/70	88.1		
	LSRC	47.4	14.2	
	V131A	98.1	<u>68.7</u>	
	Σ		82.9	94
Kerr-McGee	30/70	87.2		
	LSRC	31.5	9.5	
	V131A	99.6	<u>69.7</u>	
	Σ		79.2	91
Conoco	30/70	91.2		
	LSRC	71.9	21.6	
	V131A	100.0	<u>70.0</u>	
	Σ		91.6	100

Table 9

Material Balance of Oils
for the T102 Bottoms Samples

Participant	Sample	Wt % oils	Wt % contribution	% recovery
WV	T102 btm	19.4		
	LSRC	39.4	5.9	
	SRC	20.2	10.8	
	KMAC	1.5	<u>0.5</u>	
	Σ		17.2	88
ICRC	T102 btm	6.9		
	LSRC	47.4	7.1	
	SRC	8.9	4.7	
	KMAC	1.8	<u>0.6</u>	
	Σ		12.4	180
Kerr-McGee	T102 btm	7.4		
	LSRC	31.5	4.7	
	SRC	8.6	4.6	
	KMAC	1.5	<u>0.5</u>	
	Σ		9.8	132
Conoco	T102 btm	31.4		
	LSRC	71.9	10.7	
	SRC	41.0	21.8	
	KMAC	4.2	<u>1.3</u>	
	Σ		33.8	108

Table 10

**Material Balance of Asphaltenes
for the 30/70 Samples**

Participant	Sample	Wt % asph.	Wt % contribution	% recovery
WV	30/70	13.8		
	LSRC	60.3	18.1	
	V131A	0.3	<u>0.2</u>	
	Σ		18.3	133
ICRC	30/70	10.6		
	LSRC	47.2	14.2	
	V131A	1.6	<u>1.1</u>	
	Σ		15.3	144
Kerr-McGee	30/70	12.8		
	LSRC	65.4	19.6	
	V131A	0.4	<u>0.3</u>	
	Σ		19.9	155
Conoco	30/70	7.0		
	LSRC	22.1	6.6	
	V131A	0	<u>0</u>	
	Σ		6.6	94

Table 11

Material Balance of Asphaltenes
for the T102 Bottoms Samples

Participant	Sample	Wt % asph.	Wt % contribution	% recovery
WV	T102 btm	39.3		
	LSRC	60.3	9.0	
	SRC	58.8	31.3	
	KMAC	1.2	<u>0.4</u>	
	Σ		40.7	104
ICRC	T102 btm	48.4		
	LSRC	47.2	7.0	
	SRC	62.2	33.1	
	KMAC	2.3	<u>0.7</u>	
	Σ		40.8	84
Kerr-McGee	T102 btm	47.8		
	LSRC	65.4	9.7	
	SRC	60.7	32.3	
	KMAC	4.8	<u>1.5</u>	
	Σ		43.5	91
Conoco	T102 btm	22.7		
	LSRC	22.1	3.3	
	SRC	33.9	18.0	
	KMAC	4.9	<u>1.6</u>	
	Σ		22.9	101

Table 12

Material Balance of Benzene/Toluene Solubles
(Sum of Oils and Asphaltenes for the T102 Bottoms Samples)

Participant	Sample	Wt % oils + asph.	Wt % contribution	% recovery
WV	T102 btm	58.7		
	LSRC	99.7	14.9	
	SRC	79.0	42.0	
	KMAC	2.7	<u>0.9</u>	
	Σ		57.8	98
ICRC	T102 btm	55.3		
	LSRC	94.6	14.1	
	SRC	71.1	37.8	
	KMAC	4.1	<u>1.3</u>	
	Σ		53.2	96
Kerr-McGee	T102 btm	55.2		
	LSRC	96.9	14.4	
	SRC	69.3	36.9	
	KMAC	6.3	<u>2.0</u>	
	Σ		53.3	97
Conoco	T102 btm	54.1		
	LSRC	94.0	14.0	
	SRC	74.9	39.8	
	KMAC	9.1	<u>2.9</u>	
	Σ		56.7	105

Table 13

Material Balance of Preasphaltenes
for the T102 Bottoms Samples

Participant	Sample	Wt % preasph.	Wt % contribution	% recovery
WV	T102 btm	25.5		
	LSRC	0.3	0.0	
	SRC	20.5	10.9	
	KMAC	30.3	<u>9.7</u>	
	Σ		20.6	81
ICRC	T102 btm	28.5		
	LSRC	4.1	0.6	
	SRC	28.9	15.4	
	KMAC	34.3	<u>10.9</u>	
	Σ		26.9	94
Kerr-McGee	T102 btm	29.2		
	LSRC	3.1	0.5	
	SRC	30.7	16.3	
	KMAC	39.3	<u>12.5</u>	
	Σ		29.3	100
Conoco	T102 btm	24.3		
	LSRC	6.0	0.9	
	SRC	25.1	13.4	
	KMAC	10.6	<u>3.4</u>	
	Σ		17.7	73

Table 14

Material Balance of Residue
for the T102 Bottoms Samples

Participant	Sample	Wt % preasph.	Wt % contribution	% recovery
WV	T102 btm	15.8		
	LSRC	0	0	
	SRC	0.5	0.3	
	KMAC	67.0	<u>21.4</u>	
	Σ		21.7	137
ICRC	T102 btm	16.0		
	LSRC	0	0	
	SRC	0	0	
	KMAC	61.6	<u>19.7</u>	
	Σ		19.7	123
Kerr-McGee	T102 btm	15.6		
	LSRC	0	0	
	SRC	0	0	
	KMAC	54.4	<u>17.4</u>	
	Σ		17.4	112
Gonoco	T102 btm	21.6		
	LSRC	0	0	
	SRC	0	0	
	KMAC	80.6	<u>25.7</u>	
	Σ		25.7	119

Figure 1
Sampling Sites of SRC-I Process-Stream
Samples Used in the Round-Robin Study

Figure 2
Wilsonville's Sample Work-Up Scheme for
Dissolved Coal Slurry (V110)

NOTE: PREASPHALTENES = BENZENE INSOLUBLES - CRESOL INSOLUBLES.

Figure 3
Wilsonville's Sample Work-Up Scheme for Critical Solvent
Deashing Products and >850°F Distillate Residues

SAMPLES STUDIED: KMAC, LSRC, SRC, T102 BTM, V131A, 30170

NOTE: PREASPHALTENES = BENZENE INSOLUBLES – CRESOL INSOLUBLES.

Figure 4
Sample Work-Up Scheme Used by ICRC

Figure 5
Kerr-McGee's Sample Work-Up Scheme

NOTE: PREASPHALTENES = TOLUENE INSOLUBLES - RESIDUE.

Figure 6
Conoco's Sample Work-Up Scheme

Appendix VI-A

Determination of Percent Distillate by Vacuum Distillation
(Wilsonville Procedure No. 36025-9)

SCOPE: This method determines that fraction of the sample defined as solvent. Solvent refers to the hydrocarbon portion that can be distilled up to a corrected temperature of 925°F.

PRINCIPLE: The SRC, which is usually solid, is broken and then heated under 1-mmHg pressure to a final pot temperature of 600°F. Under these conditions, the solvent in the sample will be distilled.^a For deashing solvent determination, the receiver is immersed in a dry ice/methanol bath.

PROCEDURE:

- A. Sample is ground or broken; between 100 and 200 g is added to a tared distilling flask. Sample weight is recorded.
- B. Distillation flask is attached to an apparatus assembled as in Figure A-1.
- C. Vacuum is applied (0.1 mm or better).
- D. Apparatus is fully insulated with glass wool and the powerstats are turned on. Temperature is raised to the final temperature of 600°F.^c
- E. Powerstats are turned off and insulation is removed to facilitate cooling. To avoid explosions, sample must be cooled below 200°F before air is admitted to system.
- F. Distillation flask containing nondistillables is removed from apparatus and weighed. Weight difference from original sample weight is taken to be weight of solvent removed by distillation.

EQUIPMENT: Apparatus is illustrated in Figure A-1.

CALCULATION: $\% \text{ solvent} = \frac{(\text{sample wt} - \text{solvent-free residue wt}) \times 100}{\text{sample wt}}$

^aThis procedure may be modified readily to accommodate other SRC process samples (solid or liquid). For liquid samples (including various laboratory filtrates), the vacuum may have to be raised very slowly to prevent the lower boiling solvent fractions from flashing over. In some instances, an atmospheric cut to 600°F is necessary to prevent flashing. If, during any distillation, any part of the contents flashes over, the test must be rerun.

^bBefore vacuum is applied, a safety shield should be in position to protect the analyst from implosion and explosion. Do not manipulate the distillation apparatus while it is hot and evacuated--allow it to cool.

^cTemperature may be monitored manually using a thermometer (no mercury in thermometer) or by using a temperature controller including a thermocouple in conjunction with the heating mantles.

^dDepending on the time available for analysis and the degree of accuracy required, the percent solvent can be verified by using clean glassware and weighing each piece (Claisen head, adapter, receiver, tubing, and cold trap) before distillation. After distillation, reweighing of all apparatus should yield an additional weight equal to the loss of weight from the sample. Use of proper techniques should yield balances within 0.5 g.

Figure A-1
Apparatus for Vacuum Distillation
(Wilsonville Procedure No. 36025-9)

NOTE: CLAISEN HEAD IS WOUND WITH ASBESTOS TAPE AND HEATING WIRE (24 BS)

Appendix VI-B

Determination of Percent Cresol Insolubles in SRC Products
(Wilsonville Procedure No. 34550-21)

SCOPE: This test is designed to measure the cresol-insoluble solids in SRC.

PRINCIPLE: The procedure is based on fractional solubility in organic solvents. Because the solvent was selected to give the maximum solubility of extract, the insoluble residue represents, primarily, unreacted coal or similar material in the product. Strict adherence to all specified conditions is essential because of the empirical nature of the test.

APPARATUS: Beakers (300 mL)
Mechanical stirrer
Suction flask (100 mL)
Steam-jacketed Buchner funnel (15 cm)
Filter paper, no. 42 (15 cm)
Hot plate
Oven, 105 ± 5°C
Water aspirator
Wash bottle [for cresol (hot) methanol]
Analytical balance
Powder paper (glassine, 4-3/8 x 5-3/4, Eli Lilly Co.)

REAGENTS: Cresol
Acetone

PROCEDURE:

- A. Place 100 mL of cresol in a beaker and heat on a hot plate until vapors are visible.
- B. Prepare sample to -20 mesh. Do not crush too finely.
- C. Weigh 10-g sample on glassine paper.^a
- D. Add the sample, stirring constantly, to the hot cresol; stir the mixture for 0.5 hr. The sample can be weighed in a beaker and the hot cresol added to the sample while stirring.
- E. Weigh a No. 42 filter paper and prepare the steam-jacketed Buchner for filtering. Be sure the funnel is hot.
- F. Filter the sample and wash several times with hot cresol or until the sample does not look tacky.^b
- G. Turn off the steam and let the funnel cool. Wash the insoluble material with acetone until the sample is free of cresol.
- H. Dry the filter paper in the oven at 105°C for 30 min. Residue should be free of any cresol odor. Cool in a desiccator and weigh. Subtract weight of filter paper to obtain weight of insolubles.

CALCULATION:
$$\frac{\text{Weight of insoluble material}}{\text{weight of sample}} \times 100 = \% \text{ cresol insolubles}$$

^aSample size depends on the percent insolubles in the SRC. With a high percentage of insolubles present, a smaller sample can be used, and vice versa.

^bSome samples filter very slowly. When this occurs, a new, smaller sample should be used, or the sample should be stirred and heated for a longer period of time.

Appendix VI-C

Determination of Product Distribution by Soxhlet Extraction
(Wilsonville Procedure No. 34550-3)

- SCOPE:** This method is designed to characterize high-molecular-weight bituminous materials by separating them into three groups using solvents. Because results vary depending on conditions, the procedure is quite detailed and must be followed exactly. The method has been developed primarily to characterize coal extracts.
- PRINCIPLE:** Coal extracts are separated by solvent fractionation into the following high-molecular-weight fractions:
- A. Benzene insolubles: that fraction of the SRC that is insoluble in benzene at its atmospheric boiling point.
 - B. Asphaltenes: the fraction of the benzene-soluble SRC that is insoluble at room temperature in a mixture of 100 parts of pentane and 9 parts of benzene, when the ratio of the liquid mixture to the weight of benzene solubles is 100.
 - C. Oil: the benzene-soluble, pentane-soluble fraction of the SRC.
- EQUIPMENT:** Paper thimbles, 45 mm x 127 mm size, round-bottomed RA 98 type
 Soxhlet extractor
 Beaker A, a 600-mL Griffin beaker
 Beaker B, a 100-mL Berzelius beaker
 Beaker C, an 800-mL Griffin beaker
 Buchner funnel, with fritted disc, medium porosity, 150-mL capacity
 Wide mouth, 4-oz sample bottle
- REAGENTS:** Benzene, reagent grade
 Pentane, reagent grade
 Celite #545, analytical filter aid
 Tetrahydrofuran (THF)
- PROCEDURE:** A. Separation of Benzene-Insoluble Fraction
1. Grind an approximately 10-g sample to 100-200 mesh and place in a 1-oz bottle.
 2. Fill an alundum thimble (45 x 127 mm) with 1-2 g of celite #545. Place in a drying oven at 105°C and leave overnight. In the same manner, dry a 24-cm filter paper that has been folded into quarters.
 3. Remove thimble and filter paper from oven and place in desiccator to cool to room temperature. Then weigh the filter paper.
 4. Within 30 sec:
 - Weigh the thimble that contains celite.
 - Add 1-1.5 g of sample; weigh again. This is critical because weight gains of 1-25 mg have been observed in less than 1 min.
 5. Subtract weight of thimble and celite from weight of thimble, celite, and sample. This is the sample weight.
 6. Mix celite and sample by stirring with a microspatula. Caution: thimbles are fragile. Rinse any material left on the spatula into thimble with benzene (use less than 2 mL).
 7. Place thimble into soxhlet.

Appendix VI-C (Continued)

8. Put 3 boiling stones and about 250 mL of benzene into a 500-mL flask. Assemble soxhlet apparatus.
 9. Set powerstat to $-80-82^{\circ}\text{C}$ and turn on heat. Check carefully for overflow of thimble and plugging of capillaries as soon as reflux starts. Recycle at about 5-min intervals. Achieve a constant drop, not flow.
 10. After 3-4 hr of extraction, stop the apparatus; remove thimble and allow to drain in beaker. Careful! Remove any precipitate on outside of thimble by washing with benzene; transfer washings back into thimble.
 11. Stir material in thimble with a microspatula. Replace thimble in soxhlet and continue extraction.
 12. Stop the extraction (about 16 hr after initial 3-4 hr) after benzene comes through colorless.
 13. Allow soxhlet to cool and then drain.
 14. Remove thimble and air-dry in beaker.
 15. Place thimble in drying oven at 105°C for at least 4 hr, or overnight.
 16. Remove thimble and place in desiccator to cool to room temperature. Weigh and record weight. Subtract from the thimble/celite sample to obtain the weight of the benzene-insoluble fraction.
8. Separation of Benzene-Soluble, Pentane-Insoluble Asphaltene Fraction
1. Carefully transfer the contents of the 500-mL extraction flask into a Rotavapor evaporation flask. Rinse flask with benzene. Discard boiling stones.
 2. Remove solvent to dryness in Rotavapor.
 3. Redissolve residue with approximately 5 mL of tetrahydrofuran.
 4. Pour residue into beaker filled with 900 mL of n-pentane; stir constantly with magnetic stirring bar.
 5. Rinse flask with pentane and pour into the beaker. If necessary, use Teflon scraper to transfer all precipitate into the beaker. Do not exceed a total volume of 1,000 mL of n-pentane.
 6. Stir for about 5 min; remove the stirring bar immediately and let the precipitate settle for about 10-15 min.
 7. Place the dried, preweighed, 24-cm filter paper in a glass funnel and decant the supernatant through the filter. Then transfer the precipitate onto the filter, using additional pentane.
 8. Wash the filter with pentane; do not allow paper to dry. This is very important; otherwise, hard-to-remove oils will coat the paper. Wash with about 1,000 mL of pentane, or until the filter paper is white where the asphaltenes do not coat it.
 9. Let the filtrate drain from the filter; place the filter paper in a preweighed beaker and dry in the oven at 105°C overnight.

Appendix VI-C (Continued)

10. Remove filter paper from oven and allow to cool to room temperature in a desiccator.
11. Weigh and record. Subtract the weight of the filter paper to obtain the weight of asphaltenes.

C. Separation of Benzene-Soluble, Pentane-Soluble Oil Fraction

1. Remove the solvent from the filtrate in a Rotavapor until about 50 mL remains.
2. Transfer solvent into a preweighed beaker; rinse with a small amount of pentane.
3. Place beaker into drying oven at 105°C, let stand overnight, and then cool to room temperature in a desiccator.
4. Weigh and subtract the weight of the beaker to obtain the weight of the oils fraction.

D. Yield Calculations

To obtain the yields of the fractions, add the weights of oils, asphaltenes, and benzene insolubles (BI). Then divide this sum by the weight of the initial sample:

$$\text{Yield} = \frac{\text{wt of oils} + \text{wt of asph.} + \text{wt of BI}}{\text{wt of sample}}$$

The yield should be between 0.97 and 1.03. Then obtain the individual normalized weight-percent fractions:

$$\frac{\text{wt of oils}}{\text{wt of sample}} \times \frac{100}{\text{yield}} = \text{weight percent oils}$$

$$\frac{\text{wt of asph}}{\text{wt of sample}} \times \frac{100}{\text{yield}} = \text{weight percent asphaltenes}$$

$$\frac{\text{wt of BI}}{\text{wt of sample}} \times \frac{100}{\text{yield}} = \text{weight percent benzene insolubles}$$

Appendix VI-D

Vacuum Distillation of SRC-I Process-Stream Samples
(APCI Analytical Procedure No. 1161)

SCOPE: This distillation system is used to fractionate the total effluent generated by the SRC-I process. Selected fractions are collected to determine yield and are available for characterization studies.

PRINCIPLE: The fractions are obtained by distilling a quantity of effluent, usually 300-2,000 g, through a 15-theoretical-plate column. Conventional petroleum fractions, 420, 550, and 650°F, are removed at a 10:1 reflux ratio using normal distillation conditions. The solvent fraction, 650-1,000°F, is removed by using total liquid takeoff and increasing the temperatures of the column and head corresponding to the temperature rise of the pot. Reduced pressure is used to prevent degradation of the recovered products. An absolute pressure of 100 mm Hg is maintained to 550°F, 50 mmHg is maintained to 650°F, and the lowest pressure possible, which is usually below 1 mmHg, is maintained to 550°F. All fraction temperatures are measured at the head above the column except for the final fraction (1,000°F); the temperature in the flask at the lowest pressure is converted to a 1,000°F atmospheric equivalent. The simulated distillation technique including the American Society for Testing Materials D86 or D1160 correlation is used to determine the temperature profiles on all the fractions.

APPARATUS: A. Column

The column (Figure D-1) is constructed from a section of standard Pyrex glass tubing 25 mm internal diameter (i.d.) x 8 in. long. The middle 6 in. is packed with Reliance Glass Works Heli-Pak Packing, size 0.050 x 0.100 x 0.100 in. (stainless steel) (Catalog #3013, Reliance Glass Co., P.O. Box 825, Bensonville, Ill. 60106).

A 45/50 standard-taper male joint is joined to the bottom of the column for attachment of the pot, and the head assembly is joined to the top of the column. The column also incorporates a thermowell, which enters at the top of the packed section and extends to the center of the packing, close to the wall.

The total length (8 in.) of the column is lagged with No. 22 nichrome insulated heating wire spaced at 0.25-in. intervals; the power to the wire is controlled by a 10-A Variac. The column is then insulated to prevent heat loss.

B. Flask

The pot is a 500- or 2,000-ml round-bottomed flask with a 45/50 standard-taper female joint and a thermowell. Controlled heating is applied to the flask by using the appropriate Glascol heating mantle.

C. Head

The head (Figure D-2), a typical total condenser assembly with the capability of measuring vapor temperatures and controlling reflux ratios, was constructed by Air Products. The vapor path is lagged with No. 22 nichrome insulated heating wire spaced at 0.25-in. intervals, and a 10-A Variac controls the power to the wire.

D. Receiver

The receiver (Figure D-3) is a length of Pyrex tubing calibrated in 10-ml increments to 400 mL. The receiver can be attached to the head and to a vacuum system. Stopcocks are provided for raising the pressure to atmospheric pressure for draining and reevacuating to run pressure. The receiver was constructed by Air Products.

Appendix VI-D (Continued)

E. Auxiliary Equipment

1. Vacuum pump--Sargent Welsh Scientific Co., 33 Stern Ave., Springfield, N.J., Model 1400.
2. Magnetic stirrer--Corning Glass Works, Corning, N.Y. 14830, Hot-Plate Stirrer-PC351.
3. Closed-end mercury manometer, 0-200 mm--Air Products and Chemicals, Inc., Linwood, Pa. 19061. Drawing No. RS-349, Rev. 1.
4. Gilmanometer, low-pressure, mercury-tilt (0-5 mm)--Arthur H. Thomas, Vine & Third St., Philadelphia, Pa.
5. Nitrogen bleed valve, any fine-needle valve, 0.25-in. needle--Hoke Inc., Creskill, N.J. 07628.
6. Nitrogen rotameter, low-volume tube insert--Books Instrument Co., Hatfield, Pa. 19440.
7. Nitrogen regulator, low-pressure (10 lb), Model 2200--Air Products and Chemicals, Inc., Specialty Gases Division, Tamaqua, Pa.
8. Digimite--temperature readout, three needed, iron constantan, thermocouples rated at -300°F to +1,600°F--Thermo Electric Co., Saddle Brook, N.J. 07662.
9. Parr Instrument pressure reactor filter, Catalog No. 4551--Parr Instrument Co., Moline, Ill. 61265.

PROCEDURE: A. Operation (Refer to Figure A-5; Review Section D under This Category, Safety Precautions)

1. After melting and thoroughly mixing the sample to ensure sample homogeneity, weigh up to 2,000 g of sample into the appropriate tared 500- or 2,000-mL flask into which a stirring bar has been placed.
2. Activate magnetic stirrer at a reasonable speed.
3. Put water into head condenser and ice the dry ice trap.
4. Start vacuum pump and reduce pressure to 100 mm by using the nitrogen bleed system.
5. Apply heat to the flask through the heating mantle (see note 1 of operational notes). Adjust the heat to regulate the reflux return to the column to 165-180 drops per minute.
6. Position product takeoff stopcock so that 1 drop is collected as product, while 10 drops are returned to the column (10:1 reflux ratio).
7. Maintain these conditions (10:1 reflux ratio at 100-mm pressure) until head vapor rises to 420°F equivalent at this pressure (see operational note 2).
8. Close product takeoff stopcock, drain accumulated product into tared bottle, and weigh (see operational note 3).

Appendix VI-D (Continued)

9. Completely open stopcock and continue distillation using total takeoff until an atmospheric equivalent head-vapor temperature of 500°F is reached.
10. Return to a 10:1 reflux ratio, and make the cut point at 550°F atmospheric equivalent.
11. At the 550°F cut point, put the still on total reflux, isolate the receiver, and collect and weigh this cut as before.
12. If a 550-650°F fraction is desired, repeat steps 9 to 11 using 50-mmHg pressure (see operational note 4).
13. Turn off the heat to flask and cool the pot to 250°F. An external air jet may be used after initial cooling of flask.
14. Close nitrogen bleed and pump the still to lowest possible pressure (usually below 1 mm).
15. Adjust the heat to control drops from the head condenser as before, using a drop rate of 65-80 drops/min. Open the stopcock to the total takeoff mode. Maintain 65-80 drops/min to the product receiver. As the pot temperature rises, apply heat to both the column and the head to maintain their temperature equal to that of the pot.
16. When the pot temperature rises to an atmospheric equivalent of 1,000°F and column and head temperatures are at the same temperature, $\pm 10^\circ\text{F}$, maintain conditions until product stops coming over (about 10-15 min). This is the final cut point. If, before this condition is reached, the low-pressure manometer indicates that the pressure is rising, terminate the run immediately because this is a sign of decomposition. The cut point is acceptable even if only a 900°F equivalent head temperature is reached, because this should remove essentially all the solvent. The actual boiling range of the solvent is determined by simulated distillation.
17. As soon as heat is removed from the flask, raise the pressure to atmospheric with the nitrogen bleed. Immediately tap the pot free from the column.
18. Allow the flask to cool under a nitrogen blanket and then weigh.
19. To remove contents from the flask, chill the flask with liquid nitrogen and gently tap to break and dislodge the solid mass; transfer the solid to a suitable container.
20. Clean the column by refluxing 200 mL of pyridine. Repeat using a charge of acetone and then blow dry.
21. All products should be stored at 4°C under a nitrogen blanket.

B. Operational Notes

1. Flooding caused by too much heat may be quickly stopped by raising the pressure on the system with the nitrogen-bleed valve.
2. Solids that may build up in the head can be prevented by intermittently supplying water to the head condenser. Hold the condenser at approximately 150°F. Heat lamps must be used to keep the remainder of the product fluid.

Appendix VI-D (Continued)

3. To drain material from the receiver under vacuum, the receiver should be isolated from the rest of the system; then raise the pressure to atmospheric with a separate nitrogen source, drain, and reevacuate to run pressure before reintroducing to the system.
 4. The temperatures of cut points of fractions at times deviate from the standard cut points (int. 420-550-850°F). This procedure requires that, up to 650°F, a 10:1 reflux ratio is normally used with a pressure of 50 mmHg; total takeoff is used from 650 to 850°F (1,000°F equivalent) at the lowest possible pressure.
- C. Post Distillation Work-Up (Review Following Section on Safety Precautions)
1. Bottoms Work-Up
 - a. Grind the total bottoms that have been removed from the flask by breaking up the bulk; place the sample in a plastic bag and use a mallet. Further grinding with a mortar and pestle may be necessary; this grinding should be performed in a hood and use of a dust mask is advised.
 - b. Thoroughly mix the ground sample and remove approximately 90 g. Weigh the 90 g into the filter apparatus and add 1,200 mL of pyridine. Hold the temperature on the filter at 125°C for 1 hr; shake the filter frequently before positioning the apparatus in the filter mode. Allow filtering to continue at 2-3 lb pressure until liquid recovery ceases. Now add 400 mL of toluene to the filter to remove the residual pyridine.
 - c. Remove the filter cake from the filter, weigh, and dry in a vacuum oven at 100°C for 4 hr. Remove from oven and weigh the dried cake. This weight is the amount of insolubles and is reported as weight percent of the charge to the still.
 2. Pyridine Distillation to Recover SRC
 - a. Charge all of the pyridine plus SRC recovered from the filter back into the still.
 - b. Run at total takeoff conditions, as described earlier.
 - c. Use atmospheric pressure to a pot temperature of 400°F. Cool the still, reduce pressure to 150 mm, and continue removing product.
 - d. During the 150-mm pressure stage of the distillation, maintain the column and head temperatures at the pot temperature.
 - e. Bring all three temperatures to 400-425°F; hold this temperature until boiling stops in the flask.
 - f. Remove flask and recover solids as described earlier (Steps A-16 to A-20). This solids weight represents the amount of SRC in the charge, and may be calculated as a weight percent.
 - g. Recovered pyridine plus toluene should be discarded.

Appendix VI-D (Continued)

D. Safety Precautions

1. SRC products are harmful and may cause cancer.
2. Avoid all body contact with SRC products. If you do contact a product, wash thoroughly with soap and water. Do not use solvents to wash affected areas, because they encourage penetration into the skin.
3. Use respirator (type for hydrocarbons) and protective clothing when cleaning spills.
4.
 - a. Wear a complete set of clean work clothing every day (underwear, pants, shirt, and socks).
 - b. Do not wear shoes worn on the job for any other purpose.
 - c. Shower after every work shift.

Figure D-1
SRC Liquid Product Work-up Distillation Column

Figure D-2

SRC Liquid Product Work-up Distillation Head Assembly

Figure D-3
SRC Liquid Product Work-up Distillation
Receiver

Figure D-4
SRC Liquid Product Work-up Distillation
Flow Diagram

Appendix VI-E

Sequential Solvent Extraction
(ICRC Analytical Procedure)

SCOPE: This procedure is designed to separate a total product sample into the following fractions:

- oils: pentane soluble
- asphaltenes: pentane insoluble and benzene insoluble
- preasphaltenes: pyridine soluble and benzene insoluble
- residue: pyridine insoluble

This technique is carried out at room temperature under nitrogen, using high-quality solvent [pesticide or high-performance liquid chromatography (HPLC) grade]. The sample can be liquid, solid, or a mixture thereof, with less than 1% material boiling below 300°F. The reproducibility of the solvent-separation procedure on a total product liquid is exemplified by the following data:

	Mean (%)	Standard deviation ^a (%)
Oils	63.3	1.06
Asphaltenes	8.7	0.94
Preasphaltenes	9.7	1.23
Residue	18.2	0.31

^aThe result of five trials.

EQUIPMENT AND SOLVENTS REQUIRED:

Branson Model 350 Sonicator with 0.5-in. horn, or Heat Systems Model W375 Ultrasonic
 Millipore 142-mm pressure filter with 1,500-ml capacity; No.'s XX42-142.35 and YY-30-142-35 with 142-mm filter, 5-mm LSWP 142-50
 Glass, stainless-steel, or Teflon tubing can be used for solvent-transfer lines
 Four round-bottomed distilling flasks (1 L)
 Rotary evaporator RE 120, WWR No. 27582-406
 Vacuum pump and trap
 Nitrogen gas (0-20 psi adjustable), pressure-filter feed
 Nitrogen gas (0-20 psi adjustable), rotovapor feed
 Nitrogen liquid (1-2 L), freeze sample (Dewar)
 Solvents: n-pentane, benzene, pyridine, methanol, or methylene chloride. Grade of solvent depends upon ultimate use of sample subfractions. Pesticide, distilled in glass, or HPLC grade are acceptable.
 Fume hood, 150-200-cfm air-exchange rate
 Cooling water or heat exchanger for rotary evaporator condenser
 Balance to read weights to ± 0.005 g or better with maximum load of 500 g
 Glass Millipore, 47 mm, Model No. xx15047-00 with 5-mm No. LSWG-04700

SAFETY FEATURES:

Solvents must be used only under the fume hood. Workers must wear protective gloves and overalls for laboratory work. Hands can be mildly scrubbed with waterless hand cleaner, followed by a warm water wash. All normal safety precautions must be observed during the entire operation.

Appendix VI-E (Continued)

SAMPLE HANDLING FOR TOTAL PRODUCT LIQUIDS:

The sample selected for this procedure must represent the process unit output. Great care must be used to isolate about 5 g of gross product. Hot samples may be obtained in 8-oz glass jars.

The sample must be kept free of air (oxygen), heat, and light. Samples not ready for separation should be stored at 4°C under a blanket of nitrogen. Samples may be warmed to 65°C in the jars in an oven for 15 min and then sonicated for 15 min to induce good mixing just before a 5-g sample is procured for actual work-up.

PROCEDURE:

A. Prepare the laboratory equipment in the following order:

1. Weigh the jar containing the sample and the jar lid, record the weight, and sonicate the sample for 15 min. Mix the sample with a spatula and reweigh. Record any loss in weight as the weight of the light ends. Clean off spatula and sonicator horn by placing a tared 250-mL beaker with 200 mL of CH_2Cl_2 under the sonicator for 6 min. Evaporate CH_2Cl_2 by placing the beaker on a hot plate (at setting 2 or 3) for 1 hr. Record differences in beaker weight and subtract from weight of light ends.
2. Put Millipore filter in place after weighing the dry filter element. Ensure that all Teflon o-rings (and viton gasket) fit well, without leaks (test with n-pentane under 10 psi). No silicone gaskets or grease should be used in filter apparatus!
3. Prepare rotary evaporator bath temperature at 55-60°C for n-pentane; nitrogen flow rate should cause just a 0.25-0.5-in. dimple in the liquid in a 1-L flask.
4. Temperature of cooling liquid for rotary evaporator condenser should be less than 10°C.
- B. Tare a 600-mL heavy-walled Pyrex beaker and then add about 5 g (± 0.01 g) of the desired coal-derived sample. Obtain the sample as soon as possible after sonication, so that it is liquid. Slowly add about 100-150 mL of liquid nitrogen to the beaker to maintain a quiet solution. The total volume of liquid nitrogen used may exceed 300 mL.
- C. With a Pyrex glass stirring rod (3/8-in. diameter), grind the frozen sample to a fine powder. This step requires 5-8 min. Fill the beaker with more liquid nitrogen to maintain a volume of at least 30 mL during grinding.
- D. Allow the liquid nitrogen to evaporate to just above the solid mixture. Slowly add 100 mL of n-pentane; continue adding another 400 mL of pentane (to a total of 500 mL of pentane). Sonicate for 5 min at the 50% power level dial.
- E. Prior to decanting, wipe outside of beaker to remove water condensate. Decant supernatant into filter unit, refill beaker with 500 mL of n-pentane, and sonicate again for 3-5 min. Allow decant liquid to filter into a 500-mL flask. To ensure complete recovery of oils, do not allow filter to dry from this time on.

Appendix VI-E (Continued)

- F. Repeat step E five to eight times. If catch flask fills, transfer contents to rotary evaporator flask and begin to remove n-pentane under nitrogen at about 60°C. Transfer the solids from beaker onto the filter with small portions (25-50 mL) of pentane and wash sonicator probe and filter with pentane. Then wash sonicator again for 5-8 min with pure benzene. Set original sample aside for benzene extraction. (Do not discard beaker; hold for additional transfer of solvents to filter. This ensures removal of maximum amount of material and reduces loss.)
- G. Filter the solids, adding nitrogen pressure (5-10 psi) if needed. (The solvents can be collected from the rotary evaporator unit during the continuous solvent removal steps.)
- H. Continue solvent filtering using pentane (about 5-20 L) in a clean beaker, until the filtrate is a very light yellow. At the end of pentane extraction, switch collection flasks and add the benzene from the original sample beaker (step F).
- I. The pentane solubles from steps G and H should be held on the rotary evaporator for 2 min after the last drop of pentane has condensed in the catch flask. Remove from the rotary evaporator, clean and dry the outside of the flask, and weigh. From the difference on tare, obtain the yield of oils as x grams. Store the oils in a refrigerator at 4°C.
- J. Now extract benzene, similarly to steps G-I. Rotary evaporate in a new 500-mL, tared, round-bottomed flask under vacuum (15-20 in.) at 80°C to remove benzene. Keep adding 500-mL aliquots (totaling 5-20 L) until the filtrate is a very light yellow. Remove the flask containing benzene solubles from the rotary evaporator when two-thirds of the inner flask is evenly coated; freeze the solution in place. Quickly transfer the flask to a vacuum line (1 mmHg) with a trap, and allow flask to stand unheated to freeze-dry (sublime) the benzene in about 2 hr. Calculate the yield of asphaltenes as x grams. [If weight recovery is greater than 100%, proton nuclear magnetic resonance (¹H NMR) may be used to detect either pentane (oils), benzene (asphaltenes), or pyridine (preasphaltenes). Use CD₂Cl₂ and a 10% sample size.]
- K. After the last benzene extraction, start adding pyridine (total 5-20 L) and continue extracting as in steps G-I. Extract pyridine until the filtrate is light beige. Rotary evaporate the solvent to dryness at 100°C under 20 psi vacuum pressure. Clean rotary evaporator and condense by placing 300-500 mL of methylene chloride in a 1-L flask and rotary evaporating; discard as waste. Place 500 mL of methanol into the flask containing the pyridine solubles and shake. Pour onto a tared 47-mm Millipore glass filter (the filter may be weighed in an aluminum dish) and continue adding methanol, while shaking and scraping the flask until most of the preasphaltenes are on the filter. Wash with 100 mL of pentane to remove the methanol, which is vacuumed off. Allow filter to dry on hot plate before weighing. Reweigh rotary evaporator flask to check flask tare. Record yield of preasphaltenes as x grams.
- L. Let the residue dry in place after washing with 500 mL of methanol, 500 mL of methylene chloride, and 500 mL of pentane. Dry the filter using N₂ pressure and weigh to obtain the yield of residues as x grams.

M. Oils	A
Asphaltenes	B
Preasphaltenes	C
Residue	D
	+
	Total recovered

Original mass of sample = MS

MS - total recovered = net loss or gain

Appendix VI-E (Continued)

If weight gain is observed, leave solvent in oils or asphaltenes and test with NMR. If weight loss is observed, oils have too much volatile matter.

Results should not be reported unless >97% material is recovered. Repeat the analysis.

Add net loss to mass of oils (A + net loss) and calculate material recovery.

	<u>Recovered</u>	<u>Corrected</u>	<u>%</u>
Report: Oils	A	A + net loss	_____
Asphaltenes	B	B	_____
Preasphaltenes	C	C	_____
Residue	D	D	_____
	<u>Total recovered</u>	MS	<u>100%</u>

Samples derived during the coal conversion process can now be compared with a high degree ($\pm 1\%$) of reliability, within 10-14 hr. After the classical separation has been made, the subfractions can undergo first-level chemical characterization.

Appendix VI-F

Determination of Distillables by Vacuum Distillation
(Kerr-McGee Procedure No. ACL85-3)

INTRODUCTION: This method is used to determine the percentage of distillable organic matter in a coal-derived feed or product. The sample is distilled at a pressure of about 0.1 mmHg and a distillation pot temperature of 600°F.

SAFETY: In this procedure, the apparatus must be evacuated to 1 mmHg. Care must be taken to prevent injury from implosion.

EQUIPMENT: Distillation flask with thermowell
Column
Condenser
Product receiver
Heating mantle
Thermometers for measuring vapor and pot temperature
McLeod gauge for pressure measurement
Heat tape
Rheostats for controlling temperature

METHOD:

- A. Place a small plug of glass wool in the distillation flask thermowell and insert the thermometer.
- B. Tare the distillation flask, column, condenser, and product receivers.
- C. Measure about 100 g, weighed to the nearest 0.01 g, into the distillation flask.
- D. Lubricate the spherical joints of the distillation apparatus with a high-temperature silicone grease and connect the joints of the apparatus. Clamp the joints by means of adjustable spring clamps.
- E. Wrap the neck of the distillation flask and the column with heat tape and insulate with fiberglass wool.
- F. Start the vacuum pump and evacuate the apparatus to about 0.1 mmHg to degas the sample and then increase the pressure to about 5 mm to start the distillation.
- G. Turn on the heater and heat tracing and set the rheostats at about 60%. This will give a temperature increase of about 5°C/min.
- H. After the sample starts to melt, the distillation flask temperature will increase rapidly. Evacuate the apparatus to 0.1 mmHg after the sample is melted.

Appendix VI-F (Continued)

- I. Adjust the heat tracing so that the vapor temperature in the head is from 10 to 20°C less than the temperature in the distillation flask.
- J. During distillation, it may be necessary to use heat lamps and steam in the condenser jacket to keep the distillate fluid enough to flow into the receiver.
- K. Continue distillation until the distillation flask has reached 600°F at a pressure of 0.1 mmHg.
- L. Continue distillation at settings of (11) for 1 hr.
- M. After the end point has been reached, cool and disassemble the apparatus. Weigh and record the weights of the distillation flask, column, condenser, and receiver.

REPORTING: Report the percent of distillable (sample basis) in the column, condenser, and receiver. Also report the total percent distilled (sample basis), which is the sum of the three percentages previously reported.

Appendix VI-G

Beaker Extractions
(Kerr-McGee Procedure)

DEFINITIONS: Three fractions are defined as follows:

- Oil: Toluene and heptane soluble; determined as the difference between toluene-soluble and asphaltene content
- Asphaltene: Toluene soluble/heptane insoluble; determined directly as a heptane-insoluble residue
- Preasphaltene: Pyridine soluble/toluene insoluble; determined as the difference between the two solubilities

PROCEDURE:

- A. For both pyridine and toluene solubility procedures, digest a 10-g sample for 30 min at the solvent boiling point using a 10:1 solvent-to-feed ratio.
- B. Vacuum-filter the solutions hot through a Buchner funnel using Whatman No. 42 paper.
- C. Rinse residues with the digestion solvent and then with heptane (toluene digestion) or toluene/heptane (pyridine digestion).
- D. Determine the asphaltene content by evaporating the toluene-soluble filtrate to near-dryness on a steam bath, followed by heptane digestion and filtration.
- E. Calculate solubilities as follows:

$$\% \text{ soluble (by wt)} = \frac{\text{sample net wt} - \text{residue net wt}}{\text{sample net wt}} \times 100$$

For those samples with significant ash content (i.e., >5%), also calculate solubilities as follows:

$$\% \text{ soluble (by ash)} = 100 - \frac{\% \text{ ash (original sample)}}{\% \text{ ash (digestion residue)}} \times 100$$

The two solubility values should agree within 1%; the reported value is then taken as the average of the two solubility calculations.

Appendix VI-H

Vacuum Distillation (Conoco Procedure)

Distillations were performed in a micro-still equipped with a 50-mL pot and a ca. 9 x 1 cm column using 15 to 20 g of whole sample. Pot, column, and head (modified Claisen) were all at 290°C, giving essentially a single-plate distillation. The distillation balance is the sum of resid and distillate (including column hold-up) divided by the initial weight. For full details, see Burke and Winschel, 1982.

Appendix VI-I

Beaker Extractions (Conoco Procedure)

THF extractions were performed at ambient temperature in a pressure filter using Whatman #42 paper until the filtrate was colorless. The THF was removed from the filtrate by rotary evaporation. Samples (ca. 5 g) were either distillation bottoms or whole samples, if no distillate was assumed. The material balance of this step is 100% because results are by difference. For full details, see Burke and Winschel, 1982.

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2. DEVELOPMENT OF METHODS TO CHARACTERIZE SRC-I PROCESS SAMPLES:
DISTILLATION AND SOXHLET EXTRACTION PROCEDURES
USED BY WILSONVILLE PILOT PLANT

INTRODUCTION

Two analytical procedures used at the Wilsonville Pilot Plant were reviewed and reproduced at ICRC: (1) vacuum distillation, a test to determine the amount of distillate (<850°F) in an SRC-I process stream sample; (2) solvent fractionation by Soxhlet extraction, a test to determine the amount of benzene-insoluble material in an SRC-I process sample. ICRC's vacuum distillation yielded a reproducibility of ± 4 wt % absolute, whereas Soxhlet extraction exhibited a reproducibility of $\pm 3-6.5$ wt %. The poorer reproducibility of the Soxhlet method was due to the innate nature of the procedure.

VACUUM DISTILLATION

Vacuum distillation (Wilsonville procedure no. 36025-9) determines the amount of distillable material (<850°F) that can be obtained at reduced pressure. Wilsonville uses this technique to analyze distillates and distillation bottoms from the SRC-I process streams. See Kingsley and Schweighardt (1982) for a complete description of the process.

Results

Figure 1 illustrates ICRC's setup of procedure no. 36025-9. Reproducibility was determined by seven replicate distillations of a light solvent-refined coal (LSRC) sample. Results are listed in Table 1; the standard deviation of the data is 2.1 wt %. For the identical sample, Wilsonville determined a comparable reproducibility, 3.1 wt % standard deviation.

The repeatability of Wilsonville's results at ICRC was established by distilling seven different process stream samples (from Wilsonville

material balance run 220B) in triplicate and comparing the results with duplicate results obtained at Wilsonville (see Table 2). Means ($\bar{x}$) and standard deviations (s) were calculated for each sample. The pooled standard deviation (s_p), calculated from equation 1, showed that the precision of results obtained by both laboratories is comparable.

$$s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \dots}{(n_1 - 1) + (n_2 - 1) + \dots}} \quad (1)$$

A linear regression analysis of the means is illustrated in Figure 2. The solid line represents the values calculated from equation 2:

$$\text{wt \% ICRC} = 0.98 \text{wt \% WV} + 3.3 \quad (2)$$

The results give a correlation coefficient (r) of 0.997. The broken line represents perfect agreement between the results from both laboratories. The data points are close to the broken line, demonstrating that vacuum distillation results from both facilities are comparable.

Conclusion

The precision of ICRC's reproduction of Wilsonville's vacuum distillation is ± 3 wt % at the 95% confidence limit. The distillate results obtained by ICRC are the same as those obtained by Wilsonville within ± 4 wt %. It is believed that this agreement is acceptable for making analytical comparisons of the data from both laboratories.

SOXHLET EXTRACTION

Wilsonville uses Soxhlet extraction (procedure no. 34550-3) to determine the amount of benzene-insoluble material in an SRC-I process stream sample. After Soxhlet extraction, the benzene-soluble material is fractionated into oils and asphaltenes with pentane; this procedure is considered an integral part of Wilsonville's overall method. Thus, Wilsonville's technique yields the weight percents for benzene insolubles, oils, and asphaltenes in an SRC-I process stream sample.

Procedure

ICRC observed Wilsonville's Soxhlet extraction procedure directly and then set up the apparatus at its laboratory (see Figure 3). As discussed in previous reports (Lamb and Kingsley, 1981; Kingsley and Schweighardt, 1982), the procedure consists of two major steps:

1. The ground SRC-I process stream sample is extracted with benzene in a Soxhlet extraction apparatus for 16 to 24 hr, or until a clear extract is observed; this yields a benzene-insoluble residue and benzene-soluble extract.
2. The benzene-soluble fraction is placed in a beaker containing a large volume of pentane; asphaltenes are precipitated and the oils are solubilized.

Note that ICRC modified the Wilsonville procedure (34550-3) for safety reasons, as follows:

- ° Step 38: The beaker containing the pentane and oils filtrate was placed in a 30°C dry bath in a hood under a stream of nitrogen until all the pentane was removed.
- ° Step 40: Methylene chloride was removed from the oils fraction by placing the beaker in a 30°C dry bath in a hood under a steady stream of nitrogen. The beaker was removed 1 hr after the contents were dry.

Results

ICRC analyzed four Wilsonville SRC-I process stream samples in triplicate. Table 3 compares the analytical results to results from Wilsonville's duplicate analyses.

Standard deviations (s) and pooled standard deviations (s_p) for both laboratories for each fraction were determined using equation 1 (see Table 4). ICRC's results show precision in the 95% confidence limit of 1.4-3.0 wt %, whereas Wilsonville's results show 3.4-5.0 wt %

precision. For both laboratories, the benzene-insoluble fraction had the lowest pooled standard deviation (s_p), indicating that the initial step, Soxhlet extraction of a sample with benzene, is more reproducible than the second step, beaker precipitation of asphaltenes.

Table 5 compares mean analysis results for both laboratories. Linear regression analysis was performed, and the slopes (A), intercepts (B), and correlation coefficients were obtained from equation 3:

$$\text{wt \%}_{\text{ICRC}} = A \times \text{wt \%}_{\text{WV}} + B \quad (3)$$

When the correlation coefficients for benzene insolubles, asphaltenes, and oils are compared, that for the benzene insolubles is closest to 1.000, indicating that benzene insolubles determined by Wilsonville can be correlated with benzene insolubles determined by ICRC. The positive intercept with a slope of 1.03 indicates that Wilsonville's results for benzene insolubles are lower than those measured by ICRC. Using the linear regression equation (3), the calculated weight percents of the benzene insolubles can be determined within 4 wt % absolute.

Linear regression analysis of the oils fraction showed good comparability--the correlation coefficient is 0.996. Using equation 3, the calculated weight percent of oils in an SRC-I sample can be determined within 3 wt % absolute.

Linear regression analysis of the asphaltenes fraction showed a correlation coefficient of 0.979; the calculated weight percent of asphaltenes using equation 3 could be determined only within 6.5 wt % absolute.

Conclusion

Wilsonville's Soxhlet procedure consists of two major steps: (1) generation of benzene insolubles and (2) generation of oils and asphaltenes. Wilsonville's data for benzene insolubles can be reproduced at ICRC within 4 wt % absolute using the average of three analyses, and the oils results can be reproduced within 3 wt % absolute using the average of three analyses. However, the asphaltenes results can be reproduced

at ICRC only within 6.5 wt % absolute, also using the average of three analyses. When data from ICRC's coal process development unit are correlated with Wilsonville's data using the Wilsonville Soxhlet extraction procedure, these limits of precision for each fraction must be considered.

ACKNOWLEDGMENT

The authors wish to thank Ron Ammons of Catalytic, Inc. and Jeff Rabe of ICRC for their excellent contributions to this work. Special thanks are extended to Shirley Dukett, who modified Wilsonville's Soxhlet extraction procedure as noted and skillfully conducted the Soxhlet extractions and beaker precipitations.

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Table 1
 Reproducibility of Vacuum Distillation
 Procedure on an LSRC Sample

	wt % distilled	$\bar{x}^a$	s^b
ICRC	38.1		
	36.4		
	36.5		
	39.2	37.4	2.1
	35.9		
	34.8		
	40.7		
WV	38.5		
	34.1	36.3	3.1

^aArithmetic mean.

^bStandard deviation.

Table 2
Results of Vacuum Distillation

Process stream sample		Wilsonville			ICRC		
No.	Stream	wt % dis- tillate	$\bar{x}$	s	wt % dis- tillate	$\bar{x}$	s
67244	30/70 ^a	75.1			84.3		
		81.1	78.1	4.2	82.6	83.7	0.95
					84.2		
67245	KMAC ^b	2.8			4.2		
		3.8	3.3	0.7	1.2	3.5	1.67
					5.1		
67246	V131A				3.6		
		98.7			98.6		
		98.7	98.7	0	98.4	98.9	0.70
67247	LSRC				99.7		
		38.5			38.1	35.9	
		34.1	36.3	3.1	36.4	34.8	37.4
67248	SRC				36.5	40.7	2.06
					39.2		
		11.4			15.9	19.2	
67249	T102 btm ^c	10.5	11.0	0.6	17.7	15.9	16.2
		11.4			16.3		
		13.5	12.5	1.5	17.6	18.1	0.40
67250	V110				18.3		
		57.6			57.9		
		55.7	56.7	1.3	55.8	56.9	1.48
Pooled							
standard deviation (s_p)				1.5			1.3

^aThe 30/70 sample was a laboratory-prepared mixture of 30 wt % light solvent-refined coal (LSRC) and 70 wt % process solvent (V131A).

^bKMAC, Kerr-McGee ash concentrate.

^cT102 btm, feed to the critical solvent deashing unit.

Table 3

Comparison of Soxhlet Results from Wilsonville and ICRC

Sample	No.	wt % ben- zene insolubles		wt % asphaltenes		wt % oils		% recovery	
		WV	ICRC	WV	ICRC	WV	ICRC	WV	ICRC
LSRC	78818	0.9	1.5	43.9	41.7	55.2	54.4	95.8	97.6
		1.0	1.4	38.9	44.7	60.1	51.6	93.7	97.7
			2.1		45.5		56.2		103.8
SRC	78817	17.1	24.1	56.2	47.8	26.7	23.8	93.5	95.8
		17.4	25.1	57.3	47.0	25.3	25.0	95.7	97.1
					49.0		23.6		99.4
KMAC	78819	91.2	97.1	4.2	2.7	4.6	3.6	101.6	103.5
		93.5	98.3	2.9	2.1	3.6	2.0	100.8	102.4
			98.3		1.8		1.4		101.5
T102 btm	78816	38.7	43.2	40.2	34.1	21.1	22.0	98.6	99.4
		42.8	43.8	35.5	33.2	21.7	22.5	99.6	99.6
			44.6		33.3	24.6			102.5

Table 4

Standard Deviation and Pooled Standard Deviations
of Soxhlet Extraction Data

	<u>Benzene insolubles</u>		<u>Asphaltenes</u>		<u>Oils</u>	
	WV	ICRC	WV	ICRC	WV	ICRC
LSRC	0.1	0.4	3.5	2.0	3.5	2.3
SRC	0.2	0.9	0.8	1.5	1.0	0.8
KMAC	1.6	0.7	0.9	0.5	0.7	1.1
T102 btm	2.9	0.7	3.3	0.5	0.4	1.4
s_p	1.7	0.7	2.5	1.3	1.9	1.5

Table 5
Reproducibility of Wilsonville Soxhlet Procedure at ICRC^a

Sample	No.	wt % ben- zene insolubles		wt % asphaltenes		wt % oils	
		WV	ICRC	WV	ICRC	WV	ICRC
LSRC	78818	1.0	1.7	41.4	44.0	57.7	54.1
SRC	78817	17.3	25.0	56.8	48.2	25.9	24.1
KMAC	78819	92.4	97.9	3.6	2.2	4.1	2.3
T102 btm	78816	40.8	43.9	37.9	33.5	21.4	23.0
Slope (A)		1.03		0.91		0.95	
Intercept (B)		3.31		0.30		-0.04	
Corr. coeff.		0.998		0.979		0.996	

^a wt % ICRC = A x wt % WV + B.

Figure 1
Apparatus for Vacuum Distillation
(Wilsonville Procedure No. 36025-9)

**NOTE: CLAISEN HEAD IS WOUND
WITH ASBESTOS TAPE AND
HEATING WIRE (24 BS)**

Figure 2
Linear Regression Analysis of Wilsonville and ICRC Vacuum
Distillation Results. Comparison of Distillate Yields.

$$\text{wt\% dist. (ICRC)} = 0.98 \times \text{wt\% dist. (WV)} + 3.3 \text{ (solid line)}$$

$$r = 0.997$$

Broken line indicates perfect agreement.

Figure 3
Schematic of Wilsonville Soxhlet Extraction Procedure

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3. ROUND-ROBIN STUDY OF DISTILLATION PROCEDURES

INTRODUCTION

ICRC conducted a round-robin study among four laboratories to compare and contrast three different distillation procedures used to quantify the amount of distillate (material boiling below 850°F). Each laboratory used its own distillation setup to distill a specially selected process stream sample from the pilot plant. The distillates were then analyzed by a unique method of encapsulated simulated distillation by gas chromatography (GCSD) to quantify the <850°F fraction of the sample.

Results showed that using different laboratory setups for the same distillation procedure will affect the amount of distillate generated; however, encapsulated GCSD will help to compensate for these differences and improve agreement between laboratory data.

EXPERIMENTAL METHODS

Sample Description

The sample analyzed was collected from the distillate bottoms of the vacuum distillation tower (T102 btms) in the SRC-I Pilot Plant (run no. 235). The T102 btms material is the feed to the critical solvent deashing unit [see Kingsley and Schweighardt (1982) for a diagram showing the sampling site]. The samples were sent to each of the four laboratories participating in this study in 1-gal lots and stored in air-tight containers under nitrogen at ca. 4°C until analysis.

Analytical Methods

Four laboratories participated in this round-robin study: Conoco, Wilsonville, Kerr-McGee, and ICRC/APCI. Each laboratory distilled the T102 btms sample by three different vacuum distillation procedures. Conditions for the three procedures are outlined in Table 1. In each method, the head temperature was maintained at 25°F below the pot temperature. Each laboratory used its own glassware and distillation setup

(see Table 2 for the major features). The procedure used by Wilsonville is detailed in Appendix VI-J, that used by APCI appeared in an SRC-I Quarterly Technical Report (Kingsley and Schweighardt, 1982), and that used by Kerr-McGee is described in Appendix VI-K. Weight percents of each of the three distillates were measured to allow direct comparison of yields and to compare the boiling ranges of the distillates from the four laboratories.

The distillates were then analyzed by encapsulated GCSD, a method that allows direct weight measurement of the "GC-nonvolatiles" and of the 850°F cut point from the GC-volatile fraction of each distillate (see Figure 1). The encapsulated GCSD procedure (detailed in Moyer, 1982) involved weighing a small amount of sample into an aluminum capsule, cold-welding the capsule, and transferring the sample to the heated injector zone of a gas chromatograph, where part of the sample was volatilized, i.e., the "GC-volatile" fraction. The capsule was then punctured and the "GC-volatiles" were swept by a stream of helium carrier gas onto the GC column. The capsule was ejected after GC analysis and reweighed to obtain the weight percent of the "GC-nonvolatile" fraction (residue).

The chromatographic result for the "GC-volatiles" was interpreted using American Society for Testing Materials (ASTM) method D-2887 employing paraffinic standards for boiling-point calibration, which allows conversion of the GC results into boiling-point cuts. Table 3 lists the gas chromatographic conditions.

Using the combined results from distillation and encapsulated GCSD, we calculated the fraction boiling below 850°F for each distillation technique used by each participant.

Figure 1 illustrates the fractions obtained from both the distillation and encapsulated GCSD procedures.

RESULTS

Distillation

Table 4 summarizes the weight percent yields from each distillation method, as well as the average results ($\bar{x}$) and standard deviations (s).

The data show that method I generally produced the highest distillate yield and method II the lowest. Such yields are consistent with differences in the procedures: 600°F pot temperature at 0.1 mm Hg vacuum for method I and 554°F pot temperature at 1 mm Hg vacuum for method II. A standard deviation of 10.5 for method I indicates that this distillation produced the most varied yields, apparently due to differences in the setups used by the four laboratories (see Table 2). For example, Kerr-McGee distilled a relatively small sample (25 g) in a large (1,000-mL) distillation flask, whereas all other laboratories used samples that were at least 10 times larger in 500-mL flasks. Kerr-McGee's yields were consistently higher.

Overall, the large scatter of results (ranging from 5 to 33 wt % distillate) indicates that a specific distillation procedure will not yield the same amount of distillate if the laboratory setup differs.

Encapsulated GCSD

All the distillates were analyzed by encapsulated GCSD; results are listed in Table 5. For this study, the distillate was defined as material boiling below the 850°F cutpoint (see Figure 1a). Results in Table 5 are expressed as the percent of distillate boiling below 850°F in the "GC-volatile" fraction of the sample (<850; see Figure 1c) and the weight percent residue (wt % R) in the initial distillate, which is the "GC-nonvolatile" fraction (Figure 1b).

Results were calculated by multiplying the <850 fractions from Table 5 by the "GC-volatiles" of the distillate sample (100 -wt % R), we obtained the percent of the total fraction of distillate boiling below 850°F. These results are listed in Table 6.

Earlier work (Kingsley and Schweighardt, 1981) indicated that chromatographing distillates with lower boiling ranges is advantageous, because of the chromatographic tailing effect of heavier compounds. In this study, therefore, a distillate having its major fraction in the <850°F cut should give better GC results than one containing its largest fraction in the >850°F cut. The results in Table 6 show that more than 50% of all of Kerr-McGee's distillates boiled above 850°F, whereas distillates from the other laboratories contained a smaller fraction of

material boiling above 850°F. Thus, the Kerr-McGee distillates are higher boiling distillates, indicating that Kerr-McGee's setup generated a sample that was less suitable for routine GC analysis. Note: Such high-boiling fractions can be analyzed properly only by considering limitations of the gas chromatographic system, such as the thermal stability of the GC column. High-boiling fractions tend to show tailing toward the end of the chromatogram; this can be an indication of incomplete chromatographic elution, which can cause inaccurate area integration and, therefore, give invalid boiling-point distribution results.

Calculation of Total <850°F Distillate in the T102 Btms Sample

To combine the distillation results with the encapsulated GCSD results, the percent of material boiling below 850°F in the initial sample for each distillation was calculated using equation 1:

$$\% <850^{\circ}\text{F material} = \frac{(<850)}{100} \frac{\text{wt \% distillate}(100 - \text{wt \% R})}{100} \quad (1)$$

The <850°F fraction and wt % R are defined in Table 5. Table 7 shows the total percents of <850°F material. The combined results show a much smaller scatter ($\pm 2\%$) than those reported in Table 4 for distillation only ($\pm 10\%$), for the same distillation procedure. Distillation II in combination with encapsulated GCSD showed the lowest standard deviation ($\pm 1\%$), indicating that results from this method are the least sensitive to a particular laboratory setup. However, distillation II also yielded the least <850°F material, indicating that some <850°F distillate may have remained in the distillate bottoms. Therefore, the pressure (1 mm Hg) and final pot temperature (554°F) are insufficient to drive all <850°F material into the distillate portion of the sample.

CONCLUSIONS

The results can be summarized as follows:

- ° Four different laboratory setups using the same distillation procedures yield significantly different amounts of distillate.
- ° Results from distillation under mild conditions (554°F, 1.0 mm Hg) are less affected by variations in the laboratory setup; however, this method also generates less distillate and is unsuitable for determining the 850°F cut point.
- ° Distillation under severe conditions can produce a distillate that is unsuitable for GC analysis and cannot be used to quantify a specific cut point.
- ° Encapsulated GCSD can be used to measure the amount of nonvolatiles and volatiles in a laboratory distillate to account for differences in the laboratory setups.
- ° A combination of distillation and encapsulated GCSD provides the most precise characterization of <850°F distillate, and eliminates the discrepancies due to variations in laboratory setups.

The results from this round-robin study were discussed at a joint meeting of the participants; highlights of the discussion are included in Appendix VI-L.

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Table 1
Conditions for Three Distillation Procedures
Analyzed in Round-Robin Study

Condition	Distillation method		
	I	II	III
Final pot temperature (°F) ^a	600	554	500
Pressure (mm Hg)	0.1	1.0	0.1
End point (°F) (measured at pot temperature)	600	554	500, hold 1 hr

^aPot temperatures adjusted to atmospheric pressure are 1,370, 1,250, and 1,245°F for methods I, II, and III, respectively (according to Maxwell and Bonnell, 1955).

Table 2
Major Features of Distillation Setups in Each Laboratory^a

Laboratory	Column	Charge (g)	Size of dist. flask (mL)
(A) Conoco	Packed, heated head	400	1,000
(B) Wilsonville	Flash, short head wrapped	200	500
(C) Kerr-McGee	Flash, short head wrapped	25	500
(D) ICRC/APCI	Packed, reflux	300	500

^aFor analytical details, see Appendixes 1 and 2 and Kingsley and Schweighardt, 1982.

Table 3
Operating Conditions for Encapsulated GCSD

Sample weight	1 mg
Injector temperature	300°C
Column dimensions	36 in. x 1/8 in. outer diameter, stainless steel, dual
Packing	3% Dexsil 300 on 80/100 mesh Chromosorb W, acid-washed
Initial temperature	-30°C
Final temperature	380°C
Programming rate	16°C/min
Carrier gas	Helium, purified by catalytic dryer and oxysorb
Carrier flow	50 cm ³ /min (80 psig)
Detector temperature	350°C
Detector	Dual differential flame ionization detectors
Injection	AS-41 capsule injection

Table 4
Weight Percent Distillate from Each Distillation Procedure

Laboratory	Distillation method ^a		
	I	II	III
(A) Conoco	14.8	6.4	5.0
(B) Wilsonville	11.9	9.4	9.3
(C) Kerr-McGee	32.3	11.4	20.5
(D) APCI/ICRC	9.1	4.9	11.1
$\bar{x}$	17.1	8.0	11.5
s	10.5	3.0	6.5

^aThe reproducibility of any one distillation procedure at any one laboratory was less than ± 1 weight percent on average.

Table 5
Uncorrected Results from Encapsulated GCSD

Laboratory	Distillation method ^a					
	I		II		III	
	<850 ^b	wt % R ^c	<850 ^b	wt % R ^c	<850 ^b	wt % R ^c
(A) Conoco	57	2.0	79	2.4	81	1.9
(B) Wilsonville	68	5.7	64	2.9	72	2.4
(C) Kerr-McGee	32	3.7	47	4.2	44	9.4
(D) APCI/ICRC	63	1.7	83	10.6	62	2.5

^aThe reproducibility of the simulated distillation procedure is less than $\pm 2\%$.

^bPercent of the <850°F cut from the portion of distillate that was volatilized in the GC.

^cWeight percent of distillate that was not volatilized in the GC.

Table 6

Percent of Total Fraction of Distillate Boiling below 850°F
from Each Distillation Method Determined by Simulated Distillation

Laboratory	Distillation method		
	I	II	III
(A) Conoco	56	77	80
(B) Wilsonville	64	62	71
(C) Kerr-McGee	30	45	40
(D) APCI/ICRC	62	75	60

Table 7

Total Weight Percent of Distillate (<850°F) of T102 Btm Sample
after Adjustment by Encapsulated GCSD

Laboratory	Distillation method		
	I	II	III
(A) Conoco	8.2	4.9	4.0
(B) Wilsonville	7.5	5.8	6.5
(C) Kerr-McGee	9.6	5.1	8.1
(D) APCI/ICRC	5.6	3.6	6.7
$\bar{x}$	7.7	4.8	6.3
s	1.7	0.9	1.7

Figure 1
Diagram of Fractions Obtained from the
T102 Btms Sample by Distillation
and Gas Chromatographic Analysis

Figure 2
Distillation Curves from Encapsulated
GCSD Data for APCI Distillate (Lab D)
and Kerr-McGee Distillate (Lab C) by
Distillation Method I

Figure 3
Distillation Curve from Encapsulated
GCSD Data for the Original
T102 Btms Sample

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Appendix VI-J

Vacuum Distillation Procedure Used at Wilsonville Pilot Plant

SCOPE:

This method determines that fraction of the sample defined as solvent, that is, the hydrocarbon portion that can be distilled up to a corrected temperature of 925°F.

PRINCIPLE:

The SRC, which is usually solid, is crushed and then heated under 0.1 mm Hg to a final pot temperature of 600°F. Under these conditions, the solvent in the sample will be distilled. For deashing solvent determination, the receiver is immersed in a dry ice/methanol bath (see note A).

PROCEDURE:

- a. Grind or crush sample and add between 100 and 200 g to a tared distilling flask. Record sample weight.
- b. Attach distillation flask to an apparatus assembled as shown in Figure J-1.
- c. Apply vacuum (0.1 mm or better). (CAUTION: See note B.)
- d. Fully insulate apparatus with glass wool and turn on the powerstats. Raise temperature to the final temperature of 600°F. (See note C.)
- e. Turn off powerstats and remove insulation to facilitate cooling.
CAUTION: Sample must be cooled below 200°F before air is admitted to system to avoid explosions.

Appendix VI-J (Continued)

- f. Remove flask containing solvent-free extract from apparatus and weigh. Weight difference from original sample weight is weight of solvent removed by distillation. (See note D.)

EQUIPMENT: See apparatus shown in Figure J-1.

Temperature controller

500-cm³, one neck, 24/40, round-bottomed flask with thermometer well

GG Claisen head, 24/40

Adapter gg with vacuum adapter and drip tip

250-cm³ gg receiver flask

Two cold traps

McLeod vacuum gauge

500-mL spherical heating mantle

Two dry ice cold baths

Surge tank piping and valving

Vacuum pump capable of pulling 0.1 mm or better

Thermometer

CALCULATION: % solvent = $\frac{(\text{sample wt} - \text{solvent-free residue wt}) \times 100}{\text{sample wt}}$

REMARKS:

Note A: This procedure may be modified readily to accommodate other solid or liquid SRC process samples. In the case of liquid samples (including various laboratory filtrates), it may be necessary to raise the vacuum very slowly to prevent the lower boiling solvent fractions from flashing over. In some instances, an atmospheric cut to 600°F is necessary to prevent flashing. If any part of the contents flashes over during distillation, the test must be rerun to prevent inaccurate determination of the amount of distillate.

Appendix VI-J (Continued)

Note B: Before vacuum is applied, a safety shield should be positioned to protect the analyst from dangers of implosion and explosion. Do not manipulate the distillate apparatus while it is hot and evacuated--allow it to cool.

Note C: Temperature can be monitored manually with a thermometer (no Hg in thermowell) or a temperature controller that includes a thermocouple in conjunction with the heating mantles.

Note D: Depending on the time available for analysis and degree of accuracy required, the percent solvent can be verified by using clean glassware and weighing each of the following pieces before distillation: Claisen head, adapter, receiver, tubing, and cold trap. After distillation, reweighing all pieces of apparatus should yield an additional weight equal to the loss of weight from the sample. With good techniques, the balance should be within 0.5 g.

Note E: A total sample should be used for the composite, because of the possibility of settling or other inconsistencies.

Note F: The recovered solvent is then added to GC to determine the percent deashing solvent.

Note G: This procedure is used for all deashing solvent (DAS) determination in SRC. For determination of DAS in light SRC, a preweighed sample is put into the oven at 250°F until constant weight is attained (about 1 hr). The weight loss is that of DAS.

Figure J-1

Apparatus for Vacuum Distillation
(Wilsonville Procedure No. 36025-9)

NOTE: CLAISEN HEAD IS WOUND
WITH ASBESTOS TAPE AND
HEATING WIRE (24 BS)

Appendix VI-K

Kerr-McGee's Vacuum Distillation Procedure (-850°F Distillation)
(No. ACL 85-15)INTRODUCTION:

The purpose of this test is to determine the percentage of -850°F distillable material present in hydrotreater, liquefaction, or critical solvent deashing products. The sample is distilled for 1 hr at a pressure of approximately 0.1 mm Hg with a distillation flask temperature of 400°F.

SAFETY:

This distillation procedure requires the apparatus to be evacuated to <1 mm Hg. Care must be taken to prevent injury from implosion.

EQUIPMENT:

Laboratory timer

500-mL round-bottomed distillation flask with thermowell

Adapter

Welch vacuum pump

Product receiver

Heating mantle (Glass-Col, 270 W)

Thermometers for measuring vapor temperature and pot temperature

McLeod gauge for pressure measurement

Heat tape

Rheostats

Temperature controller (Cole-Palmer)

Two-way vacuum valve

Appendix VI-K (Continued)

OPERATING PARAMETERS:

Flask temperature	400°F
Head temperature	400 ± 20°F
Pressure	≤0.1 mm Hg
Sample size	25 g
Time of distillation	1 hr at 400°F

METHOD:

1. Place a small plug of glass wool in the distillation flask thermowell and insert the thermocouple.
2. Tare the distillation flask to the nearest 0.1 g.
3. Measure approximately 25 g weighted to the nearest 0.01 g into the distillation flask.
4. Lubricate the ground-glass joints of the distillation apparatus with a high-temperature silicone grease and connect the joints.
5. Wrap the neck of the distillation flask and the adapter with a heating mantle and heat tape and insulate with fiberglass wool.
6. Start the vacuum pump and evacuate the apparatus to approximately 5 mm Hg to degas the sample. Isolate the system from the vacuum pump by using the vacuum valve.
7. Turn on the temperature controller, heating mantle, and heat tracing. Set the rheostats such that the final flask temperature is reached in approximately 25 min.
8. After the flask temperature reaches 400°F, start timer and carefully open the vacuum valve and evacuate the system to 0.1 mm Hg.

Appendix VI-K (Continued)

9. The heat tracing should be adjusted so that the vapor temperature in the head is maintained at $\pm 20^{\circ}\text{F}$ of the temperature in the distillation flask.
10. Continue the distillation for 1 hr taking pressure measurements every 30 min.
11. Upon completion of the distillation, cool and disassemble the apparatus. Weigh and record the weight of the distillation flask.

CALCULATIONS:

$$-850^{\circ}\text{F, wt \%} = \frac{A - C}{A - B} \times 100$$

where: A = gross wt, flask + sample (initial)

B = tare wt, flask

C = gross wt, flask + sample (final)

Appendix VI-L

Highlights of Discussion of Round-Robin Results
(from Joint Meeting of Participants at Birmingham,
Alabama, June 30, 1982)

Two main conclusions were derived from the data:

- ° Different laboratory setups generate different amounts of distillate from the SRC-I process stream sample.
- ° Using distillation in combination with encapsulated GCSD to define the 850°F cut point greatly improves agreement between laboratories.

Discussion centered on two major topics:

1. The distillation setup, in particular, use of a reflux column, the effect of sample size, and the location of pressure measurement.

Participants decided that an approach similar to that used by the ASTM should be followed; i.e., every step of the distillation procedure should be standardized and the exact glassware should be specified. The following guidelines were proposed: 100-g sample size; 0.1-mm Hg pressure measured at the head; 600°F final pot temperature; heat temperature within 25°F of pot temperature; end point defined as pot temperature at 600°F for 1 min.

2. GCSD conditions, with major emphasis on: choice of detector, mode of integration, correlations with Wilsonville GCSD, column selection, and choice of calibration standard.

These guidelines for the GCSD procedure were proposed: time slice integration; Dexsil 300 GC column; aromatic boiling-point calibration standard. A final decision on the choice of detector (FID or TCD) was not reached.

Appendix VI-L (Continued)

To finalize the distillation and encapsulated GCSD procedures for determining the <850°F fraction of a coal liquefaction sample, the participants decided on the following action items:

- (1) The APCI distillation laboratory should develop a standard distillation procedure incorporating the approved guidelines mentioned above.
- (2) The APCI distillation laboratory should investigate the effect of sample size on the overhead yield of distillation by running a series of distillations of differing sample sizes (down to approximately 100 g) using K125 material.
- (3) Kerr-McGee should investigate the effect of measuring the distillation pressure at different points, most notably, before and after any cryo traps.
- (4) ICRC should derive a correlation between the Wilsonville GCSD and encapsulated GCSD.
- (5) The APCI GC laboratory should investigate the effect of the FID vs. TCD response (weight or volume percent).