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EFFECTS OF SOLVENT CHARACTERISTICS ON WYODAK COAL LIQUEFACTION

Annual Technical Progress Report
for the Period May, 1977 - April, 1978

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EFFECTS OF SOLVENT CHARACTERISTICS ON WYODAK COAL LIQUEFACTION

II. ABSTRACT

On May 1, 1976, a contract was awarded to the University of Wyoming for the investigation of the effects of solvent characteristics on Wyodak coal liquefaction. The principal investigators on the program are Dr. Howard F. Silver, Department of Mineral Engineering, and Dr. Robert J. Hurtubise, Department of Chemistry. This report summarizes the work of the second year of this project.

During the past year, Wyodak coal liquefaction runs have been completed using nine different solvents derived from Wyodak coal recycle solvent from the Wilsonville, Alabama SRC plant. Results suggest that the effectiveness of the solvents studied tends to improve as the boiling range of the solvent increases. Further, mildly hydrogenated Wyodak solvents appear to be more effective than either unhydrogenated or severely hydrogenated solvent.

In addition, 13 additional solvents have been prepared from a Kentucky coal-derived recycle solvent produced at the SRC plant in Tacoma, Washington; from Pittsburgh Seam coal-derived anthracene oils from the Clairton works of U. S. Steel; and from Hanna coal-derived in situ coal gasification tars produced at Hanna, Wyoming. Coal liquefaction runs have been initiated using these solvents.

Open column and high-performance liquid chromatography have been used to separate monophenols from recycle solvents. Fluorescence spectroscopy has been employed for identification and characterization of the monophenols. Nitrogen type analysis shows that nitrogen compounds in coal-derived liquids contain a high percentage of quinoline types which may be difficult to remove.

III. OBJECTIVE AND SCOPE OF WORK

The objective of this proposed research is to investigate the effects of solvent characteristics on the extent of Wyodak coal liquefaction, asphaltene formation, and nitrogen removal during the non-catalytic hydrogenation of Wyodak coal.

The research is divided into three major areas as follows:

1. Reactor Experiments
   Processing Wyodak coal in a series of solvents to include solvent refined coal (SRC) process recycle oils, coal tar distillates and other solvents, both as received and modified, for example by prehydrogenation or blending, under reaction conditions representative of SRC processes.

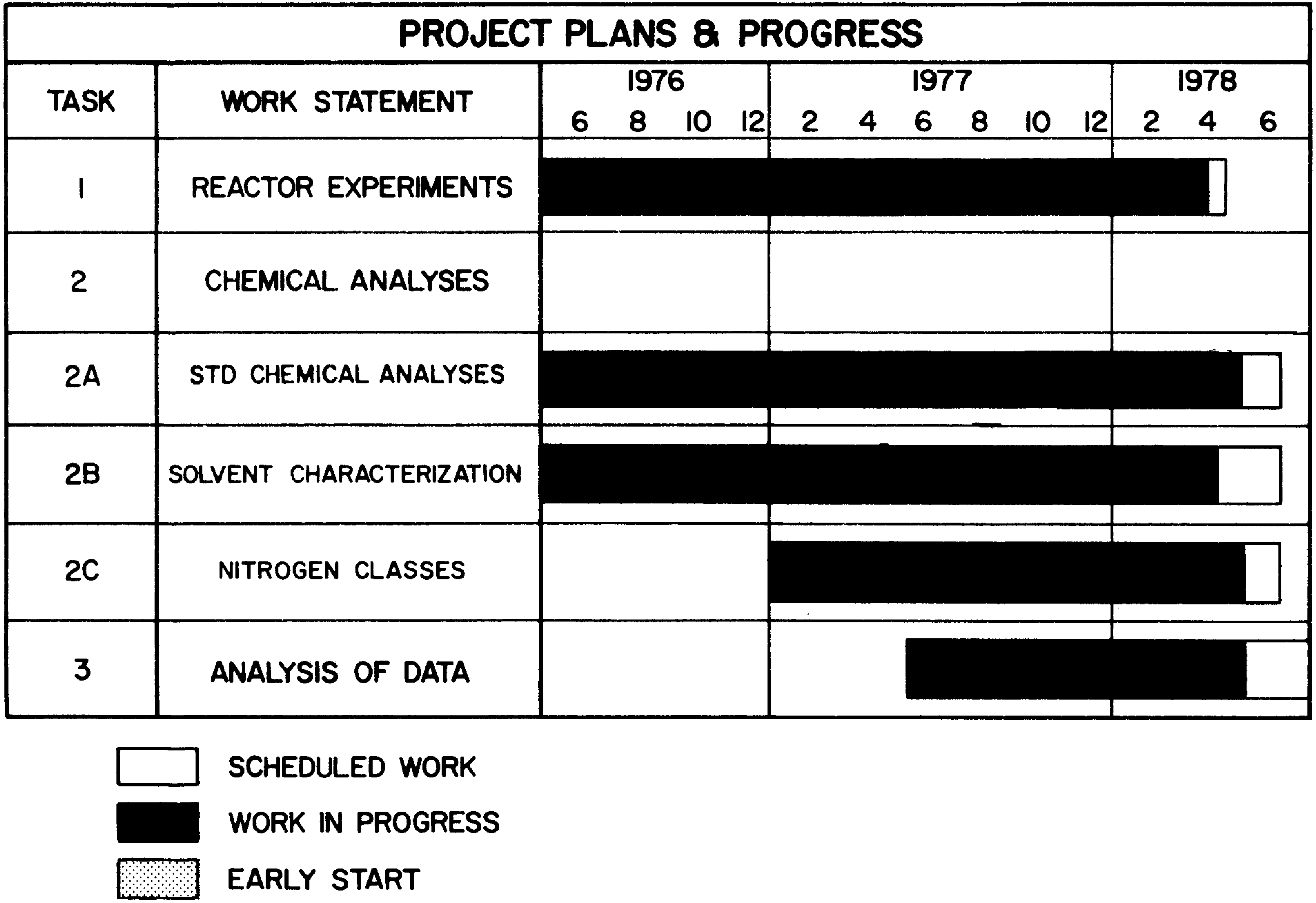
2. Chemical Analyses
   a. Standard Chemical Analyses
      Use of accepted analytical procedures to evaluate both chemical and physical properties of both the reactants and products from the reactor.

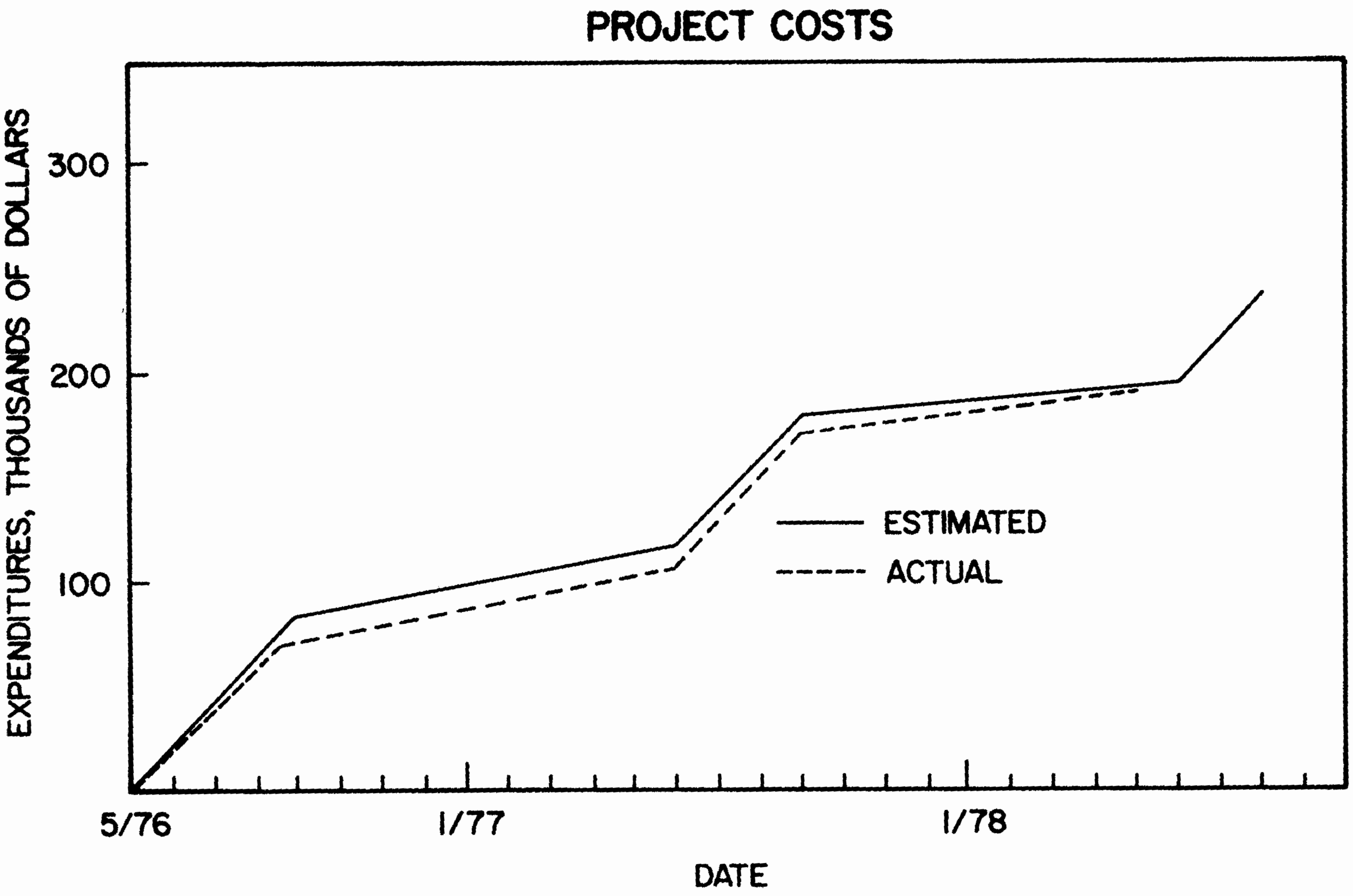
   b. Solvent Characterization
      Measurement of changes in the chemical characteristics of the solvents and the relative concentrations of aromatic, hydroaromatic, and aliphatic hydrocarbons in the solvents.

   c. Nitrogen Classes
      Estimation of the concentration of nitrogen classes (quinoline, indole, aryl-amine, alkyl-amine and amide) using non-aqueous potentiometric titration and infrared spectroscopy.

3. Analysis of Data
   Evaluation of the precision of the reaction data and correlation of the variables studied.

IV SUMMARY OF PROGRESS TO DATE




PROJECT COSTS
EXPENDITURES, THOUSANDS OF DOLLARS
300
200
100
5/76
1/77
1/78
DATE
ESTIMATED
ACTUAL

V. DETAILED DESCRIPTION OF TECHNICAL COAL LIQUEFACTION EXPERIMENTS

EQUIPMENT AND PROCEDURES

Liquefaction Experiments and Standard Chemical Analyses

Experimental Wyodak coal solvent preparation and coal liquefaction experiments have been carried out using a 2 liter Autoclave Magnedrive reactor (Catalog No. AO-6206) shown in Figure 1. The outside diameter of this reactor is 8 inches, the inside diameter is 3 1/2 inches, and the inside depth is 13 inches. The material of construction for the reactor body and cover is 347 stainless steel. The maximum working pressure of this unit is 10,000 psi at 900°F Rupture discs rated at 7900 psi have also been provided on the hydrogen inlet and outlet lines of this reactor.

The reactor is equipped with a cooling coil, an agitator shaft with an attached propeller, a baffle assembly, and a thermowell. Material of construction for all of these parts is 316 stainless steel. A cooling coil is provided with snap-on water hose connections. Hydrogen inlet and outlet, openings to a pressure gauge, thermowell, sampling tube, and a vent to a third rupture disc are also provided in the reactor cover. The vent and the opening to the sampling tube are plugged.

The magnedrive reactor is provided with a ceramic heater wired in three equally dispersed 220 volt, 60 cycle single phase circuits of 1.7 kw each. Two circuits are provided with on-off control, and the third circuit is provided with a variable transformer control.

Magnets are used to rotate the agitator. External magnets, in an outer steel housing, are rotated by a 1/4 HP AC motor. These external magnets in turn actuate internal magnets mounted on a square rotor shaft. The driven agitator shaft is, thus, completely sealed within the unit, and the conventional stuffing box and packing are eliminated. A water jacket is located just above the openings on the reactor cover. When the reactor is in operation, cold water is circulated through the jacket, and this prevents the shaft from being heated to a point where the alignment of the internal magnets is affected.

Tubing used in the remainder of the reactor section is 1/4 inch O.D. type 304 stainless steel rated at 70,000 psi. Valves used in the system are either Aminco or High Pressure Equipment Company Incorporated valves. All are type 316 stainless steel rated at 30,000 psi.

The reactor temperatures are measured with a Leeds and Northrup millivolt potentiometer (Catalog No. 8686) using 20 gauge iron-constantan thermocouples. Two thermocouples are provided for the reactor. One is used to measure the temperature in the lower wall just outside the reacting solid-liquid phase. A reference thermocouple and ice bath are also provided. Reactor pressures are measured using a 0-10,000 psi Aminco gauge (Catalog No. 47-8210).

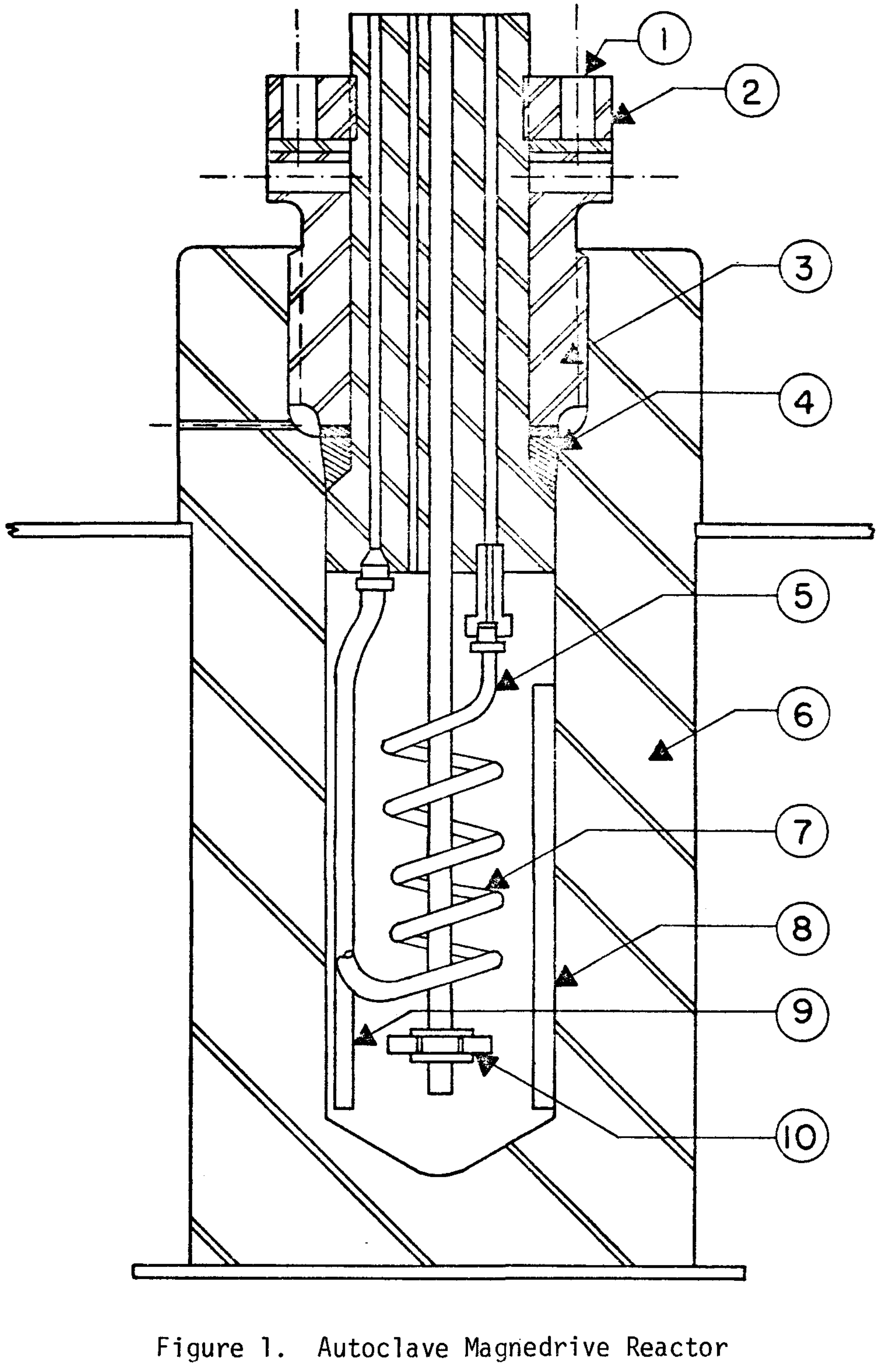


Figure 1. Autoclave Magnedrive Reactor

All high pressure equipment is located in special high pressure cells. The cell walls are made of 1/4 inch steel plate over 1 5/8 inch wood backed by a 1/8 inch steel plate. A fan rated at 1300 CFM and suitable duct work circulate air through the laboratory containing the high pressure cells. The fan changes the air in the laboratory every 2.7 minutes to minimize the possibility of explosion by leaking gases.

Wyodak coal from the Roland Smith seam in the Belle Ayr Mine of the Amax Coal Co., used in these experiments was supplied by Catalytic Inc., from their operation at the Southern Services Inc., SRC plant in Wilsonville, Alabama. A quantity of unground coal (1/2-2 inches) sufficient for 5-10 runs is ground and pulverized, as described in the appendix, and stored in sealed glass bottles. Analyses of the samples of coal used, based on accepted analytical procedures, are presented in Table I.

TABLE I

ANALYSES OF WYODAK COAL

	C-1	C-2	C-3	C-4	C-5
PROXIMATE ANALYSIS WT% (MF BASIS)					
Volatile Matter	43.0	42.4	42.5	43.0	
Fixed Carbon	49.3	49.5	49.5	49.4	
Ash	7.7	8.1	8.0	7.6	
ULTIMATE ANALYSIS WT% (MF BASIS)					
Carbon	68.9	68.8	68.7	68.2	67.3
Hydrogen	5.0	5.0	5.0	4.8	4.8
Sulfur	0.5	0.4	0.4	0.5	0.6
Nitrogen	1.0	1.0	1.0	0.9	1.0
Oxygen (by difference)	16.9	16.7	16.9	18.0	18.2
Ash	7.7	8.1	8.0	7.6	8.1
SCREEN SIZE (TYLER), WT%					
+65	0	0	34.9	27.4	
65/100	15.2	5.7	13.5	16.2	
100/150	17.2	12.1	9.6	11.1	
150/200	16.1	19.5	9.2	8.8	
200/325	20.4	15.0	7.4	9.6	
325/PAN	31.1	52.7	25.4	26.9	
SULFUR FORMS, WT% (MF BASIS)					
Organic Sulfur	0.38	0.33			
Pyritic Sulfur	0.07	0.07			
Sulfate Sulfur	0.04	0.04			
Total Sulfur	0.49	0.44			

The initial solvent used in this work was a recycle solvent derived from the liquefaction of Wyodak coal at the Southern Services Inc., SRC plant in Wilsonville, Alabama, in 1975. Other solvents used include Pittsburgh Seam coal-derived anthracene oil cuts supplied from the Clairton Works of Unites States Steel Corporation, a recycle solvent derived from the liquefaction of Kentucky coal at the Pittsburgh and Midway SRC plant in Tacoma, Washington, and an in situ gasification coal tar produced by the Laramie Energy Research Center at Hanna, Wyoming.

As hydrogen donor capacity is believed to be an important characteristic of coal liquefaction solvents, the hydrogen donor capacity of several of these solvents was increased using a "light" hydrogenation. This consisted of reacting the solvents under an initial hydrogen pressure of 2000 psig at 700°F for one hour over a Co-Mo on Al_2O_3 catalyst (Nalcomo 471) which had been thermactivated at 1000°F for 2 hours in a muffle furnace. Other solvents were hydrogenated under "moderate" reactor conditions using an initial hydrogen pressure of 3000 psig at 700°F for one hour over Nalcomo 471 while still others were hydrogenated under "severe" reactor conditions using an initial hydrogen pressure of 3000 psig at 800°F for one hour over the same Co-Mo catalyst.

In addition, the as-received and hydrogenated Wyodak coal-derived recycle solvents were fractionated into light and heavy fractions. Table II, on the next page, is a description of the solvents prepared for this study while Table III, following Table II, contains the properties of the solvents.

The properties of the hydrogen charged to the reactor are presented in Table IV. The properties of Nalcomo 471 hydrogenation catalyst used in this work and supplied by Nalco Chemical Company, are presented in Table V.

TABLE IV

PROPERTIES OF HYDROGEN

Grade	Extra Dry
Purity	99.8% (Min.)
Dew Point	-75°F (Max.)
Cylinder Pressure	2000 psig

TABLE II

DESCRIPTION OF SOLVENT

Solvent	Description	Hydrogenation Conditions
F-1	Wilsonville Recycle⁽¹⁾	None
F-2	Wilsonville Recycle⁽¹⁾	Light
F-3	Wilsonville Recycle⁽¹⁾	Severe
F-1 LT	-500°F F-1 distillate	
F-2 LT	-500°F F-2 distillate	
F-3 LT	-500°F F-3 distillate	
F-1 Hvy	+500°F F-1 residue	
F-2 Hvy	+500°F F-2 residue	
F-3 Hvy	+500°F F-3 residue	
F-4	USS 230-315(2)	None
F-5	USS 315-355(3)	None
F-6	USS 355-450(4)	None
F-7	Tacoma Recycle(5)	None
F-8	USS 230-315(2)	Light
F-9	USS 230-315(2)	Moderate
F-10	USS 315-355(3)	Light
F-11	USS 315-355(3)	Moderate
F-12	USS 355-450(4)	Light
F-13	USS 355-450(4)	Moderate
F-14	Tacoma Recycle(5)	Light
F-15	Tacoma Recycle(5)	Moderate
F-16	Coal Gasification Tar(6) Oil	None

Notes:

1) Wilsonville Recycle: Recycle solvent from SRC process at Wilsonville, Alabama, using Wyodak coal
2) USS 230-315: United States Steel Pittsburgh Seam anthracene oil 230-315°C fraction
3) USS 315-355: United States Steel Pittsburgh Seam anthracene oil 315-355°C fraction
4) USS 355-450: United States Steel Pittsburgh Seam anthracene oil 355-450°C fraction
5) Tacoma Recycle: Recycle solvent from SRC process at Tacoma, Washington, using Kentucky 14 coal
6) Coal Gasification Tar Oil: Tar oil product from an in situ coal gasification project near Hanna, Wyoming, conducted by Laramie Energy Research Center

TABLE III
SOLVENT DISTILLATIONS AND ANALYSES

SOLVENT	F-1	F-2	F-3	F-1 LT	F-2 LT	F-3 LT	F-1 HV	F-2 HV	F-3 HV	F-4	F-5	F-6
SPECIFIC GRAVITY (60/60)	1.023	1.015	0.991	0.990	0.986	0.959	1.055	1.051	1.038	1.0639	1.1377	1.1871
°API (60/60)	6.8	7.9	11.3	11.4	12.0	16.0	2.6	3.1	4.8	1.5	- 7.1	-12.3
DISTILLATION, °F VOLUME % OVER												
0/5	265/425	200/350	200/300	330/425	175/405	195/300	460/490	480/505	475/515	495/500	505/545	645/670
10/30	435/470	420/460	415/450	430/435	415/435	405/415	505/555	515/555	525/565	500/510	570/640	680/715
50	520	515	490	445	445	430	610	600	610	520	655	745
70/90	590/715	575/690	540/630	465/500	465/500	455/490	660/780	655/755	655/765	545/600	700/770	---/---
95/100	770/---	755/---	700/---	---/---	---/---	---/---	---/---	790/---	800/---	635/---	---/---	---/---
END POINT (VOL%)	97	97	98	90	90	94	93	96	95	98	93	62
TEMP. AT END POINT (°F)	800	800	755	500	500	500	800	800	800	660	800	800
WT% DISTILLED												
WATER	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
350°F -	2.1	3.6	6.0	2.06	3.62	8.28	0.10	0.30	0.78	0.0	0.0	0.0
350°-500°F	41.0	37.8	46.7	85.15	84.33	82.18	7.78	3.01	1.00	15.0	0.0	0.0
500°-650°F	37.9	40.6	36.7	12.79	12.05	9.54	56.81	63.23	66.16	82.5	33.9	0.0
650°-800°F	14.5	13.9	9.3	0.0	0.0	0.0	27.63	29.06	27.45	0.0	58.3	62.0
800°F +	4.5	4.1	1.3	0.0	0.0	0.0	7.68	4.41	4.69	2.5	7.8	38.0
ULTIMATE ANALYSIS, WT%												
C	87.95	87.92	88.43	86.74	86.95	87.82	88.07	88.08	88.97	89.25	90.38	91.60
H	8.49	9.07	9.25	9.07	9.19	9.55	8.46	8.50	8.81	7.31	6.51	6.11
N	0.49	0.45	0.34	0.23	0.22	0.25	0.70	0.60	0.46	1.27	1.03	1.12
S	0.13	0.12	0.04	0.15	0	0	0.31	0.10	0.06	0.75	0.81	0.75
O	2.94	2.44	1.94	3.81	3.64	2.38	2.46	2.72	1.70	1.42	1.27	0.42
WT% TETRALIN	2.27	2.74	6.12	5.74	6.00	13.00	0	0	0	0	0	0
VABP (°F)	546	532	505	455	452	439	622	616	624	535	667	806
ALIPHATIC/AROMATIC RATIO	3.20	4.51	6.39	2.63	2.88	4.73	5.38	4.82	6.40	0.44	0.14	0.14
NONPOLAR SOLUBILITY PARAMETER, λ, AT 25°C	9.62	9.59	9.49	9.43	9.43	9.30	9.80	9.80	9.77	9.70	10.00	10.10
SOLUBILITY PARAMETER, δ, CORRECTED TO 25°C	9.87	9.84	9.82	9.91	9.80	9.63	9.84	9.80	9.55	10.24	10.35	9.75

TABLE V

PROPERTIES OF CATALYST

Catalyst Designation	Nalcoma 471
Supplier	Nalco Chemical Co.
Composition, Weight %	12.5% MoO_3 3.5% CoO .05% Na_2O 0.03% Fe 0.3% SiO_2
Physical Properties	
Surface Area, m^2/gm	226
Pore Volume, cm^3/gm	0.40
Density (lb_m/ft^3)	42
Strength, Crushing, lb_f	14
Form	1/8" extrudate

In preparing to make a run, the quantities of solvent, coal and/or catalyst used in a particular run are first weighed on an Ohaus triple beam balance of 2610 gram capacity and then added directly to the reactor. Hydrogen from commercial cylinders is then used to flush any air from the closed reactor, and the reactor is pressurized for leak tests.

In order to obtain hydrogen at the desired pressure level of the run, the hydrogen is compressed in an auxiliary water compression system. This compression system consists of a Sprague hydraulic pump and a compression cylinder fabricated from a drill collar. After pressurizing the reactor to the desired initial hydrogen pressure, the reactor agitator is turned on for a few minutes, and then the sealed reactor is allowed to stand for approximately 12 hours. If the pressure in the reactor shows no decrease over this period, except for a decrease observed when the agitator is activated, the run is initiated.

At the conclusion of a run, the reactor is allowed to cool to room temperature, and the gases are vented into a gas sampling system. The gas sampling system consists of two aircraft-type stainless steel oxygen tanks and a manifold for connecting the tanks to the reactor. The tanks have a capacity of 2100 cubic inches each. The manifold consists of 1/2 inch O.D. soft black iron pipe and fittings. The manifold is connected to the reactor by stainless steel and tygon tubing. The gas sample tanks and manifold are equipped with quick disconnect fittings. Four tanks can be connected to the manifold at one time. Manifold pressure is measured by two 5000 series gauges manufactured by the U.S. Gauge Corp. One gauge has a range of 30 inches mercury vacuum to 60 psi. The other has a range from 0 to 100 psi.

The gas analysis equipment is that necessary to determine molecular weights and also a component analysis. Glass balloons of approximately 220 ml capacity and an Ainsworth Right-A-Weigh type SC automatic single pan balance of 200 gram capacity are used for molecular weight determination. A Hewlett Packard HP 5840A chromatograph is used to determine gas composition. Gas sample tanks can be connected directly to this unit.

After the gases are vented from the reactor, the reactor cover is removed using an overhead crane. Liquid product from the opened reactor is then siphoned into a glass flask, and any solid particles remaining in the reactor are removed with a hand scraper. This total mixture is then centrifuged in an International Company centrifuge at 1500 RPM to separate solids and liquids. Samples of the oil wet solids and samples of liquid product are then analyzed for N and S to provide a basis for estimating the H_2S and NH_3 produced during the reaction.

Approximately 50 gms of toluene are then added to 100 gms of liquid product, called decant oil, in a tared 500 ml distilling flask. The flask is then placed in a heating mantle and fitted with a Dean Stark receiver and reflux condenser. The mixture is allowed to boil for approximately 12 hours, following ASTM D-95 procedures, in order to remove any water contained in the decant oil.

The distillation flask containing the water-free decant oil is then fitted with an ASTM D-1160 distillation head and a receiver. A toluene cut and a decant oil cut at 350°F, corrected from 585 mm of Hg, Laramie atmospheric pressure, to 760 mm of Hg, are then made.

At this point, the distillation residue is cooled and vacuum of approximately 2 mm of Hg is applied to the distillation flask. Cuts at 350-500°F, 500-650°F, and 650-800°F are taken. This distillation is a modified ASTM D-1160 distillation.

Samples of vacuum distillation residue, boiling above 800°F and called solvent refined coal, SRC, are then placed in a soxhlet extractor. One set of duplicate samples is extracted with pyridine, a second set with benzene, and a third set with hexane. An ultimate analysis of an SRC sample is also performed, and a nitrogen analysis is performed on the benzene insoluble SRC. Samples of the benzene soluble SRC in the benzene used for extraction are then stored for use in the nitrogen type analysis procedure.

Finally, samples of the centrifuge residue are also extracted with pyridine, benzene, and hexane in the soxhlet extractors. The benzene insoluble centrifuge residue is analyzed for ash and for sulfur in the ash to provide a basis for calculating the weight percent coal liquefaction.

Solvent Chracterization

Separation and identification of hydroaromatics

The high-performance liquid chromatograph used in the determination of tetralin and naphthalene in recycle solvents is a Waters model ALC/GPC 244 equipped with a model 6000-A pump, a U6K injector, and a free standing ultraviolet detector set at 254 nm. A stainless steel tube 11 cm x 0.23 mm I.D. attached to the exit port of the detector cell is used in sample collection. A μ-bondapak C_{18} column with methanol:water (65:35) at a flow rate of 1 ml/min is employed, and a 10 mv recorder completes the system.

The columns used in open column chromatography are 50 cm x 11 mm I.D. Pyrex (Corning No. 2145) and are dry packed to a height of 35 cm with aluminum oxide activity II-III according to Brockmann (aluminum oxide from I.C.N. Life Sciences, Cleveland, Ohio, and Brinkmann, Westbury, N.Y., were used interchangeably). Columns packed with silica gel (Brinkmann) are prepared in the same manner. Brinkmann ALOX N/UV 254 thin-layer chromatoplates are used in the thin-layer chromatography (TLC) work with n-hexane as the mobile phase.

Reagents used are pure grade (99% min) n-hexane obtained from Phillips Chemical, glass distilled methanol from Burdick and Jackson, and glass distilled water which are filtered prior to mixing. Napthalene (99+%) and tetralin (99%) have been obtained from Aldrich and used as received. All other chemicals are obtained from commercially available sources and are purified when necessary.

In this analysis, F-1 and F-2 solvents were found to contain hexane insolubles while F-3 was soluble in hexane. In analyzing F-3, a 20 g sample was brought to volume with n-hexane in a 100 volumetric flask. Aliquots of 25 ml were added to each of three 50 ml volumetric flasks. Standard additions of 50 mg and 100 mg each of tetralin and napthalene were added volumetrically to two of the flasks, respectively. All three flasks were diluted to volume with n-hexane. Aliquots of 1 ml of each of the solutions were pipetted onto the top of each of three aluminum oxide columns. Elution was performed with n-hexane. Work with standards showed that the tetralin was eluted totally in the first 15 ml (Fraction 1) and the napthalene in 15-55 ml (Fraction 2). Fraction 1 was collected in a 25 ml volumetric flask and Fraction 2 in a 50 ml volumetric flask, each flask diluted to the appropriate volume with n-hexane.

Hexane insolubles in the F-1 and F-2 solvents coat the volumetric glassware when the sample solution is less that about 25% w/v in n-hexane. In this case, the volume displacement has been found to be approximately 0.5 ml for a 20 g sample. To minimize this source of error, a solution of 20 g sample in approximately 120 ml n-hexane is made and swirled in a sealed flask. After at least two hours, most of the solid material coats the flask, and the remaining solution is rinsed into a 250 ml volumetric flask, then made up to volume. Three aliquots of 25 ml each are prepared as before, but the standard addition quantities are 20 mg and 50 mg for both tetralin and napthalene. Aliquots of 2 ml are pipetted onto the aluminum oxide columns and Fraction 1 and Fraction 2 collected.

Determination of the quantity of tetralin in F-1, F-2, and F-3 is accomplished by an injection of 10μl each of the unknown and of the two standard addition solutions that were passed through the alumina oxide columns onto the μ-bondapak C_{18} columns with the detector at 0.01 absorbance units. The heights of the tetralin peaks are all measure and "normalized" to the peak height of the only other predominant chromatographic peak in Fraction 1 which has been identified an indan. This internal reference peak represents the same amount of indan present in the individual solvent and the two standard addition solutions. Normalization of all the tetralin peak heights to a constant indan peak height compensates for the nonreproducible injections inherent in the HPLC system. A standard addition curve is prepared by plottin peak height vs mg tetralin added. The line intersecting the peak height axis is extrapolated to zero peak height to obtain the tetralin concentration in the prepared solution. From this value the percentage tetralin is calculated (Figure 2). Results of this work are incorporated into Table III.

Injections of 10 μl at 0.1 absorbance units have been used for the determination of napthalene. Peak heights are normalized to the predominant peak at 18.4 ml elution volume which is believed to be composed mainly of biphenyl and 2-methylnapthalene. The percentage napthalene is calculated in the same manner as tetralin.

High-performance liquid chromatography (HPLC) was not employed to separate hydroaromatics other than tetralin in recycle solvents because the HPLC unit was being used to separate monophenols from recycle solvents. However, results from dry-column chromatography, thin-layer chromatography, ultraviolet spectroscopy, and luminescence spectroscopy indicate the presence of phenanthrene and possible hydrophenanthrenes in the recycle solvents. Work is continuing to separate polycyclic aromatic hydrocarbons and hydroaromatics from recycle solvents.

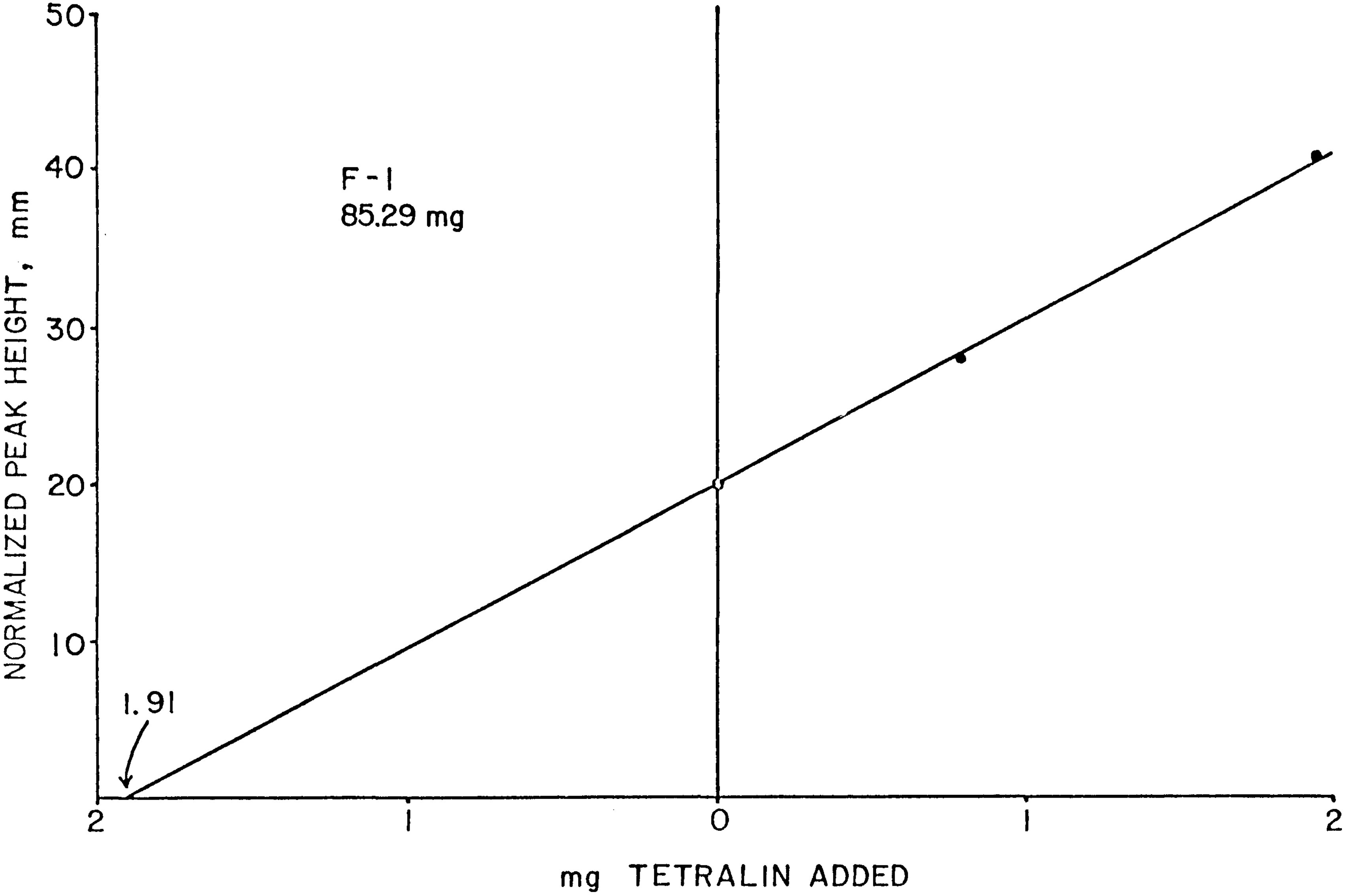
Separation of Monophenols

Considerable effort was expended in developing separation methods for monophenols in recycle solvents. After several experiments with various chromatographic systems and monophenol standards the following approach was developed. Initially, silica gel was slurry packed into a glass column with n-hexane:toluene (96:4) and then 0.1 ml of concentrated hydrochloric acid was placed onto the silica gel column. The sample (F-1, F-2, or F-3) was then eluted with n-hexane:toluene (96:4) which separated hydroaromatics, polycyclic aromatic hydrocarbons, and ethers from other compounds. Next, chloroform saturated with hydrochloric acid was employed as a mobile phase. This mobile phase separated ortho-substituted phenols. Finally, chloroform-ether (90:10) saturated with hydrochloric acid was used as a mobile phase. With this mobile phase non-ortho-substituted phenols were separated from polyphenols. The ortho-substituted and non-ortho-substituted phenol fractions were collected and further separated by HPLC using a μ-bondapak-NH_2 column and a n-heptane:isopropanol (99:1) mobile phase. From the ortho-substituted phenol fraction 25 subfractions were collected from the HPLC column, and 30 subfractions were collected for the non-ortho-substituted fraction.

Aromatic to Aliphatic Hydrocarbon Ratios

In 1972, C.H. Wright and D.E. Severson proposed that solvent effectiveness could be measured by determining the aromatic to aliphatic hydrogen ratio using infrared absorbance.(1) As this ratio appeared to decrease as the effectiveness of the solvent increased, R.P. Anderson proposed using the aliphatic to aromatic hydrogen ratio. Details of the procedures used to determine this ratio are presented in the Appendix. Results obtained are included in Table III.

FIGURE 2



Standard addition curve for determination of tetralin

Nitrogen Type Analyses

Selected samples of process solvent and benzene soluble SRC made during these studies have been analyzed for nitrogen type distribution. Following procedures reported by Wang (2), titration techniques are used to determine quinoline type, amide type, and amine type heterocyclics, and infrared analyses are used to determine indole heterocyclics.

All titrations are made using a Precision-Dow Recordomatic titrometer. This instrument has standard glass and calomel electrodes.

In some of the titration analyses, an aliquot of the oil sample to be titrated is weighed into a 100 ml beaker and dissolved in 15 ml of benzene. Then, 30 ml of either acetic anhydride or acetic acid is added to the beaker, and the resulting mixture is titrated immediately with 0.1 N perchloric acid dissolved in purified dioxane. Quinoline is used to standardize the perchloric acid.

Aliquots of the oil samples to be titrated are also dissolved in 50 ml of a 0.1 M solution of acetic anhydride in acetic acid and 5 ml of benzene. Samples prepared in this manner are stirred for one hour prior to titration.

Infrared analyses of selected oil samples are made on a Beckman ACTA MIV spectrophotometer at LERC. The samples to be analyzed are dissolved in carbon tetrachloride such that the concentration of oil is approximately 5 to 10 gms/liter of CCl_4. The samples are then scanned in the region of 3600 to 3200 cm^{-1} using cells that provide a one cm path through the samples in both the sample and reference beams. The average absorptivity for the N-H stretch of the indole compound is taken as 16.85/gm N/liter/cm.

The weight percent indole type nitrogen in the oil sample is then found by dividing the absorbance of the sample, defined as the height of the peak measured at 3480 cm-1 from a baseline drawn across the shoulders of the peak by the average absorptivity of the N-H stretch of the indole type heterocyclic.

RESULTS

Liquefaction Experiments and Standard Chemical Analyses

As part of each experimental run, material balances have been made around each step of the operating procedures. Experimental data obtained and detailed material balances for each step in the liquefaction experiments have been included in the appendix along with discussions of the methods used to distribute losses incurred at each point in the procedure.

A summary of the net yields of hydrogen-free gases, water, liquid products, and solids produced for each 100 gms of moisture-free coal charged to the reactor is presented in Table VI. The sum of these products should equal 100 plus the gms of hydrogen consumed per 100 gms of moisture-free coal, where

$$\text{Hydrogen Consumption} = \frac{H_c - H}{C_{MF}} \times 100$$

where H_C = gms H_2 charged to the reactor

H = gms H_2 recovered from the reactor

and C_{MF} = gms moisture-free coal charged to the reactor.

Benzene insoluble conversion, defined as

$$X = \frac{C_{MF} - R}{C_{MAF}} \times 100$$

where R = gms of benzene insoluble centrifuge residue

and C_{MAF} = gms of moisture-ash free coal charged to the reactor

has been used as a preliminary indication of the extent to which the coal is converted to liquids and gases.

The weight percent liquefaction is reported to more closely represent conversions obtained in demonstration plant units and is based on determining unreacted benzene insoluble solids from an ash balance corrected for sulfates and for benzene insoluble liquids (3). In this work, weight percent liquefaction is defined as

$$W = \frac{C_{MF} - R_{AF}}{C_{MAF} + SO_3}$$

where R_{AF} = gms of benzene insoluble residue calculated from an SO_3 free mineral balance and corrected for benzene insoluble liquids

and $C_{MAF} + SO_3$ = gms of moisture-ash free coal plus gms of SO_3 in coal mineral matter.

Values of the wt % ash and wt % sulfur in the ash of the benzene insoluble residue required for this calculation are presented in Table VI.

TABLE VI
SUMMARY OF LIQUEFACTION RESULTS

RUN NUMBER	32	32b	32c	33	34	35	36	37	38	39	40	41	41b
COAL	C-3	C-4	C-4	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-4	C-4	C-4
SOLVENT	F-1	F-1	F-1	F-2	F-3	F-1LT	F-2LT	F-3LT	F-1HV	F-2HV	F-3HV	F-1LT	F-1LT
SOLVENT/COAL (WT/WT)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
REACTION TEMP. (°F)	825	825	825	825	825	825	825	825	825	825	825	825	825
TIME AT REACTION TEMP. (MIN.)	0	0	0	0	0	0	0	0	0	0	0	0	0
INITIAL P(H_2) (PSIG)	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
MAXIMUM P(H_2) (PSIG)	4200	4200	4250	3600	3475	4425	4400	4375	4225	4050	4300	4450	4350
YIELDS (WT % MF COAL)													
H_2-FREE GAS	15.2	13.5	13.4	11.2	9.8	14.7	14.9	13.6	16.4	13.5	14.7	14.9	13.4
WATER	4.3	4.3	2.9	1.9	(0.7)	4.1	1.5	(0.3)	6.6	6.8	0.6	1.5	1.4
-350 °F	12.1	10.6	10.5	9.8	5.9	11.5	11.5	14.3	5.6	6.4	6.0	12.5	13.2
350-500 °F	(5.6)	(1.3)	(5.4)	0.6	(1.6)	(21.1)	(17.1)	(14.5)	(10.2)	0.0	(0.5)	(12.3)	(13.1)
500-650 °F	(10.6)	(7.0)	(7.8)	(5.6)	(4.4)	(2.2)	4.1	2.3	(0.8)	(0.4)	(6.9)	(1.2)	(2.9)
650-800 °F	6.9	1.7	5.0	9.6	13.4	10.6	11.2	10.2	(0.7)	0.3	6.5	14.1	12.9
+800 °F	42.9	48.9	52.4	51.0	48.1	47.4	46.0	38.6	58.0	57.5	50.9	46.0	46.1
SOLIDS	37.1	30.9	30.9	24.4	32.9	37.8	29.0	37.5	26.2	18.6	28.9	26.3	31.1
TOTAL	102.3	101.6	101.9	102.9	103.4	102.8	101.1	101.7	101.1	102.7	100.2	101.8	102.1
H_2 CONSUMPTION (WT % MF COAL)	4.4	1.3	1.9	2.8	3.4	2.1	1.1	1.8	1.2	2.7	0.3	1.7	2.1
LIQUID PRODUCT DENSITY (°API)	2.9	2.6	2.2	4.0	5.5	7.5	7.8	10.3	0.5	0.6	1.9	7.9	7.6
ULTIMATE ANALYSIS OF SRC (WT %)													
HYDROGEN	5.99	6.20	6.40	6.52	6.49	5.94	6.26	6.52	6.11	6.35	6.70	6.04	6.21
CARBON	87.34	83.54	85.26	85.49	86.17	83.10	85.78	85.62	83.79	80.21	84.92	84.26	84.61
NITROGEN	1.24	1.29	0.85	1.20	1.35	1.39	1.30	1.48	1.35	1.27	1.17	1.05	1.25
SULFUR	0.20	0.22	0.20	0.17	0.14	0.30	0.18	0.18	0.25	0.24	0.12	0.25	0.17
OXYGEN	5.23	8.75	7.29	6.62	5.85	9.27	6.48	6.20	8.50	11.93	7.09	8.40	7.76
ASH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
BENZENE INSOLUBLE CONV.	67.6	74.8	74.8	82.1	71.8	67.5	77.2	67.8	80.1	88.3	76.9	79.8	74.6
BENZENE INSOLUBLE													
CENTRIFUGED RESIDUE													
WT % ASH	20.11	21.14	22.18	30.65	21.16	21.11	25.69	21.89	22.91	30.67	23.10	25.67	21.88
WT % S IN ASH	3.07	3.08	3.23	3.27	3.07	3.15	3.09	2.71	2.97	2.32	2.91	3.16	3.12
WT % LIQUEFACTION	74.5	75.7	77.4	83.5	72.4	73.8	79.8	75.8	79.2	84.2	79.4	80.1	75.9

TABLE VI
SUMMARY OF LIQUEFACTION RESULTS

RUN NUMBER	42	43	44	45	46	47	48	49	50	51	52	53	54
COAL	C-4	C-4	C-4	C-4	C-4	C-5	C-5	C-5	C-5	C-5	C-5	C-5	C-5
SOLVENT	F-2LT	F-3LT	F-1HV	F-2HV	F-3HV	F-4	F-5	F-6	F-7	F-4	F-5	F-6	F-7
SOLVENT/COAL (WT/WT)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
REACTION TEMP. (°F)	825	825	825	825	825	825	825	825	825	825	825	825	825
TIME AT REACTION TEMP. (MIN.)	0	0	0	0	0	0	0	0	0	0	0	0	0
INITIAL P(H_2) (PSIG)	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
MAXIMUM P(H_2) (PSIG)	4450	4575	4425	4125	4325	4350	4325	4300	4300	4400	4150	4300	4475
YIELDS (WT % MF COAL)													
H_2-FREE GAS	12.0	13.1	16.0	14.0	14.7	16.0	16.6	16.3	16.6	17.1	14.8	16.7	18.8
WATER	1.9	(1.8)	(0.1)	9.7	2.7	(0.1)	1.4	2.8	6.8	(1.9)	0.8	4.4	3.6
-350 °F	10.9	11.8	15.1	9.9	3.8	5.7	9.5	3.0	7.2	8.7	15.5	4.0	8.2
350-500 °F	(4.0)	1.3	0.5	0.3	2.8	21.0	0.0	2.1	2.5	17.5	0.0	0.0	2.3
500-650 °F	2.1	5.4	(10.4)	(2.2)	(13.2)	(44.9)	(19.3)	7.7	(6.1)	(33.7)	(4.8)	11.0	(3.1)
650-800 °F	13.3	12.9	(0.8)	(0.1)	7.1	16.1	3.4	(28.4)	(7.5)	10.3	(9.8)	(24.3)	(10.6)
+800 °F	44.6	47.3	60.1	54.0	56.5	53.2	70.7	34.8	65.5	55.2	68.3	39.4	68.9
SOLIDS	21.1	11.9	21.9	17.1	28.8	35.3	20.1	64.8	17.9	30.1	18.0	50.9	15.0
TOTAL	101.9	101.9	102.3	102.7	103.2	102.3	102.4	103.1	102.9	103.3	102.8	102.1	103.1
H_2 CONSUMPTION (WT % MF COAL)	1.9	2.1	2.0	2.7	3.3	2.5	2.4	3.1	2.9	3.3	2.7	2.1	3.1
LIQUID PRODUCT DENSITY (°API)	7.1	9.7	-1.5	0.1	-0.1	-1.2	-14.0	----	-2.9	-1.4	-10.8	----	-2.4
ULTIMATE ANALYSIS OF SRC (WT %)													
HYDROGEN	6.28	6.53	5.85	6.25	6.39	5.92	5.25	5.14	6.09	5.81	5.21	5.08	6.01
CARBON	84.58	85.21	82.70	78.88	82.14	85.11	82.43	84.30	82.35	86.51	83.38	84.59	83.52
NITROGEN	1.54	1.52	1.12	1.38	1.25	2.05	1.40	1.21	1.57	1.95	1.56	1.38	1.48
SULFUR	0.24	0.18	0.37	0.31	0.21	0.29	0.47	0.47	0.38	0.31	0.51	0.49	0.38
OXYGEN	7.36	6.56	9.96	13.18	10.01	6.05	5.04	2.94	4.85	4.92	3.62	2.85	4.12
ASH	0.0	0.0	0.0	0.0	0.0	0.58	5.41	5.94	4.76	0.50	5.72	5.61	4.49
BENZENE INSOLUBLE CONV.	85.4	95.4	84.5	89.7	77.3	68.3	72.2	----	76.1	73.0	68.7	----	82.5
BENZENE INSOLUBLE CENTRIFUGED RESIDUE													
WT % ASH	26.28	27.73	22.93	28.70	22.63	20.94	22.36	12.62	25.66	23.79	20.97	16.35	30.68
WT % S IN ASH	3.00	3.36	2.86	2.66	3.04	3.53	2.84	4.88	2.78	3.54	2.91	4.43	2.80
WT % LIQUEFACTION	80.3	81.4	76.4	83.0	79.6	74.0	78.1	86.5	80.6	80.0	72.5	85.9	86.3

In addition to the standard ultimate analysis of the SRC product presented in Table VI, the SRC product was also analyzed for unreacted coal, preasphaltenes, asphaltenes, and oils. Unreacted coal is defined as pyridine insoluble SRC; preasphaltenes are defined as pyridine soluble, benzene insoluble SRC; asphaltenes are defined as benzene soluble, hexane insoluble SRC; and oils are defined as hexane soluble SRC. The results of this analysis are presented in Table VII.

Solvent Characterization

Chromatographic Correlation Factor

A correlation factor was developed which relates log k' values on μ-bondapak C_{18} for polycyclic aromatic hydrocarbons (PAH), alkyl-substituted aromatic hydrocarbons and hydroaromatics to certain structural features of the compounds. The capacity factor, k' was calculated by $k'=(V_R-V_m)/V_m$ where V_R (ml) is the measured retention volume and V_m(ml) is the column void volume. In practice, the correlation factor can be used to predict the approximate retention volume region for a sought-after compound in a reversed-phase high-performance liquid chromatographic system. Alternatively, speculation as to the identity of a chromatographic peak can be made with the correlation factor. The correlation factor will be employed to characterize PAH and hydroaromatics in recycle solvents and other coal derived samples. Details on the correlation factor have been published. (J. F. Schabron, R. J. Hurtubise, and H. F. Silver, Anal. Chem. 49, 2253 (1977).)(4)

Separation of Monophenols

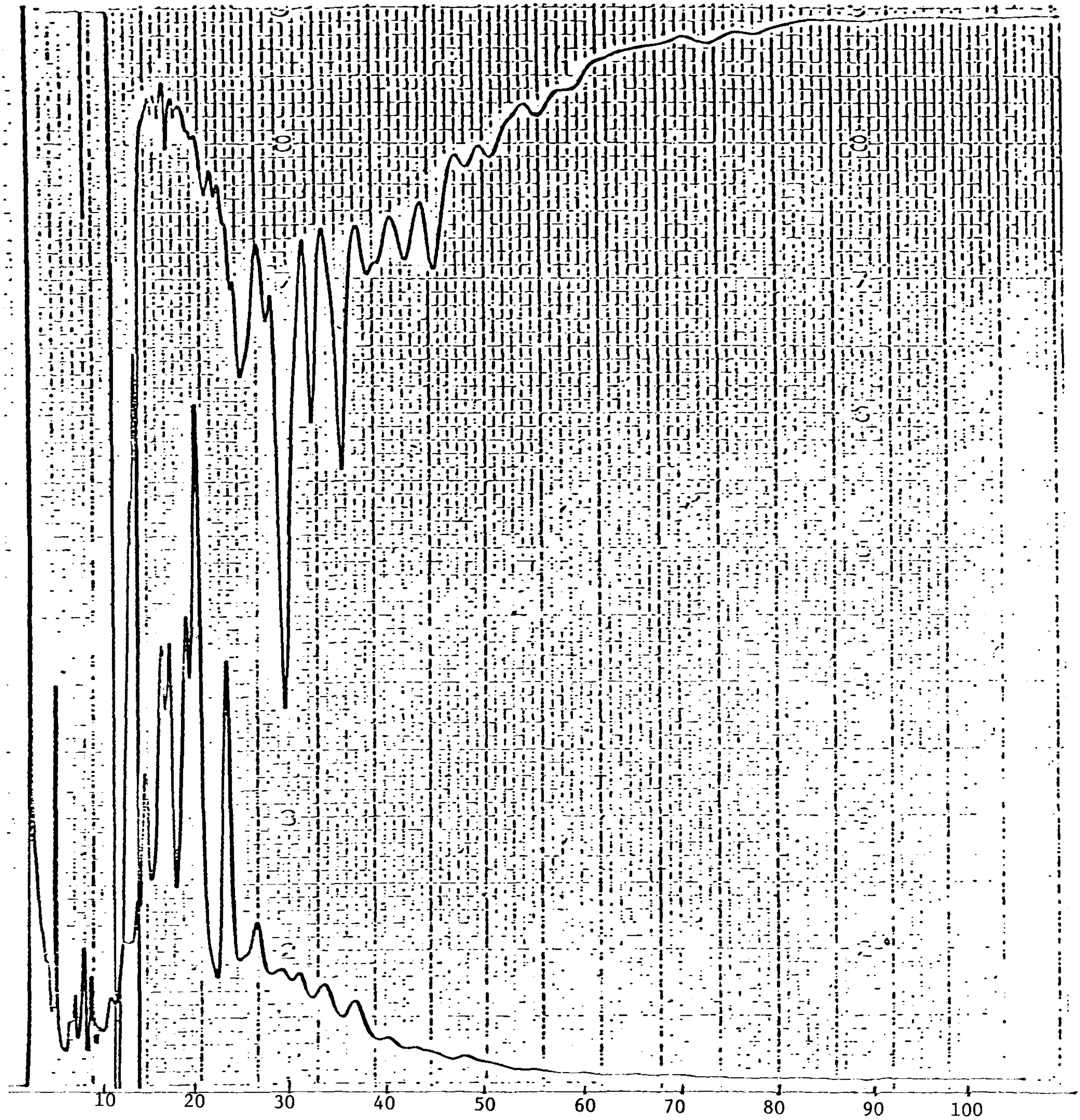
A series of various chromatographic systems have been used to separate monophenols from recycle solvents. Figures 3 and 4 show representative chromatograms from the μ-bondapak-NH_2 column of the ortho-and non-ortho-substituted fractions for F-1, respectively. Figures 5 and 6 illustrate representative chromatograms from the μ-bondapak-NH_2 column of the ortho-and non-ortho-substituted fractions for F-3, respectively. Comparison of the chromatograms show that F-3 ortho-and non-ortho samples contain less phenolic material than F-1-ortho and non-ortho samples. The several ortho-and non-ortho substituted fractions for F-1 from the μ-bondapak-NH_2 column were further separated by HPLC employing a μ-bondapak C_{18} column and a methanol:water (65:35) mobile phase. Figures 7 and 8 show chromatograms from the μ-bondapak C_{18} column for one of the non-ortho fractions and one of the ortho fractions, respectively. These chromatograms illustrate the complexity of the individual fractions and the numerous monophenols in F-1, F-2, and F-3. Fluorescence and ultraviolet spectroscopy along with the chromatographic data have been used to identify phenol, o-cresol and p-cresol in F-1, F-2, and F-3. Work is continuing to isolate and identify other monophenols in F-1, F-2, and F-3. From the chromatographic and spectroscopic information obtained so far it will be possible to identify tentatively or speculate on the structures of several of the monophenols. This aspect is being worked on presently and will be reported later.

Quantitation of Phenol

A method was developed for determining phenol in F-1, F-2, and F-3. Phenol was separated in two steps by isolating the non-ortho fraction with silica gel and mobile phases discussed earlier and using HPLC with a μ-bondapak

TABLE VII
SRC SOLUBILITY ANALYSES

RUN	WT % UNREACTED COAL AND PREASPHALTENES	WT % ASPHALTENES	WT % OILS
32	37.3	50.7	12.0
32b	34.2	35.8	30.0
32c	32.9	44.0	23.1
33	18.1	50.5	31.4
34	20.7	42.1	37.2
35	43.7	41.2	15.1
36	38.8	45.4	15.8
37	37.1	34.6	28.3
38	39.3	30.5	30.2
39	28.4	24.9	46.7
40	23.5	33.5	43.0
41	36.9	52.6	10.5
41b	43.4	46.1	10.5
42	42.4	38.2	19.4
43	31.5	43.7	24.8
44	29.7	46.8	23.5
45	35.6	37.4	27.0
46	29.2	26.6	44.2
47	29.5	50.1	20.4
48	45.1	33.3	21.6
49	40.7	17.1	42.2
50	35.2	29.6	35.2
51	38.5	46.6	14.9
52	47.1	36.4	16.5
53	42.4	19.7	37.9
54	37.2	33.2	29.6

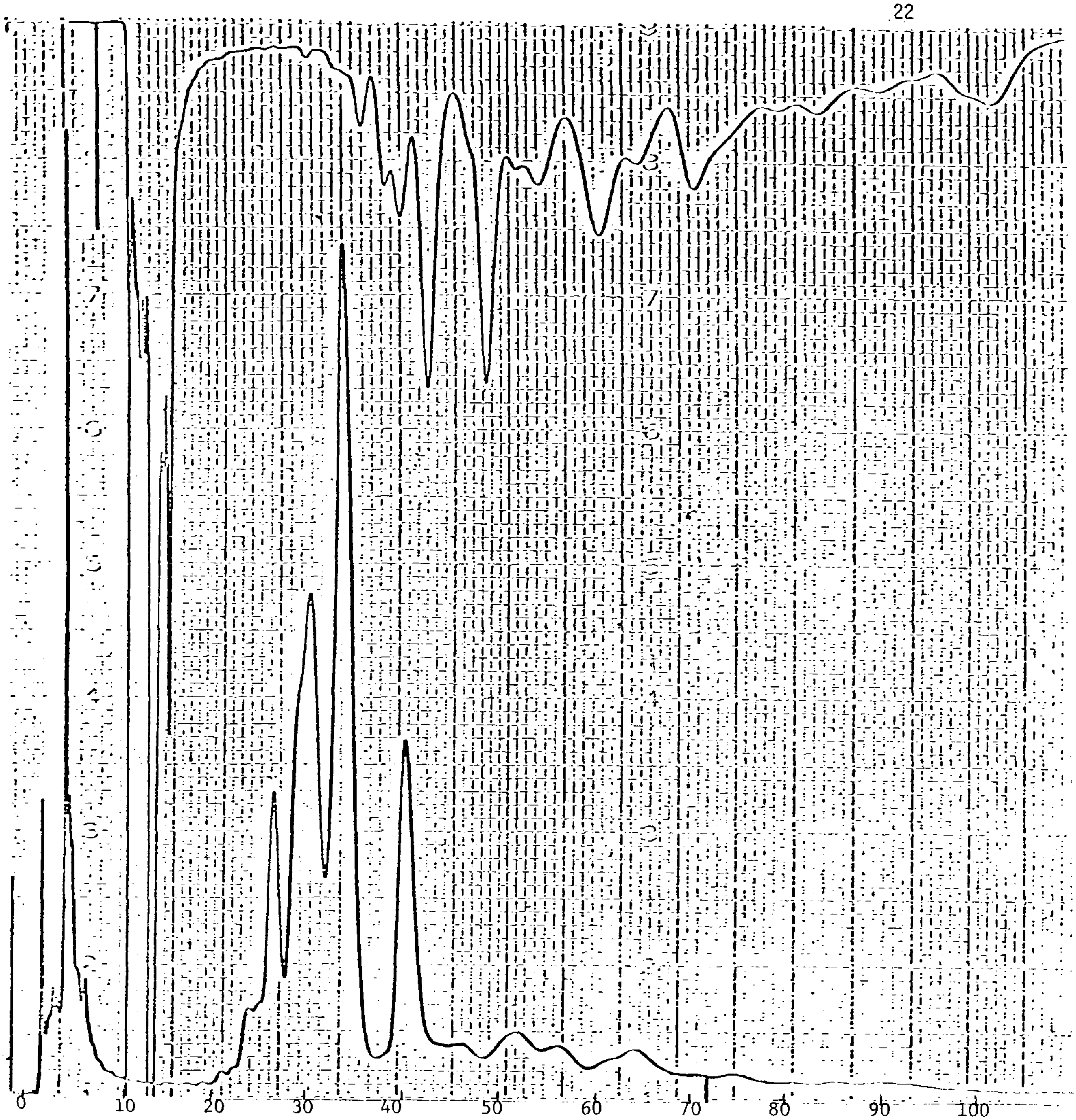


Sample: 10μL F-1- Ortho frac. from silica gel, evap'd to 2 mL

Column: μ-Bondapak NH_2, n-heptane:isopropyl alcohol 99:1 2mL/min

Sensitivity: 0.1 AUFS at 254 nm (top) 0.2 AUFS at 280 nm (bottom)

Figure 3

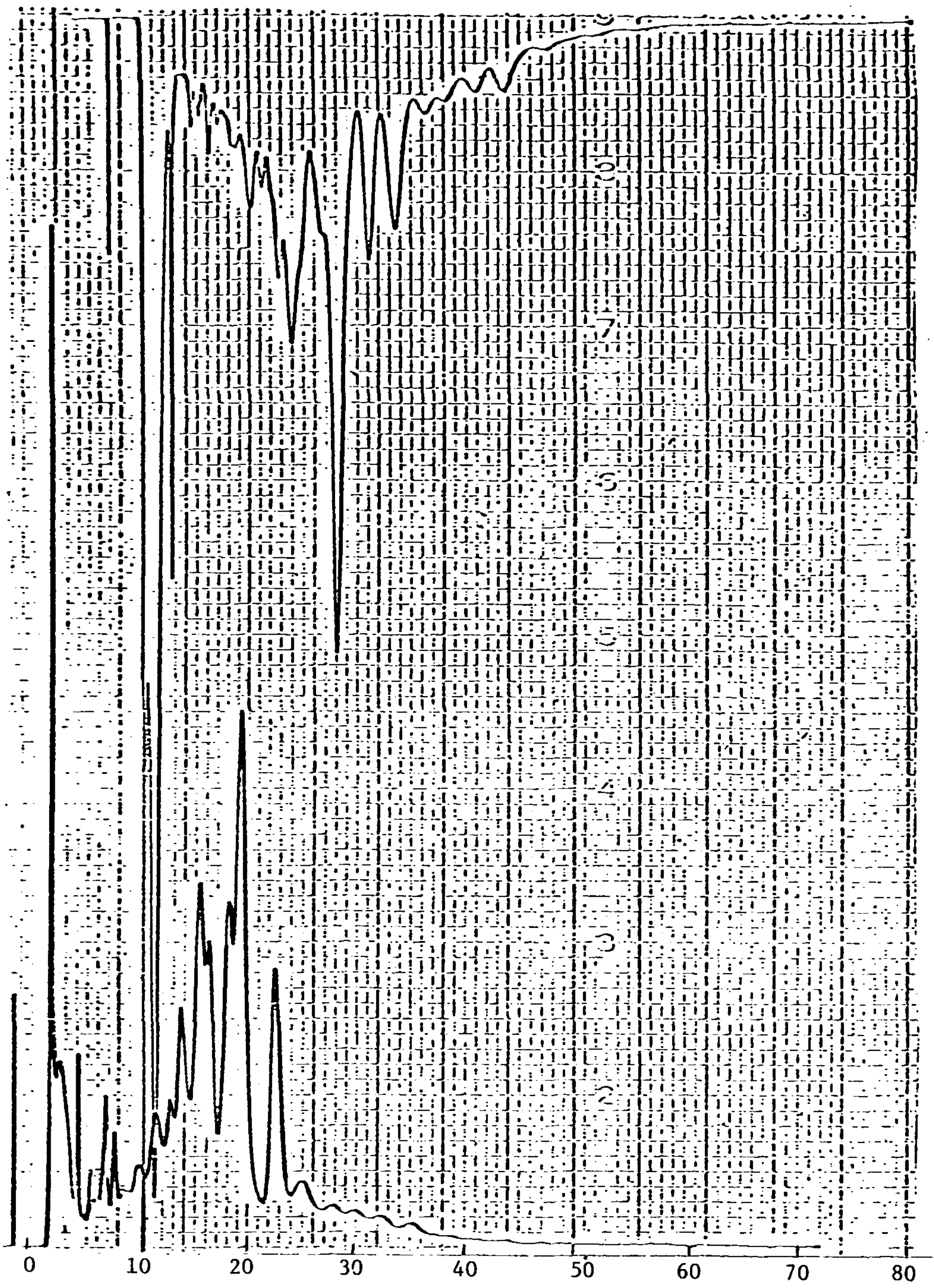


Sample: 10μL F-1 nonortho frac. from silica gel evap'd to 2 mL

Column: μ-Bondapak NH_2, n-heptane:isopropyl alcohol 99:1 2mL/min

Sensitivity: 0.1 AUFS at 254 nm (top), 0.2 AUFS at 280 nm (bottom)

Figure 4

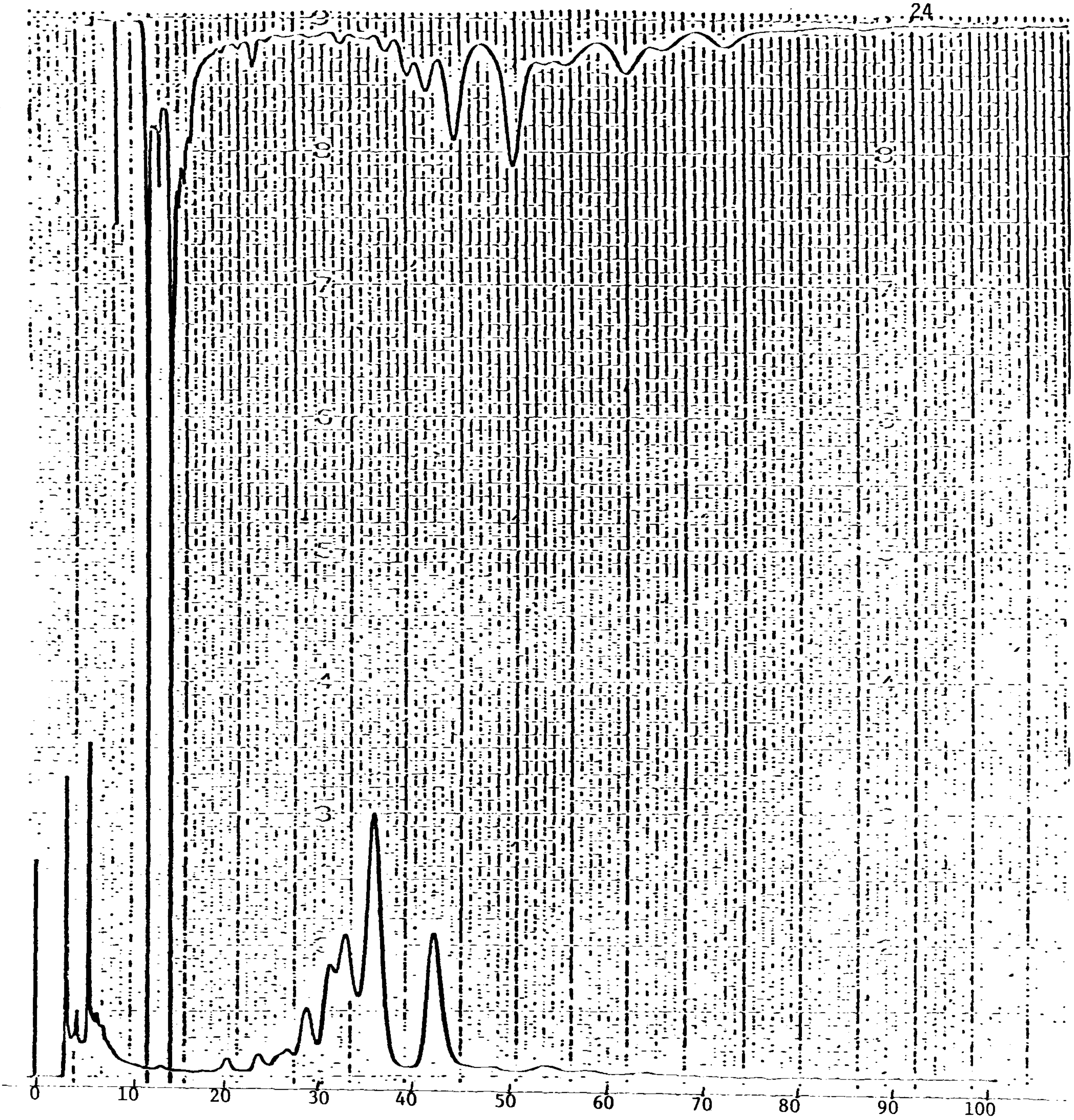


Sample: 10μL F-3 ortho- sub. frac. from silica gel, evap'd to 2 mL

Column: μ-Bondapak NH_3, n-heptane:isopropyl alcohol 99:1 2ml/min

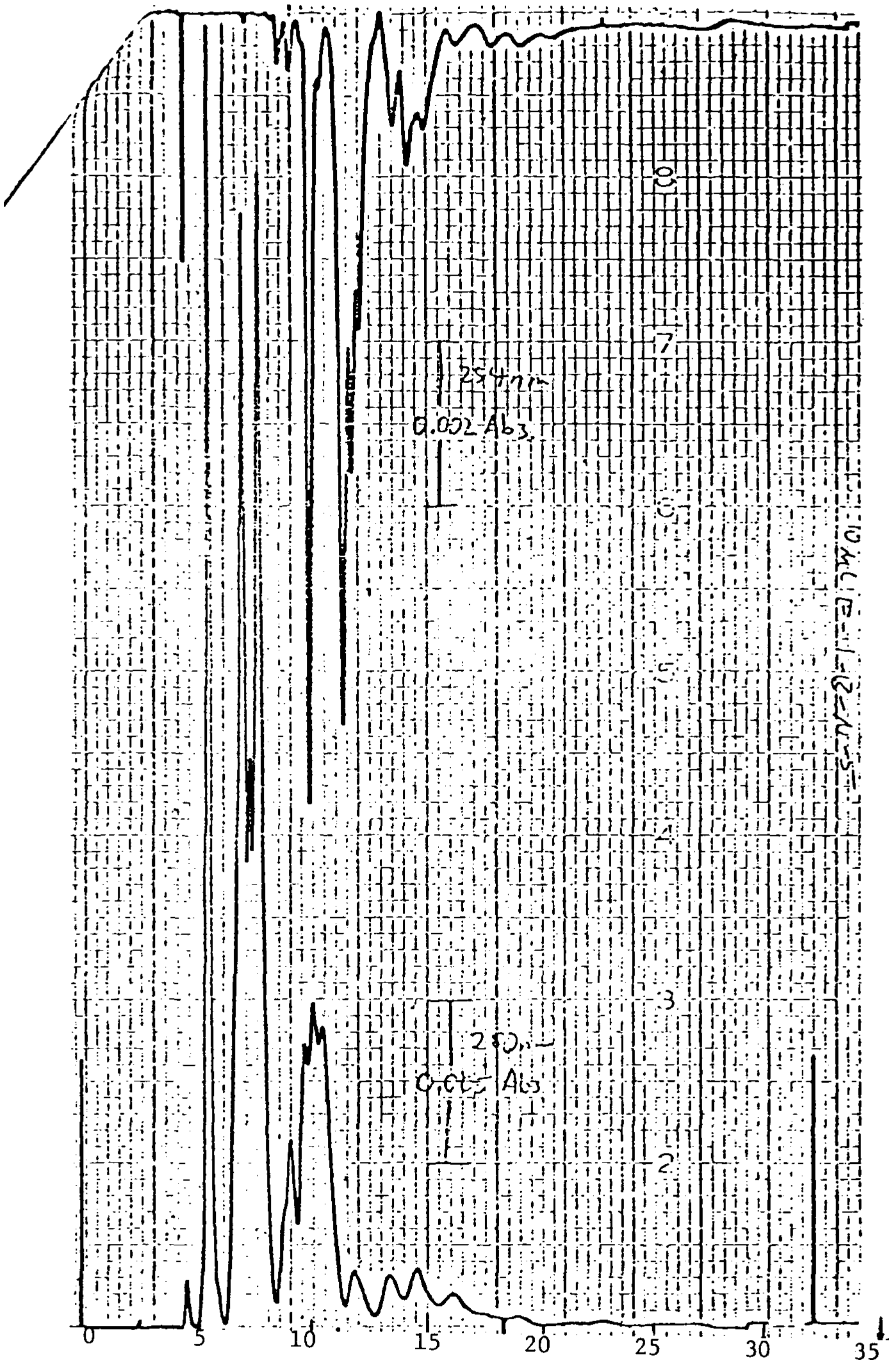
Sensitivity: 0.1 AUFS (top) 254 nm, 0.2 AUFS, 280 nm (bottom)

Figure 5



Sample: 10μL F-3 nonortho frac. from silica gel, evap'd to 2 mL
Column: μ-Bondapak NH_2, n-heptane:isopropyl alcohol 99:1, 2 mL/min
Sensitivity: 0.1 AUFS 254 nm (top) 0.2 AUFS 280 nm (bottom)

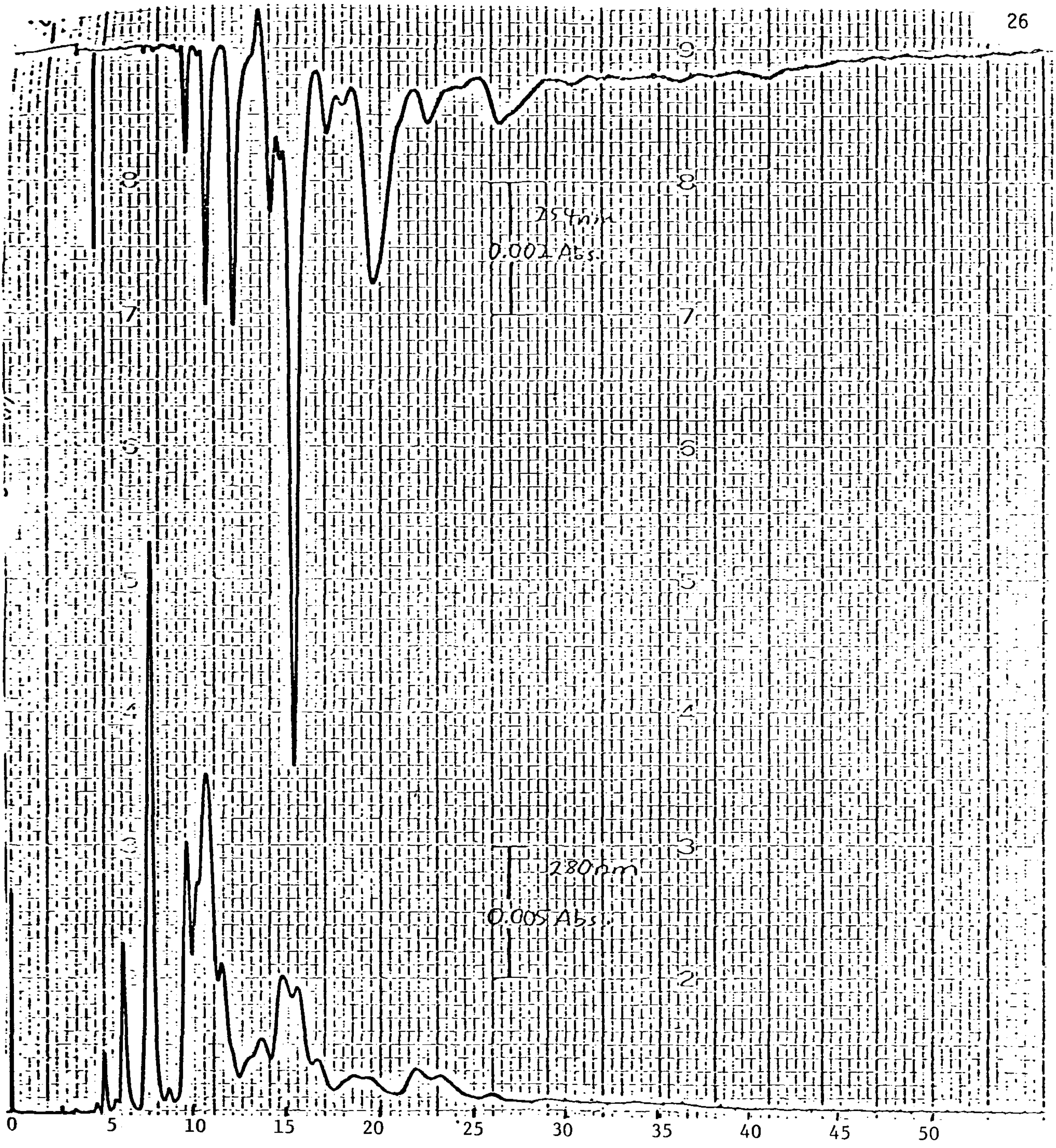
Figure 6



Sample: μ-NH_2 Fraction F-1 N-4

Conditions: $1C_{18}$ column, H_2O:MeOH 35:65 1mL/min

Figure 7



Sample: μ-NH_2 Fraction F-1 0-6

Conditions: $1C_{18}$ column, H_2O:MeOH 35:65 1mL/min

Figure 8

C_{18} column and methanol:water (65:35) mobile phase. The phenol content for F-1, F-2, and F-3 are given below.

F-1	2.32%
F-2	1.77%
F-3	0.87%

Percent recovery and reproducibility experiments were not performed for the phenol analytical method so no statement can be made about the accuracy or precision of the method. However, several experiments were run that indicate the percentages reliable.

Nitrogen Classes

The procedures used to determine classes of nitrogen compounds in coal liquids are discussed in the appendix. A summary of the results obtained is summarized in Tables VIII and IX.

Unidentified nitrogen is the difference between the total nitrogen in the benzene soluble SRC and the sum of the identified nitrogen compounds. The relatively large percentages of unidentified nitrogen compounds found in the benzene soluble SRC may be a result of the manner in which the total benzene soluble nitrogen is determined, that is, by difference between the total nitrogen in the SRC and in the benzene insoluble SRC. Another possible explanation is that while the SRC is extracted with benzene at the boiling point of benzene, the nitrogen type analyses is conducted in benzene at room temperature. A portion of the benzene soluble SRC may precipitate out as a result of this temperature change.

TABLE VIII

WT. % NITROGEN TYPES IN SOLVENT

Solvent	Quinoline	Indole	Aryl Amines	1° and 2° Alkyl Amines	Amides	Unidentified	Total N
F1	.310	.081	.036	.062	.006	(.005)	.49
F1 LT	.170	.030	.011	0	0	.019	.23
F1 HV	.407	.099	.037	.010	.011	.136	.70
F2	.186	.082	.078	.062	.013	.029	.45
F2 LT	.118	.021	.043	.026	.006	.006	.22
F2 HV	.245	.115	.126	.050	.016	.048	.60
F3	.109	.079	.177	.009	(.018)	(.016)	.34
F3 LT	.040	.033	.181	.010	(.019)	.005	.25
F3 HV	.161	.111	.063	.002	.071	.052	.46

( ) -- negative value

TABLE IX

WT. % NITROGEN TYPES IN SOLUBLE SRC

Run	Quinoline	Indole	Aryl Amines	1° and 2° Alkyl Amines	Amides	Unidentified	Total N
28	.535	.333	0	.023	.123	.511	1.53
29	.551	.385	0	.005	.130	0	1.07
30	.558	.359	.004	.104	.100	.035	1.16
31	.567	.360	.015	.096	.152	.220	1.41
32	lost sample						
32b	.345	.192	.042	.030	.059	.712	1.38
32c	.409	.136	.016	.003	.121	.055	.74
33	.505	.343	.006	.015	.180	.074	1.12
34	.490	.410	.020	.051	(.071)	.339	1.31
35	.419	.172	.080	.131	.056	.532	1.39
36	.406	.126	.082	.119	.046	.341	1.12
37	.473	.109	.075	.076	.104	.523	1.36
38	.480	.218	.027	.041	.014	.650	1.43
39	.404	.168	.039	.181	(.037)	.388	1.18
40	.356	.147	.126	.080	(.036)	.291	1.00

(   ) -- negative value

Table IX (CONT.)

Run	Quinoline	Indole	Aryl Amines	1° and 2° Alkyl Amines	Amides	Unidentified	Total N
41	.446	.147	.080	.119	.024	.104	.92
41b	.422	.191	.066	.126	(.036)	.135	.94
42	.483	.206	.012	.110	.032	.617	1.46
43	.484	.161	.111	.087	.068	.499	1.41
44	.420	.139	.016	.075	.058	.252	.96
45	.478	.200	.003	.092	.067	.580	1.42
46	.412	.196	.131	.014	.028	.399	1.18

( ) -- negative value

DISCUSSION OF RESULTS

Correlations of Solvent Effectiveness

Attempts have been made to correlate the effectiveness of a solvent in liquefying Wyodak coal at 2000 psig initial hydrogen pressure and zero minutes at 825°F as a function of a solvent property. Properties used which might indicate the hydrogen donor capacity of the solvents include

1. Wt. % Tetralin in Solvent
2. Wt. % H_2 in Solvent
3. Solvent H/C ratio

and 4. Aliphatic to Aromatic Hydrogen Ratio in Solvent

As shown in Figure 9, based on the data available at this point in the project, no apparent correlation exists between wt. % coal liquefaction and wt. % tetralin in the solvent. In fact, the more effective solvents contained no tetralin. Further, no apparent correlation could be found between wt. % coal liquefaction and either wt. % H_2 in the solvent or solvent H/C ratio. However, as shown in Figure 10, a correlation may exist between wt. % coal liquefaction and aliphatic to aromatic hydrogen ratio in the solvent. However, it appears that at least two lines are required to represent the data shown in Figure 10.

Other solvent parameters evaluated include physical properties such as

5. Watson Characterization Factor, K
6. Solubility Parameter, δ
7. Non-Polar Solubility Parameter, λ

and 8. Volumetric Average Boiling Point, VABP

while reaction parameters evaluated include

9. Hydrogen consumption

and 10. Maximum reactor pressure

Of these parameters, the most promising appears to be the VABP of the solvent, as shown in Figure 11. Again, it appears that at least two different lines are required to represent the data. Whether the two lines required on Figures 10 and 11 are due to scatter in the data or indicate that two parameters, one chemical to denote hydrogen donor capacity and one physical to denote the compatability of the solvent and the dissolved coal, remains to be demonstrated.

The data points shown on Figures 9, 10, and 11 are based on results of two or more duplicate coal liquefaction runs. However, no obvious improvement

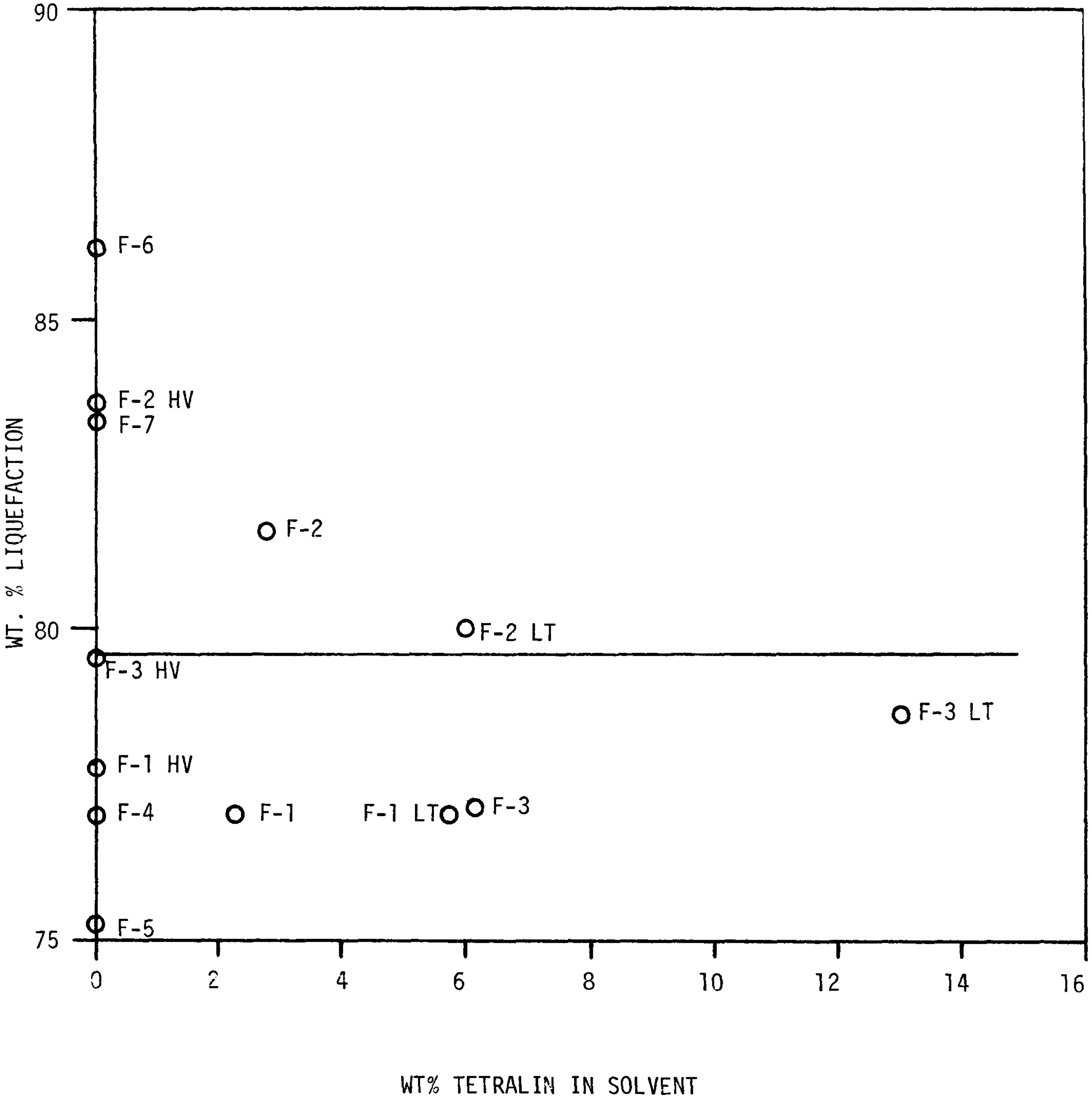


FIGURE 9- WT. % LIQUEFACTION VS. WT. % TETRALIN IN SOLVENT

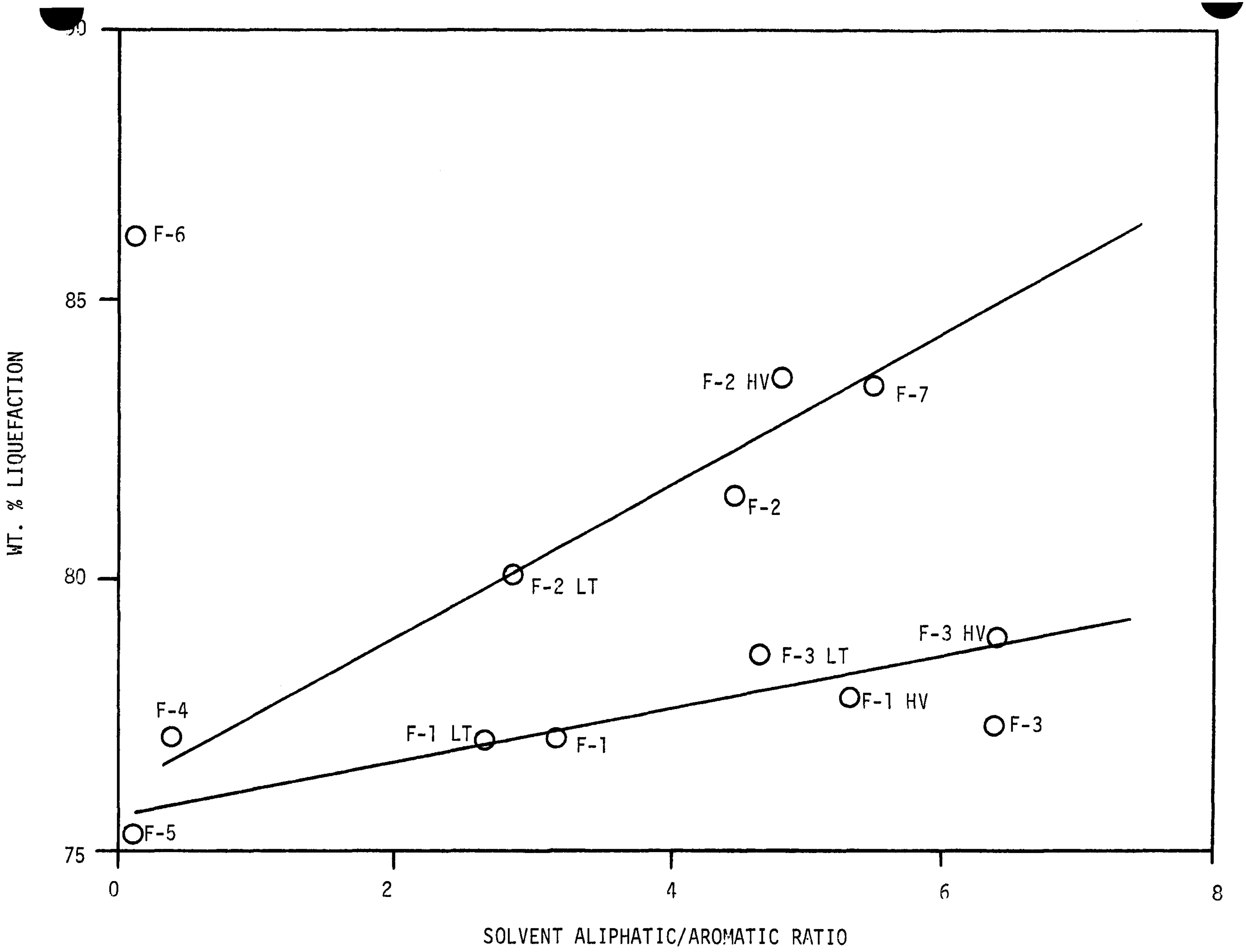


FIGURE 10- WT. % LIQUEFACTION VS. SOLVENT ALIPHATIC/AROMATIC RATIO

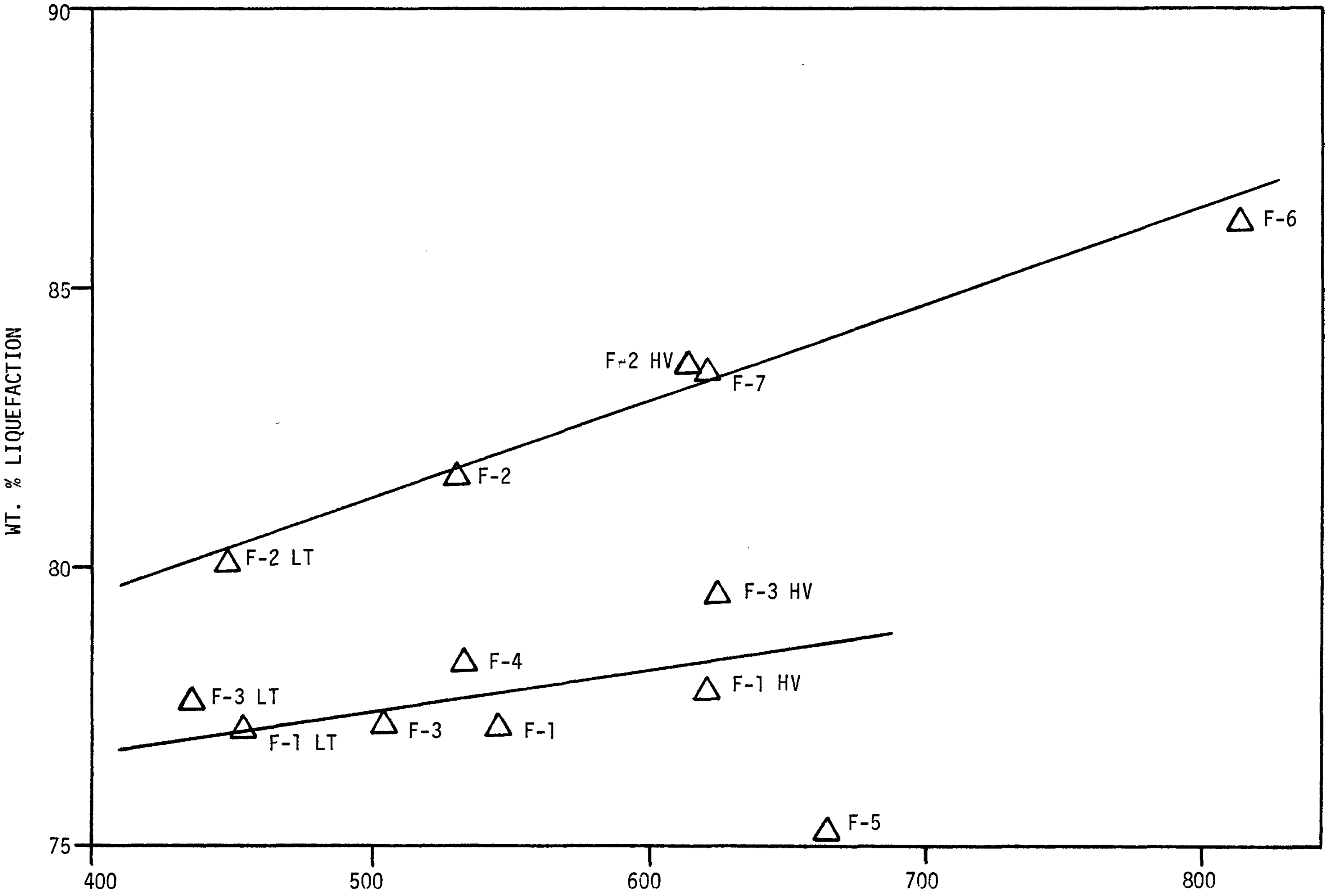


FIGURE 11- WT. % LIQUEFACTION VS. SOLVENT VABP. (°F)

in the correlation was obtained in Figure 11 when either wt. % tetralin in the solvent or aliphatic to aromatic hydrogen ratio of the solvent was used as a third parameter.

Correlation of Product Yields

As the volumetric average boiling point of the solvent appeared to produce a reasonable correlating parameter for the wt. % liquefaction of Wyodak coal, this parameter was also used in an attempt to correlate product yields. Figure 12 is a plot of the net C4-800 °F yield of liquid product representing recovered solvent, based on the difference in the quantity of solvent charged and the C4-800 °F liquid recovered as a function of the solvent VABP. It should be pointed out that the solvents all had initial boiling points above 175 °F and that many of the solvents had end points well above 800 °F. As shown on Figure 12, the quantity of recovered solvent appears to decrease as the VABP of the solvent increases. Again, similar to the results presented in Figure 11, two lines appear to be necessary to represent the data.

In Figure 13, the yield of +800 °F liquid product, called SRC, is shown as a function of solvent VABP, while in Figure 14, the yield of benzene soluble SRC, or asphaltenes and oils, is shown as a function of solvent VABP. In both cases, the yield of SRC and benzene soluble SRC increases with solvent VABP.

Correlation of Product Nitrogen Distribution

The wt. % N in the products obtained in liquefying Wyodak coal at 2000 psig initial hydrogen pressure and zero minutes at 825 °F is shown as a function of solvent VABP in Figure 15. Analysis of the data shows that the total grams of nitrogen in the SRC and in the solid residue is very nearly the same as the grams of nitrogen charged in the coal. Further, the grams of nitrogen in the SRC increases as the VABP of the solvent increases, perhaps reflecting the fact that the nitrogen content of the solvents also increases as the VABP of the solvent increases. However, the total SRC produced increases at a more rapid rate that the grams of N in the SRC with increasing solvent VABP. Thus, the wt. % N in the SRC decreases with increasing solvent VABP.

Further, the grams of nitrogen contained in the liquid product representing recovered solvent is definitely lower than the grams of nitrogen in the solvent charged.

Interestingly, the grams of nitrogen in the total F-1 solvent appear to have decreased from 1.48 grams to 1.18 grams when F-1 was used to liquefy Wyodak coal and from 1.48 to 1.02 grams when F-1 solvent was hydrogenated at 3000 psig initial hydrogen pressure for one hour at 800 °F over a Co-Mo catalyst to produce F-3 solvent. This difference could almost be attributed to the difference in reaction time and temperatures, suggesting that the Co-Mo fouled rapidly and had little effect on the reaction.

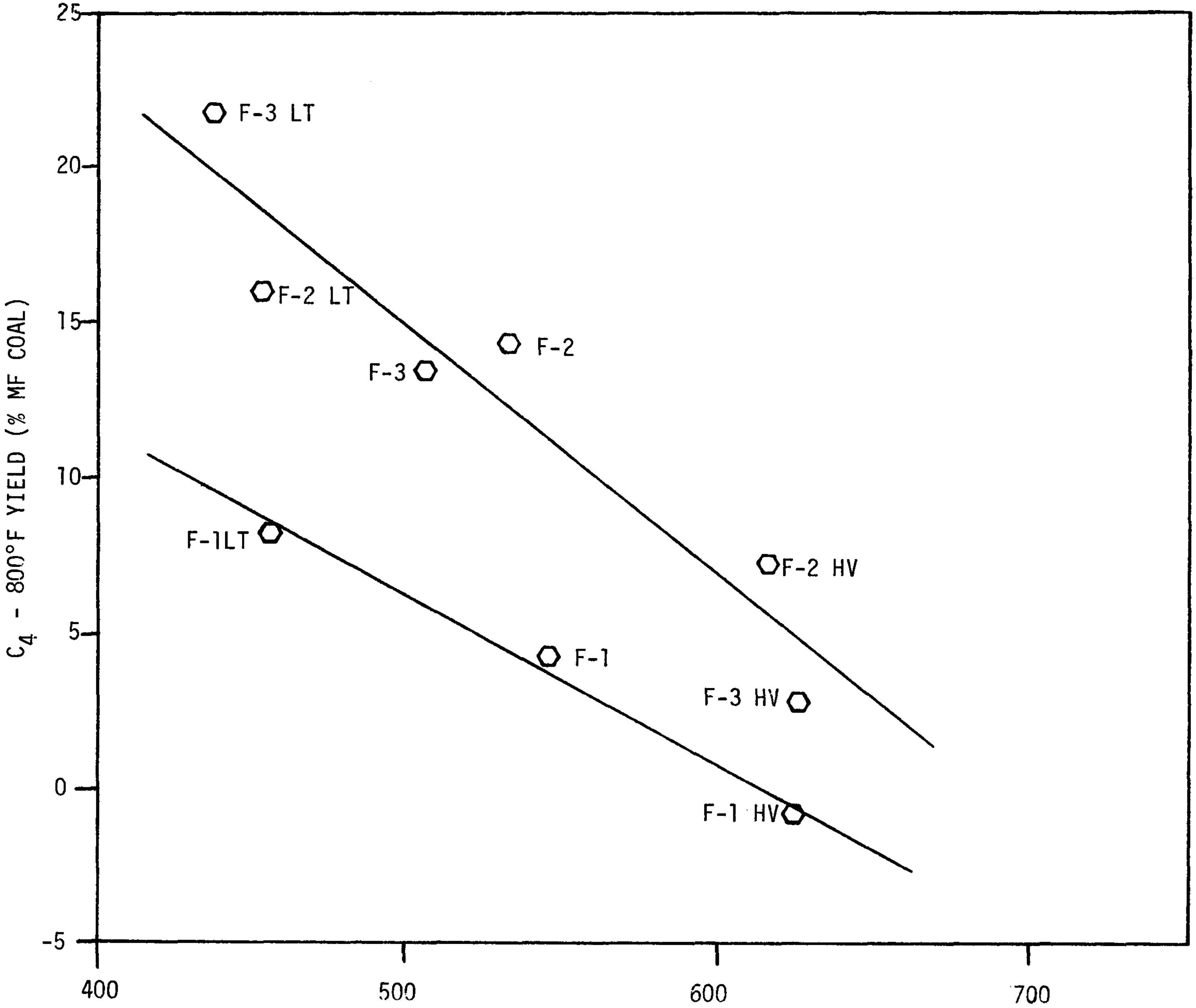


FIGURE 12- NET LIQUID YIELD VS. SOLVENT VABP

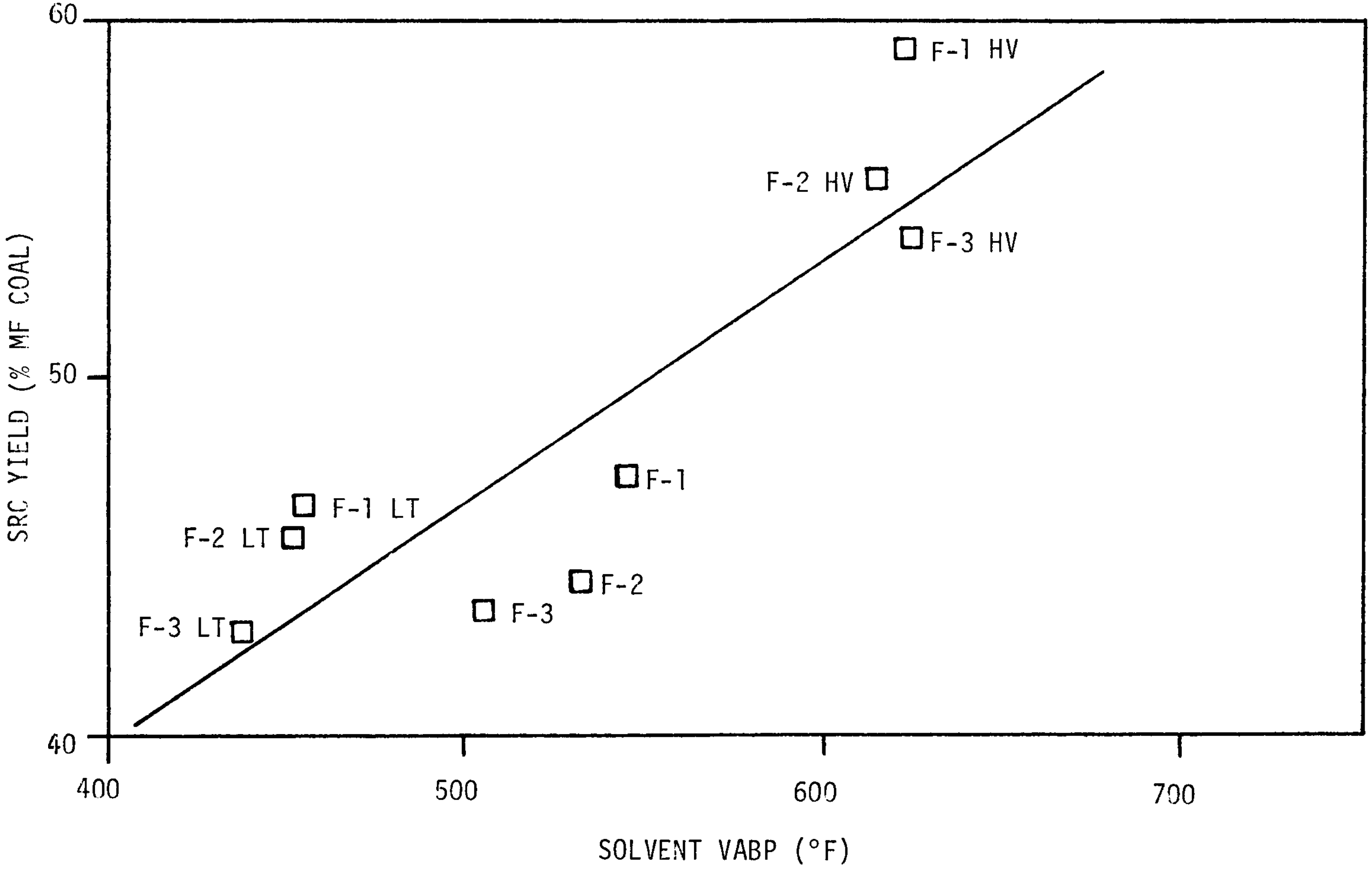


FIGURE 13- SRC YIELD VS. SOLVENT VABP

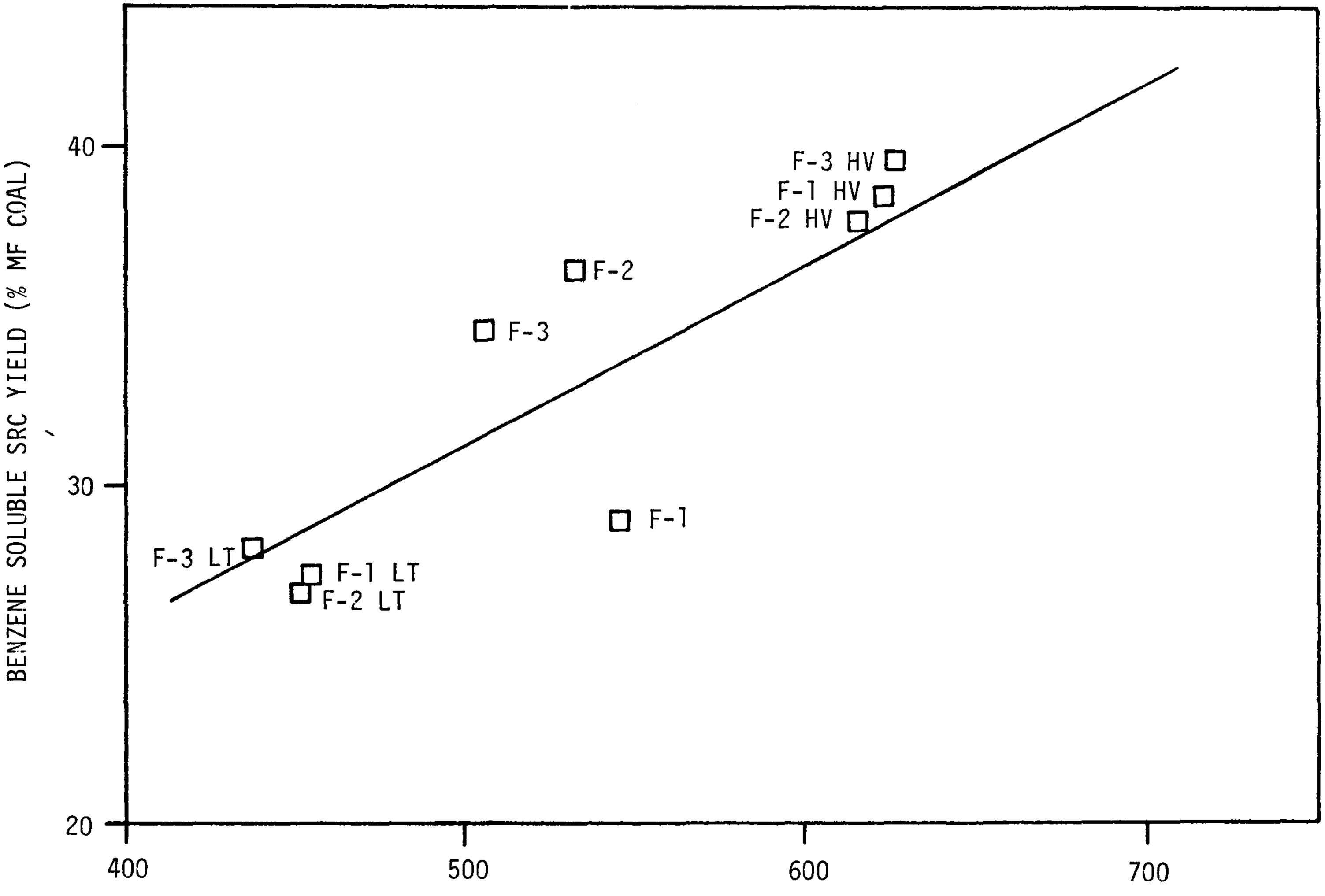


FIGURE 14- BENZENE SOLUBLE SRC YIELD VS. SOLVENT VABP

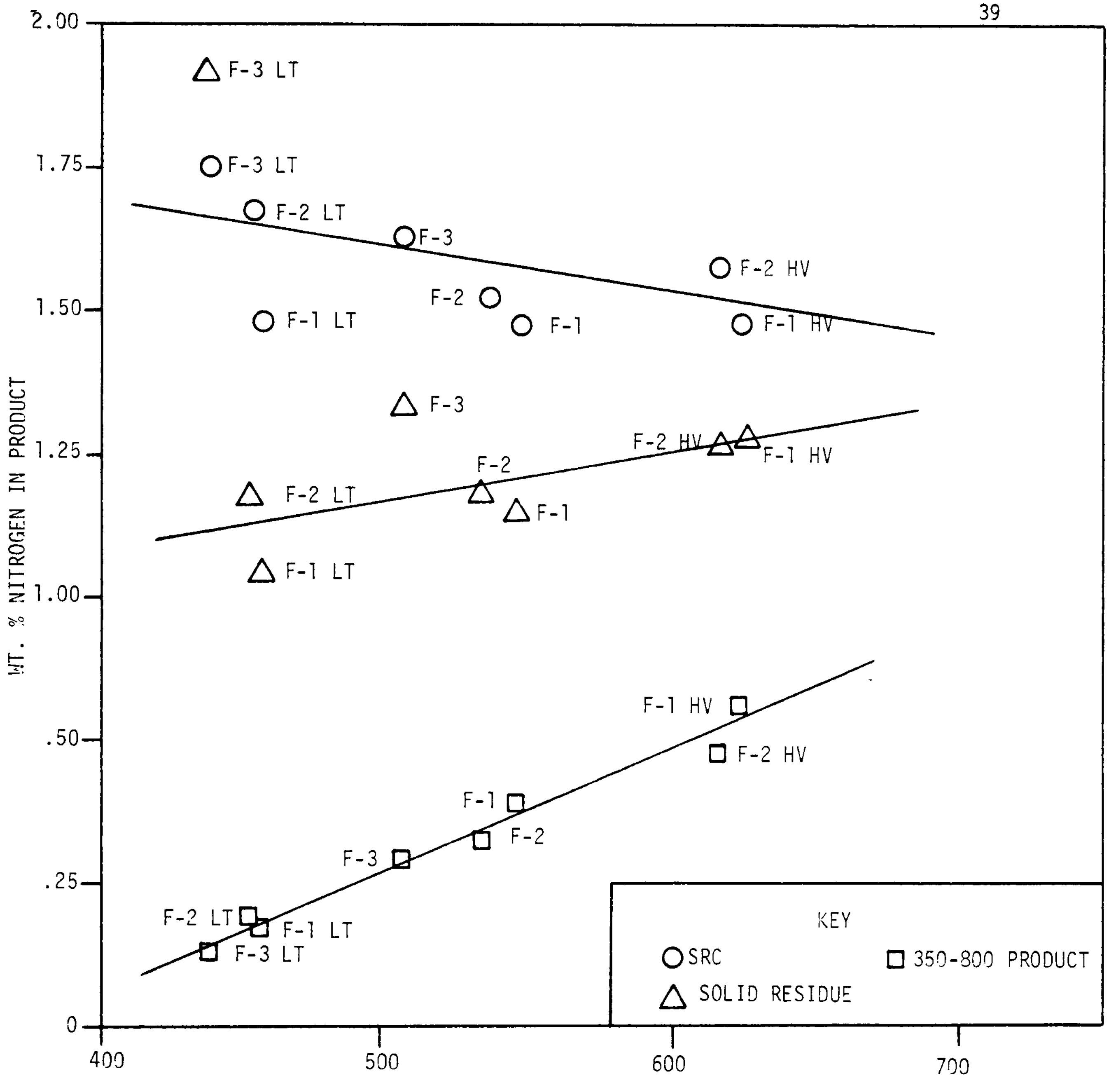


FIGURE 15- WT.% NITROGEN IN PRODUCTS VS. SOLVENT VABP (°F)

SUMMARY AND CONCLUSIONS

Solvents of varying hydrogen donor capacity and boiling range have been prepared and batch reaction conditions which give results reasonably similar to results obtained in flow systems processing Wyodak coal have been selected. Preliminary results also indicate that there is a difference in the effect of the solvents studied on the extent of Wyodak coal liquefaction, asphaltene production and nitrogen removal. Although there seems to be a trend of increasing solvent effectiveness with increasing solvent boiling range, it appears that more than one solvent property will be required to produce a statistically significant correlation of the results.

A quantitative method has been developed for determining tetralin and napthalene in solvent boiling range coal liquids. Some polycyclic aromatic hydrocarbons have been characterized using fluorescence emission spectra directly from the surface of chromatoplates with a Schoeffel spectrodensitometer. Separation schemes have been developed for the isolation of monophenols from recycle solvents. Several phenols have been identified tentatively.

Procedures have also been developed to determine the classes of nitrogen compounds in solvents and in SRC. Preliminary results indicate a high percentage of quinoline-type nitrogen compounds in coal liquids.

Future liquefaction work will be directed toward evaluating a wider range of solvents for correlation purposes. Correlation work will be extended to combine a chemical property of the solvent, perhaps to indicate the hydrogen donor capacity of the solvent, and a physical property of the solvent which would indicate the compatability of the coal liquid fragments with the solvent. Future solvent characterization work will continue in three areas: a) isolation and identification of oxygen containing compounds in liquefaction solvents, b) isolation and identification of other hydroaromatics in these solvents, and c) development of fluorescent profile techniques to determine changes in solvent composition due to the liquefaction reaction.

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APPENDIX

EXPERIMENTAL RESULTS

INTRODUCTION

In order to determine the effect of reaction conditions on solvent hydrogenation and on coal liquefaction, it has been necessary to make material balances around each step of the experimental procedure. All material balances have been adjusted to account for material lost in handling.

REACTOR DATA

During the investigation, a Wyodak coal-derived recycle solvent from the Southern Services inc., SRC plant in Wilsonville, Alabama, was used directly as received and as modified by hydrogenation in a batch autoclave. In addition, three different anthracene oils produced at the Clairton works of U.S. Steel from Pittsburgh Seam Coal, a Kentucky coal-derived recycle solvent from the Pittsburgh and Midway SRC plant in Tacoma, Washington, and an in situ coal gasification coal tar produced by the Laramie Energy Research Center at Hanna, Wyoming, were prepared for use as received and as modified by hydrogenation in a batch autoclave. In the solvent modification runs, preweighed amounts of solvent and a Co-Mo catalyst (Nalcomo 471) are added to the reactor. In the coal liquefaction runs, preweighed amounts of Wyodak coal and solvent are added to the reactor. The reactor is then flushed three times with low pressure hydrogen and then pressurized to the desired initial run pressure. The quantity of hydrogen charged to the reactor for each run is calculated from an equation of state using reactor temperature and pressure measurements, an estimate of the portion of the reactor volume occupied by the hydrogen, and tabulated compressibility factors for hydrogen. An allowance is made for the hydrogen which dissolves in the solvent when the magnetic stirrer is initially activated at room temperature.

After the reactor is checked for leaks by maintaining pressure over an extended period of time, the run is started. Cooling water is first started through the water jacket above the reactor cover. The reactor temperature and pressure and the temperature of the outer surface of the reactor is recorded. Full power is then turned on to the heating mantle. Power input is such that the reactor is heated at a rate of about 5°F per minute. After the first 30 minutes of heating, the agitator is turned on. Reactor temperature and pressure are recorded at frequent intervals during the heating period. Reactor temperatures are also recorded continuously on a Brown Electronik recorder.

The power input is cut to about 1/3 as the desired reaction temperature is approached. The reactor temperature is then brought smoothly to the desired operating temperature by passing compressed air at room temperature through the cooling coil. Temperature and pressure are recorded frequently while the reactor is at operating temperature. At the end of the run period, all power to the heating mantle is cut off and the cooling air passed through the cooling coil. Fifteen minutes later a final reading of the reactor temperature and pressure is taken and the agitator is turned off. The reactor is then allowed to cool overnight.

The products removed from the reactor consist of gases, liquids, called decant oil, and solids. Gases are first vented from the reactor through a manifold into successive gas sample tanks which had been pre-evacuated to approximately one in. of Hg total pressure until a vacuum attained in the reactor. This is done to minimize the quantity of gases which could flash into the atmosphere when the reactor is opened. Next, the gases in the sample tanks are allowed to mix through the manifold so that there will be sufficient pressure in all tanks to permit gas samples to be withdrawn. The quantity of gases collected in the sample tanks is then calculated from the ideal gas law using measurements of the molecular weight determined gravimetrically.

After the gases have been recovered, the reactor is opened and the liquid is siphoned out. Solids adhering to the reactor walls are scrapped out and added to the recovered liquid. The total recovered liquid and solid mixture is then weighed. The liquid-solid product recovered from the reactor is then centrifuged. The solid-free liquid is weighed and its specific gravity is measured with an API hydrometer.

The centrifuge residue, consisting of solid material coated with solvent, is then placed in a soxhlet extractor and washed with benzene until the benzene is clear. The washed residue is then dried and weighed.

The experimental material balance is then adjusted to a no loss basis using the data obtained from the product separation and analyses steps of the experimental procedure. Because pressure tests indicated that the gas sample system did not leak, no losses are attributed to the gases. Rather, all losses are attributed to the liquid product from the catalytic runs and are divided proportionally between the liquid and solid products in the coal liquefaction runs. However, the gas yield is adjusted to account for the ammonia and hydrogen sulfide which remain in solution in the liquid. The total grams of hydrogen sulfide produced are estimated from a sulfur balance and the grams of ammonia produced are estimated from a nitrogen balance.

Results of both the unadjusted and adjusted reactor material balances are presented in Table A-1.

GAS ANALYSIS DATA

Gas analyses are being performed to determine the molecular weight and composition of the gaseous products. Glass balloons of approximately 220 ml capacity and a Ainsworth Right-A-Weigh-type SC automatic single pan balance of 200 gram capacity is used for molecular weight determination.

The molecular weight of the gas is determined by weighing the glass balloons filled with the gas sample. Air standards are also run and the specific gravity (Air = 1.0) of the gas is determined. The molecular weight is then calculated by taking the product of the molecular weight of air and the specific gravity of the sample gas. The total weight of gases recovered is then calculated by taking the product of the sample molecular weight and the gram moles of gas taken from the reactor.

TABLE A-1
OPERATING RESULTS

RUN NUMBER	32	32b	32c	33	34	35	36	37	38	39	40	41
OPERATING CONDITIONS												
CHARGE												
COAL	C-3	C-4	C-4	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-4	C-4
SOLVENT	F-1	F-1	F-1	F-2	F-3	F-1LT	F-2LT	F-3LT	F-1HV	F-2HV	F-3HV	F-1LT
CATALYST												
OPERATING TEMPERATURE, °F	825	825	825	825	825	825	825	825	825	825	825	825
TIME AT TEMPERATURE, MIN.	0	0	0	0	0	0	0	0	0	0	0	0
INITIAL HYDROGEN PRESSURE, psi	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
MAXIMUM HYDROGEN PRESSURE, psi	4200	4200	4250	3600	3475	4425	4400	4375	4225	4050	4300	4450
OPERATING RESULTS												
CHARGE, gms												
HYDROGEN	16.6	16.4	16.4	16.6	16.4	16.3	16.4	16.5	16.4	16.4	16.6	16.4
SOLVENT	299.7	300.7	302.4	299.0	299.2	299.9	300.2	301.1	299.9	300.3	299.8	301.2
COAL	147.5	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0
CATALYST												
TOTAL	463.8	467.1	468.8	465.6	465.6	466.2	466.6	467.6	466.3	466.7	466.4	467.6
PRODUCT (RAW DATA), gms												
HYDROGEN	10.1	14.4	13.6	12.4	11.4	13.2	14.7	13.8	14.6	12.4	16.1	13.9
H_2-FREE GASES	20.3	19.2	18.9	15.8	14.1	20.4	21.5	19.5	22.9	19.1	20.3	20.4
DECANT OIL, SOLIDS, WATER, DISSOLVED H_2S & NH_3	396.3	422.7	426.1	414.0	410.5	412.4	424.2	420.0	377.1	387.1	397.6	417.9
CATALYST												
LOSSES	37.1	10.8	10.2	23.4	29.6	20.2	6.2	14.3	51.7	48.1	32.4	15.4
TOTAL	463.8	467.1	468.8	465.6	465.6	466.2	466.6	467.6	466.3	466.7	466.4	467.6
PRODUCT (ADJUSTED DATA), gms												
HYDROGEN	10.1	14.4	13.6	12.4	11.4	13.2	14.7	13.8	14.6	12.4	16.1	13.9
H_2-FREE GASES	21.2	20.0	19.8	16.6	14.5	21.5	22.1	20.3	24.4	19.8	21.1	21.7
WATER	9.3	7.3	6.5	4.4	0.8	9.5	4.1	0.7	11.4	14.0	7.4	6.2
DECANT OIL	368.6	379.4	383.3	396.0	390.2	366.6	382.8	376.9	377.0	393.3	380.3	387.4
SOLID RESIDUE	54.6	46.0	45.6	36.2	48.7	55.4	42.9	55.9	38.9	27.2	41.5	38.4
CATALYST												
TOTAL	463.8	467.1	468.8	465.6	465.6	466.2	466.6	467.6	466.3	466.7	466.4	467.6
WT % RECOVERED	92.3	97.7	97.8	95.0	93.6	95.7	98.7	96.9	88.9	89.7	93.0	96.7

TABLE A-1
OPERATING RESULTS

RUN NUMBER	41b	42	43	44	45	46	47	48	49	50	51	52	53
OPERATING CONDITIONS													
CHARGE													
COAL	C-4	C-4	C-4	C-4	C-4	C-4	C-5	C-5	C-5	C-5	C-5	C-5	C-5
SOLVENT	F-1LT	F-2LT	F-3LT	F-1HV	F-2HV	F-3HV	F-4	F-5	F-6	F-7	F-4	F-5	F-6
CATALYST													
OPERATING TEMPERATURE, °F	825	825	825	825	825	825	825	825	825	825	825	825	825
TIME AT TEMPERATURE, MIN.	0	0	0	0	0	0	0	0	0	0	0	0	0
INITIAL HYDROGEN PRESSURE, psi	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
MAXIMUM HYDROGEN PRESSURE, psi	4350	4450	4575	4425	4125	4325	4350	4325	4300	4300	4400	4150	4300
OPERATING RESULTS													
CHARGE, gms													
HYDROGEN	16.3	16.3	16.2	16.6	16.6	16.5	16.4	16.7	16.9	16.6	16.7	16.9	16.8
SOLVENT	303.3	301.0	301.8	299.8	299.5	301.5	301.1	300.9	292.5	301.6	299.7	301.8	307.0
COAL	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0	150.0
CATALYST													
TOTAL	469.6	467.3	468.0	466.4	466.1	468.0	467.5	467.6	459.4	468.2	466.4	468.7	473.8
PRODUCT (RAW DATA), gms													
HYDROGEN	13.4	13.5	13.2	13.8	12.6	11.7	12.8	13.2	12.5	12.4	11.9	12.9	13.7
H_2-FREE GASES	17.9	17.1	19.0	21.6	20.2	20.8	21.0	22.0	21.6	22.8	22.6	20.5	22.2
DECANT OIL, SOLIDS, WATER, DISSOLVED H_2S & NH_3	413.6	435.9	409.6	406.9	425.3	410.2	423.2	381.7	382.0	389.4	410.5	404.6	388.8
CATALYST													
LOSSES	24.7	0.8	26.2	24.1	8.0	25.3	10.5	50.7	43.3	43.6	21.4	30.7	49.1
TOTAL	469.6	467.3	468.0	466.4	466.1	468.0	467.5	467.6	459.4	468.2	466.4	468.7	473.8
PRODUCT (ADJUSTED DATA), gms													
HYDROGEN	13.4	13.5	13.2	13.8	12.6	11.7	12.8	13.2	12.5	12.4	11.9	12.9	13.7
H_2-FREE GASES	18.9	17.6	19.3	23.0	20.8	21.6	23.5	23.8	23.3	24.4	25.1	21.9	24.3
WATER	10.8	6.4	1.4	6.6	16.5	7.1	3.2	8.3	10.9	12.6	0.6	3.1	11.0
DECANT OIL	382.6	398.9	416.8	391.6	390.9	385.3	376.2	393.4	320.0	392.4	384.7	404.2	350.8
SOLID RESIDUE	43.9	30.9	17.3	31.4	25.3	42.3	51.8	28.9	92.7	26.4	44.1	26.6	74.0
CATALYST													
TOTAL	469.6	467.3	468.0	466.4	466.1	468.0	467.5	467.6	459.4	468.2	466.4	468.7	473.8
WT % RECOVERED	94.7	99.8	94.4	94.8	98.3	94.6	97.8	89.2	90.6	90.7	95.4	93.4	89.6

TABLE A-1
OPERATING RESULTS

RUN NUMBER	54	55	55b	56	57	57b	58	59	59b	60	61	61b	62
OPERATING CONDITIONS													
CHARGE													
COAL	C-5												
SOLVENT	F-7	F-4	F-4	F-4	F-5	F-5	F-5	F-4	F-4	F-4	F-5	F-5	F-5
CATALYST		Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo
OPERATING TEMPERATURE, °F	825	700	700	700	700	700	700	700	700	700	700	700	700
TIME AT TEMPERATURE, MIN.	0	60	60	60	60	60	60	60	60	60	60	60	60
INITIAL HYDROGEN PRESSURE, psi	2000	2000	2000	2000	2000	2000	2000	3000	3000	3000	3000	3000	3000
MAXIMUM HYDROGEN PRESSURE, psi	4475	3375	3300	3375	3325	3175	3350	5300	5050	4875	4825	4825	5500
OPERATING RESULTS													
CHARGE, gms													
HYDROGEN	16.9	10.6	10.7	10.6	11.2	11.3	11.2	15.2	15.4	15.2	16.3	16.2	16.1
SOLVENT	301.1	1002.0	1001.2	999.9	1000.1	1000.0	1000.0	1001.1	1004.6	1000.0	1000.2	1000.0	1000.0
COAL	150.0												
CATALYST		60.5	60.0	58.5	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
TOTAL	468.0	1073.1	1071.9	1069.0	1071.3	1071.3	1071.2	1076.3	1080.0	1075.2	1076.5	1076.2	1076.1
PRODUCT (RAW DATA), gms													
HYDROGEN	12.6	0.9	3.0	0.5	2.5	2.2	2.3	4.7	6.2	4.5	4.9	5.3	4.8
H_2-FREE GASES	25.0	0.6	2.0	0.2	0.6	1.1	0.6	1.0	1.1	1.7	1.5	0.7	1.1
DECANT OIL, SOLIDS WATER, DISSOLVED H_2S & NH_3	410.9	972.8	993.2	993.9	997.9	995.9	992.9	1025.9	1004.5	1000.3	997.0	999.7	1014.6
CATALYST		60.5	60.0	58.5	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
LOSSES	19.5	38.3	13.7	15.9	10.3	12.1	15.4	(15.3)	8.2	8.7	13.1	10.5	(4.4)
TOTAL	468.0	1073.1	1071.9	1069.0	1071.3	1071.3	1071.2	1076.3	1080.0	1075.2	1076.5	1076.2	1076.1
PRODUCT (ADJUSTED DATA), gms													
HYDROGEN	12.6	2.9	3.0	2.5	2.5	2.2	2.3	4.7	6.2	4.5	4.9	5.3	4.8
H_2-FREE GASES	26.3	1.6	2.0	2.2	0.6	1.1	0.6	1.0	1.1	1.7	1.5	0.7	1.1
WATER	14.7												
DECANT OIL	393.3	1008.1	1006.9	1005.8	1008.2	1008.0	1008.3	1010.6	1012.7	1009.0	1010.1	1010.2	1010.2
SOLID RESIDUE	21.1												
CATALYST		60.5	60.0	58.5	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
TOTAL	468.0	1073.1	1071.9	1069.0	1071.3	1071.3	1071.2	1076.3	1080.0	1075.2	1076.5	1076.2	1076.1
WT % RECOVERED	95.8	96.4	98.7	98.5	99.0	98.9	98.6	101.4	99.2	99.2	98.8	99.0	100.4

TABLE A-1
OPERATING RESULTS

RUN NUMBER	63	63b	64	65	65b	66	67	67b	68	69	69b	70
OPERATING CONDITIONS												
CHARGE												
COAL												
SOLVENT	F-6	F-6	F-6	F-6	F-6	F-6	F-7	F-7	F-7	F-7	F-7	F-7
CATALYST	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo
OPERATING TEMPERATURE, °F	700	700	700	700	700	700	700	700	700	700	700	700
TIME AT TEMPERATURE, MIN.	60	60	60	60	60	60	60	60	60	60	60	60
INITIAL HYDROGEN PRESSURE, psi	2000	2000	2000	3000	3000	3000	2000	2000	2000	3000	3000	3000
MAXIMUM HYDROGEN PRESSURE, psi	3250	3275	3300	4575	5025	4800	3325	3325	3400	5100	6025	5100
OPERATING RESULTS												
CHARGE, gms												
HYDROGEN	11.7	11.8	11.7	16.7	16.6	16.1	10.7	10.7	10.8	15.5	15.4	15.5
SOLVENT	992.0	997.0	1001.8	1002.1	1026.0	1024.4	1000.2	1000.0	1000.0	1000.0	1000.0	1000.1
COAL												
CATALYST	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
TOTAL	1063.7	1063.8	1073.5	1078.8	1102.6	1100.5	1070.9	1070.7	1070.8	1075.5	1075.4	1075.6
PRODUCT (RAW DATA), gms												
HYDROGEN	1.4	2.4	2.6	4.9	4.6	4.7	8.3	9.6	10.4	12.6	12.7	14.2
H_2-FREE GASES	1.7	0.9	1.5	0.9	1.6	1.4	0.9	0.8	1.0	0.8	1.4	0.8
DECANT OIL, SOLIDS, WATER, DISSOLVED H_2S & NH_3	934.0	976.6	982.9	966.0	992.4	989.4	989.8	993.1	992.1	992.5	1055.4	991.8
CATALYST	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
LOSSES	66.6	28.9	26.5	47.0	44.0	45.0	11.9	7.2	7.3	9.6	(54.1)	8.8
TOTAL	1063.7	1068.3	1073.5	1078.8	1102.6	1100.5	1070.9	1070.7	1070.8	1075.5	1075.4	1075.6
PRODUCT (ADJUSTED DATA), gms												
HYDROGEN	1.4	2.4	2.6	4.9	4.6	4.7	8.3	9.6	10.4	12.6	12.7	14.2
H_2-FREE GASES	1.7	0.9	1.5	0.9	1.6	1.4	0.9	0.8	1.0	0.8	1.4	0.8
WATER												
DECANT OIL	1000.6	1000.5	1009.4	1013.0	1036.4	1034.4	1001.7	1000.3	999.4	1002.1	1001.3	1000.6
SOLID RESIDUE												
CATALYST	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
TOTAL	1063.7	1068.8	1073.5	1078.8	1102.6	1100.5	1070.9	1070.7	1070.8	1075.5	1075.4	1075.6
WT % RECOVERED	93.7	97.3	97.5	95.6	96.0	95.9	98.9	99.3	99.3	99.1	105.0	99.2

A Hewlett-Packard Model 5840A gas chromatograph is used to analyze gas compositions. Gases are injected into the column using a six port valve (HP 18815A) connected directly to the gas sample tank. Sample size is 17 μl. A Matheson high purity mixture is used to calibrate the machine. A 12 ft. Porapak QS 50-80 mesh column is used for all runs. Gases quantitatively analyzed are hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and propane. A temperature program is used to achieve satisfactory separation. Liquid nitrogen is used to cool the chromatograph oven at the starting temperature of -40°C. This temperature is held for 4 minutes. The oven is then heated at 10°C/min to 125°C. This temperature is held for 4 minutes to complete the run. Each run lasts approximately 25 minutes.

Although the odor of H_2S and NH_3 could be detected from the reactor product, neither product showed up on the chromatograms of gases sampled from the reactor. Therefore, it is assumed that essentially all the H_2S and NH_3 is absorbed in the water produced during the liquefaction reaction and condensed before the reactor is opened. Because of the problems encountered in determining H_2S and NH_3 in the gas products, the H_2S and NH_3 produced in the reaction were calculated from S and N balances. Any difference between the S and N contents of the coals and solvents charged and the S and N contents of the oil covered centrifuge residues and the centrifuge decant oil was assumed to be due to H_2S plus NH_3 in the product. The N and S analyses of the wet centrifuge residue and the centrifuge decant oils is presented in Table A-2. The calculated grams of H_2S and NH_3 not found in the gases are added to the total gas produced and subtracted from the liquid water produced, as determined from an ASTM D-95 Dean Stark distillation using toluene.

Results of both the unadjusted and adjusted gas product material balances are presented in Table A-3.

DISTILLATION DATA

The initial step in the distillation procedure is to add approximately 100 grams of centrifuged, solid-free coal liquid and 50 grams of toluene to a tared 500 ml. distilling flask containing a magnetic stirring bar and boiling chips. The distilling flask is then placed in a heating mantle and fitted with a Dean Stark receiver and reflux condenser. The magnetic stirrer is turned on and the power to the heating mantle is turned on to approximately 20 percent of maximum. The Dean Stark distillation is continued overnight or until no more water is removed from the sample. The power to the heating mantle is then turned off and the apparatus cooled to room temperature. The water and toluene in the receiver are drawn off separately and weighed. The distilling flask is also weighed. All weights are recorded for material balance calculations. Calculated weights of H_2S and NH_3 are subtracted from the liquid water recovered and added to the gas product.

The 500 ml. distilling flask containing the residue from the Dean Stark distillation is then fitted with a ASTM D-1160 distillation head open to the atmosphere, a thermometer, a condenser, and receiving cylinders. Three receiving cylinders are attached to a three-way distillation udder so that low boiling liquid product weights can be measured directly. The magnetic stirrer is started and the power to the heating mantle is turned to 30-35 percent of full capacity.

Vapor temperatures and volumes distilled over into a receiving

TABLE A-2
CENTRIFUGE PRODUCT CHEMICAL ANALYSES

Run Number	Decant Oils (WT%) Nitrogen	Decant Oils (WT%) Sulfur	Centrifuge Residues (WT%) Nitrogen	Centrifuge Residues (WT%) Sulfur
32	.57	.09	.67	.25
32b	.55	.06	.72	.30
32c	.56	.06	.66	.30
33	.57	.07	.60	.43
34	.45	.07	.69	.28
35	.36	.08	.46	.34
36	.37	.05	.55	.32
37	.24	.12	.62	.24
38	.74	.10	.82	.24
39	.69	.08	.85	.35
40	.49	.05	.66	.24
41	.31	.03	.52	.34
41b	.36	.05	.61	.29
42	.37	.05	.62	.37
43	.41	.04	.83	.28
44	.74	.10	.86	.28
45	.67	.14	.74	.31
46	.47	.08	.73	.16
47	1.05	.25	1.06	.53
48	.91	.52	1.06	.41
49	1.03	.43	(Oil & Residue)	
50	.82	.15	1.06	.56
51	1.03	.28	1.13	.47
52	.93	.54	1.16	.56
53	.98	.42	(Oil & Residue)	
54	1.03	.19	.91	.30

TABLE A-3
GAS ANALYSES

RUN NUMBER	32	32b	32c	33	34	35	36	37	38	39	40	41	41b
RAW DATA, gms													
HYDROGEN	10.1	14.4	13.6	12.4	8.3	13.1	14.7	13.8	14.6	12.4	16.1	13.9	13.4
HYDROGEN SULFIDE													
CARBON MONOXIDE	1.0	1.5	1.4	1.4	0.9	1.7	1.6	1.5	1.4	1.5	1.3	1.6	1.3
CARBON DIOXIDE	11.8	11.7	11.3	9.8	6.4	13.4	13.7	12.0	12.5	10.2	12.2	12.6	11.8
METHANE	3.8	3.1	3.2	2.1	1.4	2.7	2.9	2.7	3.8	3.4	3.0	3.3	2.6
ETHYLENE													
ETHANE	2.3	1.8	1.9	1.3	0.9	1.5	1.8	1.6	2.7	2.1	1.9	1.8	1.4
PROPANE	1.4	1.2	1.2	1.1	0.7	1.0	1.5	1.8	2.4	1.8	1.8	1.1	0.8
TOTAL	30.4	33.7	32.6	28.1	18.6	33.4	36.2	33.4	37.4	31.4	36.3	34.3	31.3
ADJUSTED DATA, gms													
HYDROGEN	10.1	14.4	13.6	12.4	11.4	13.1	14.7	13.8	14.6	12.4	16.1	13.9	13.4
HYDROGEN SULFIDE	0.4	0.5	0.5	0.3	0.1	0.4	0.1	0.0	1.0	0.4	0.3	0.7	0.7
AMMONIA	0.5	0.3	0.4	0.5	0.3	0.7	0.5	0.8	0.5	0.3	0.5	0.6	0.3
CARBON MONOXIDE	1.0	1.5	1.4	1.4	1.2	1.7	1.6	1.5	1.4	1.5	1.3	1.6	1.3
CARBON DIOXIDE	11.8	11.7	11.3	9.8	8.9	13.4	13.7	12.0	12.5	10.2	12.2	12.6	11.8
METHANE	3.8	3.1	3.2	2.1	1.9	2.7	2.9	2.7	3.8	3.4	3.0	3.3	2.6
ETHYLENE													
ETHANE	2.3	1.8	1.9	1.3	1.2	1.5	1.8	1.6	2.7	2.1	1.9	1.8	1.4
PROPANE	1.4	1.2	1.2	1.1	1.0	1.0	1.5	1.8	2.4	1.8	1.8	1.1	0.8
TOTAL	31.3	34.5	33.5	28.9	26.0	34.5	36.8	34.2	38.9	32.1	37.2	35.6	32.3
MOLECULAR WEIGHT													
COMPONENT ANALYSIS, UNADJUSTED	5.33	4.32	4.44	4.23	4.13	4.67	4.52	4.45	4.67	4.61	4.19	4.52	4.34
DENSITY MEASUREMENTS	4.96	3.75	3.88	4.39	4.27	3.72	4.13	3.70	4.25	3.82	4.12	3.91	3.56

TABLE A-3
GAS ANALYSES

RUN NUMBER	42	43	44	45	46	47	48	49	50	51	52	53
RAW DATA, gms												
HYDROGEN	13.5	13.2	13.8	12.6	11.7	12.9	13.2	12.5	12.4	11.9	12.9	13.7
HYDROGEN SULFIDE												
CARBON MONOXIDE	1.4	1.3	1.4	1.6	1.4	1.4	1.4	1.4	1.4	1.6	1.4	1.5
CARBON DIOXIDE	10.8	11.3	12.4	10.9	11.8	13.2	14.5	14.4	12.5	13.6	13.7	14.9
METHANE	2.8	3.2	3.4	3.5	3.1	3.4	2.6	2.4	4.1	4.0	2.5	2.5
ETHYLENE												
ETHANE	1.4	1.8	2.4	2.4	2.2	1.7	1.9	1.9	2.7	1.9	1.7	1.8
PROPANE	0.7	1.3	2.0	1.9	2.4	1.3	1.5	1.5	2.2	1.5	1.3	1.6
TOTAL	30.6	32.1	35.4	32.9	32.6	33.9	35.1	34.1	35.3	34.5	33.5	36.0
ADJUSTED DATA, gms												
HYDROGEN	13.5	13.2	13.8	12.6	11.7	12.9	13.2	12.5	12.4	11.9	12.9	13.7
HYDROGEN SULFIDE	0.2	0.3	1.1	0.3	0.4	1.6	1.2	1.3	1.3	1.7	1.0	1.4
AMMONIA	0.3	0.0	0.3	0.3	0.4	0.9	0.6	0.4	0.3	0.8	0.4	0.7
CARBON MONOXIDE	1.4	1.3	1.4	1.6	1.4	1.4	1.4	1.4	1.4	1.6	1.4	1.5
CARBON DIOXIDE	10.8	11.3	12.4	10.9	11.8	13.2	14.5	14.4	12.5	13.6	13.7	14.9
METHANE	2.8	3.2	3.4	3.5	3.1	3.4	2.6	2.4	4.1	4.0	2.5	2.5
ETHYLENE												
ETHANE	1.4	1.8	2.4	2.4	2.2	1.7	1.9	1.9	2.7	1.9	1.7	1.8
PROPANE	0.7	1.3	2.0	1.9	2.4	1.3	1.5	1.5	2.2	1.5	1.3	1.6
TOTAL	31.1	32.4	36.8	33.5	33.4	36.4	36.9	35.8	36.9	37.0	34.9	38.1
MOLECULAR WEIGHT												
COMPONENT ANALYSIS, UNADJUSTED	4.23	4.50	4.73	4.74	5.05	4.82	4.89	4.98	5.12	5.23	4.77	4.80
DENSITY MEASUREMENTS	3.65	3.74	4.03	3.99	3.73	3.99	3.99	4.04	4.16	4.07	3.90	4.17

TABLE A-3
GAS ANALYSES

RUN NUMBER	54	55	55b	56	57	57b	58	59	59b	60	61	61b	62
RAW DATA, gms													
HYDROGEN	12.6	0.9	3.0	0.5	2.5	2.2	2.3	4.7	6.2	4.5	4.9	5.3	4.8
HYDROGEN SULFIDE													
CARBON MONOXIDE	1.3												
CARBON DIOXIDE	13.2												
METHANE	4.3	0.3	1.1	0.1	0.3	0.5	0.3	0.7	0.8	1.2	0.5	0.4	0.5
ETHYLENE													
ETHANE	3.3	0.2	0.5	0.1	0.2	0.3	0.2	0.3	0.3	0.5	0.7	0.2	0.3
PROPANE	3.0	0.1	0.5		0.1	0.3	0.1		0.1		0.3	0.1	0.3
TOTAL	37.7	1.5	5.1	0.7	3.1	3.3	2.9	5.7	7.4	6.2	6.4	6.0	5.9
ADJUSTED DATA, gms													
HYDROGEN	12.6	0.9	3.0	0.5	2.5	2.2	2.3	4.7	6.2	4.5	4.9	5.3	4.8
HYDROGEN SULFIDE	1.3												
AMMONIA	0.0												
CARBON MONOXIDE	1.3												
CARBON DIOXIDE	13.2												
METHANE	4.3	0.3	1.1	0.1	0.3	0.5	0.3	0.7	0.8	1.2	0.5	0.4	0.5
ETHYLENE													
ETHANE	3.3	0.2	0.5	0.1	0.2	0.3	0.2	0.3	0.3	0.5	0.7	0.2	0.3
PROPANE	3.0	0.1	0.5		0.1	0.3	0.1		0.1		0.3	0.1	0.3
TOTAL	39.0	1.5	5.1	0.7	3.1	3.3	2.9	5.7	7.4	6.2	6.4	6.0	5.9
MOLECULAR WEIGHT													
COMPONENT ANALYSIS, UNADJUSTED	5.35	3.15	3.17	2.69	2.48	2.85	2.56	2.38	2.31	2.66	2.19	2.23	2.40
DENSITY MEASUREMENTS	4.35	----	3.79	----	2.76	2.91	2.72	2.55	2.48	2.61	2.37	2.40	2.40

TABLE A-3
GAS ANALYSES

RUN NUMBER	63	63b	64	65	65b	66	67	67b	68	69	69b	70
RAW DATA, gms												
HYDROGEN	1.4	2.4	2.6	4.9	4.6	4.7	8.3	9.6	10.4	12.6	12.6	14.2
HYDROGEN SULFIDE												
CARBON MONOXIDE												
CARBON DIOXIDE												
METHANE	0.6	0.4	0.6	0.4	0.7	0.7	0.5	0.5	0.5	0.4	0.5	0.4
ETHYLENE												
ETHANE	0.7	0.3	0.7	0.3	0.5	0.5	0.3	0.2	0.3	0.2	0.3	0.2
PROPANE	0.4	0.1	0.3	0.1	0.4	0.2	0.1	0.1	0.2	0.2	0.6	0.1
TOTAL	3.1	3.2	4.2	5.7	6.2	6.1	9.2	10.4	11.4	13.4	14.0	14.9
ADJUSTED DATA, gms												
HYDROGEN	1.4	2.4	2.6	4.9	4.6	4.7	8.3	9.6	11.4	12.6	12.6	14.2
HYDROGEN SULFIDE												
AMMONIA												
CARBON MONOXIDE												
CARBON DIOXIDE												
METHANE	0.6	0.4	0.6	0.4	0.7	0.7	0.5	0.5	0.5	0.4	0.5	0.4
ETHYLENE												
ETHANE	0.7	0.3	0.7	0.3	0.5	0.5	0.3	0.2	0.3	0.2	0.3	0.2
PROPANE	0.4	0.1	0.3	0.1	0.4	0.2	0.1	0.1	0.2	0.2	0.6	0.1
TOTAL	3.1	3.2	4.2	5.7	6.2	6.1	9.2	10.4	11.4	13.4	14.0	14.9
MOLECULAR WEIGHT												
COMPONENT ANALYSIS, UNADJUSTED	4.09	2.63	3.02	2.33	2.63	2.52	2.18	2.14	2.17	2.12	2.20	2.09
DENSITY MEASUREMENTS	2.99	2.60	3.70	2.44	2.80	2.67	2.03	2.28	2.40	2.10	2.29	2.33

cylinder are recorded at the first drop and at 5 ml. to 10 ml. intervals. The distillation is continued until all toluene and the coal liquid boiling below 350°F are removed. The heating mantle power is then turned off and the apparatus cooled to room temperature. The distillate is then weighed and recorded for material balance calculations. All vapor temperatures are corrected from 585 millimeters, Laramie atmospheric pressure, to 760 millimeters of mercury.

The apparatus containing the 350°F+ residue is then connected to a vacuum system. A cold trap is connected to the condenser outlet and is placed in a dry ice-acetone mixture. The magnetic stirrer in the distillation flask is then activated, the vacuum pump turned on, and the power to the heating mantle turned on to 30-35 percent of maximum. The pressure in the system is then adjusted to 2 millimeters of mercury, and maintained at this level throughout the vacuum distillation. Vapor temperatures and volumes distilled over into the receiving flask are recorded at the first drop and at frequent intervals. All vapor temperatures are corrected to 760 millimeters. The power to the heating mantle is then turned off and the apparatus cooled to room temperature under a residual vacuum.

After the apparatus has cooled, the distillate fractions boiling between 350°-500°F, 500°-650°F and 650°-800°F are weighed and stored. The cold trap is removed and allowed to warm enough so that frost no longer forms on the side. The cold trap is then weighed, and the material collected in the cold trap is added to the minus 350°F distillate. No water has been observed to be present in the cold trap for any of the runs. The distillation residue boiling above 800°F and called solvent refined coal, SRC, is weighed and set aside for further analyses. All weights are recorded for material balance calculations.

Results of the unadjusted and adjusted distillation material balances are presented in Table A-4.

SOLUBILITY DATA

The total liquid-solid product from the reactor is centrifuged to produce a solid-free liquid and an oil-coated solid residue. The oil is separated from the centrifuge residue by washing a sample of the residue with pyridine, a second sample of residue with benzene and a third sample of residue with hexane in 250 ml. soxhlet extractors. Extractions are continued overnight or until the wash solvent appeared to be clear. Material balances around the centrifuge residue extractions showed significant losses (in the order of 20% to 30%). These losses are arbitrarily assigned to the soluble portion of the product. All extractions are performed in duplicate and the adjusted results of these experiments are summarized in Table A-5.

In addition, soxhlet extractions are also performed on the solid-free liquid product boiling above 800°F called SRC. Duplicate samples are extracted with pyridine, a second set of duplicate samples are extracted with benzene and a third set of duplicate samples are extracted with hexane. Material balances indicated an average closure of approximately 95%. The benzene benzene-soluble product is stored in glass sample bottles for

TABLE A-4
DISTILLATION DATA

RUN NUMBER	32	32b	32c	33	34	35	36	37	38	39	40	41	41b
DEAN STARK													
CHARGE, (gms)													
TOLUENE	50.3	50.4	50.3	50.0	44.8	48.5	50.4	50.0	51.4	52.2	51.5	51.1	55.5
DECANT OIL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
TOTAL	150.3	150.4	150.3	150.0	144.8	148.5	150.4	150.0	151.4	152.2	151.5	151.1	155.5
PRODUCT													
TOLUENE	18.5	19.2	19.2	19.8	21.2	20.3	20.2	20.8	18.0	18.2	19.1	19.5	18.5
WATER	2.7	2.1	1.9	1.3	0.3	2.8	1.2	0.4	3.3	3.6	2.1	1.9	3.0
DECANT OIL & TOLUENE	127.7	128.4	127.8	127.9	122.6	124.4	128.7	128.0	129.3	129.9	130.0	128.8	133.3
LOSSES	1.4	0.7	1.4	1.0	0.7	1.0	0.3	0.8	0.8	0.5	0.3	0.9	0.7
TOTAL	150.3	150.4	150.3	150.0	144.8	148.5	150.4	150.0	151.4	152.2	151.5	151.1	155.5
WT % RECOVERY	99.1	99.5	99.1	99.3	99.5	99.3	99.8	99.5	99.5	99.7	99.8	99.4	99.5
DISTILLATION													
CHARGE, (gms)	127.7	128.4	127.8	127.9	122.6	124.4	128.7	128.0	129.3	129.9	130.0	128.8	133.3
PRODUCT, (gms)													
TOLUENE	30.2	30.6	29.5	28.6	21.6	27.2	30.0	28.0	32.3	33.2	30.4	30.8	36.4
350 °F-	6.3	3.2	5.2	6.4	7.6	5.6	6.4	12.0	2.3	2.6	4.2	5.7	5.8
350-500 °F	30.3	33.2	29.7	28.4	35.1	59.4	58.7	59.6	2.1	2.2	0.5	60.5	60.8
500-650 °F	25.9	26.7	26.4	28.3	26.4	9.4	10.8	8.5	43.4	46.3	48.5	9.4	8.8
650-800 °F	14.1	11.9	13.1	14.0	12.2	4.2	4.3	4.0	21.1	21.4	23.6	5.3	4.6
800 °F +	20.2	22.3	23.3	22.0	19.2	18.4	17.6	15.2	28.1	23.8	22.4	17.1	16.5
LOSSES	0.7	0.5	0.6	0.2	0.5	0.2	0.9	0.7	0.0	0.4	0.4	0.0	0.4
TOTAL	127.7	128.4	127.8	127.9	122.6	124.4	128.7	128.0	129.3	129.9	130.0	128.8	133.3
WT % RECOVERY	99.5	99.6	99.5	99.8	99.6	99.8	99.3	99.5	100.0	99.7	99.7	100.0	99.7
ADJUSTED MATERIAL BALANCE													
CHARGE, (gms)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
PRODUCT, (gms)													
H_2O (ℓ) + dissolved NH_3+H_2S	2.7	2.1	1.9	1.3	0.3	2.8	1.2	0.4	3.3	3.6	2.1	1.9	3.0
350 °F-	6.4	5.7	5.6	6.3	6.8	6.1	7.2	12.2	2.2	2.5	2.8	6.2	6.3
350-500 °F	30.4	31.3	29.7	28.4	35.1	59.3	58.8	59.7	2.1	2.2	0.6	60.4	60.8
500-650 °F	26.0	26.7	26.4	28.2	26.4	9.3	10.9	8.5	43.4	46.4	48.5	9.3	8.8
650-800 °F	14.2	11.9	13.1	13.9	12.2	4.1	4.3	4.0	21.0	21.5	23.6	5.2	4.6
800 °F +	20.3	22.3	23.3	21.9	19.2	18.4	17.6	15.2	28.0	23.8	22.4	17.0	16.5
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

TABLE A-4
DISTILLATION DATA

RUN NUMBER	42	43	44	45	46	47	48	49	50	51	52	53	54
DEAN STARK													
CHARGE, (gms)													
TOLUENE	50.0	51.5	51.5	50.4	50.0	50.0	50.0	50.0	50.8	50.5	50.0	50.0	50.0
DECANT OIL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
TOTAL	150.0	151.5	151.5	150.4	150.0	150.0	150.0	150.0	150.8	150.5	150.0	150.0	150.0
PRODUCT													
TOLUENE	19.6	20.6	51.5	17.1	19.5	19.9	18.3	17.9	17.8	19.6	17.9	17.8	17.5
WATER	1.7	0.4	2.0	4.2	2.0	1.5	2.5	3.8	3.5	0.8	1.1	3.6	3.9
DECANT OIL & TOLUENE	128.0	129.7	92.5	127.9	127.7	128.3	127.7	127.6	128.4	128.2	127.7	127.5	127.7
LOSSES	0.7	0.8	5.5	1.2	0.8	0.3	1.0	0.7	1.1	1.9	3.3	1.1	0.9
TOTAL	150.0	151.5	151.5	150.4	150.0	150.0	150.0	150.0	150.3	150.5	150.0	150.0	150.0
WT % RECOVERY	99.5	99.5	96.4	99.2	99.5	99.8	99.3	99.5	99.3	98.7	97.8	99.3	99.4
DISTILLATION													
CHARGE, (gms)	128.0	129.7	92.5	127.9	127.7	128.3	127.7	127.6	128.4	128.2	127.7	127.5	127.7
PRODUCT, (gms)													
TOLUENE	29.7	30.4	0.0	32.0	29.4	29.7	29.8	31.3	32.3	29.4	29.0	31.0	31.6
350 °F-	5.7	9.2	0.0	3.5	1.8	2.3	3.2	1.2	2.5	2.3	5.0	1.5	2.3
350-500 °F	61.1	59.6	5.5	2.3	1.8	20.1	0.0	0.9	0.9	18.1	0.0	0.0	0.7
500-650 °F	9.7	8.8	38.9	45.6	45.8	48.0	18.3	3.3	39.4	50.9	23.3	4.7	40.1
650-800 °F	4.8	4.5	20.3	21.3	23.7	6.4	44.7	42.3	19.9	3.8	39.5	42.9	18.7
800 °F +	16.1	16.5	27.3	22.8	24.7	22.7	31.0	48.4	33.7	22.8	30.5	48.0	33.5
LOSSES	0.9	0.7	0.5	0.4	0.5	(0.9)	0.7	0.2	(0.3)	0.9	0.4	(0.6)	0.8
TOTAL	128.0	129.7	92.5	127.9	127.7	128.3	127.7	127.6	128.4	128.2	127.7	127.5	127.7
WT % RECOVERY	99.3	99.5	99.5	99.7	99.6	100.7	99.5	99.8	100.2	99.3	99.7	100.5	99.4
ADJUSTED MATERIAL BALANCE													
CHARGE, (gms)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
PRODUCT, (gms)													
H_2O (ℓ) + DISSOLVED NH_3+H_2S	1.7	0.4	2.0	4.2	2.0	1.5	2.5	3.8	3.5	0.8	1.1	3.6	3.9
350 °F-	6.6	10.1	5.5	3.8	2.0	2.2	3.4	1.3	2.6	3.3	5.6	1.6	2.8
350-500 °F	61.1	59.7	6.0	2.3	1.8	19.9	0.0	0.9	0.9	18.2	0.0	0.0	0.8
500-650 °F	9.7	8.8	38.9	45.6	45.8	47.8	18.4	3.3	39.4	51.0	23.3	4.4	40.2
650-800 °F	4.8	4.5	20.3	21.3	23.7	6.2	44.7	42.3	19.9	3.9	39.5	42.6	18.8
800 °F +	16.1	16.5	27.3	22.8	24.7	22.4	31.0	48.4	33.7	22.8	30.5	47.8	33.5
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

TABLE A-5
WEIGHT % INSOLUBLES

	CENTRIFUGE RESIDUE			SOLIDS FREE SRC (800 °F +)		
RUN	PYRIDINE	BENZENE	n-HEXANE	PYRIDINE	BENZENE	n-HEXANE
32	26.2%	32.7%	45.6%	----	37.3%	88.0%
32b	26.9	35.5	47.0	4.0	34.2	70.0
32c	29.3	36.5	43.7	1.6	32.9	76.9
33	31.3	31.8	47.2	4.0	18.1	68.6
34	28.7	32.9	47.2	3.8	20.7	62.8
35	38.0	45.7	56.3	7.0	43.7	84.9
36	35.0	38.8	51.6	1.3	38.8	84.2
37	28.0	35.0	47.6	4.3	37.1	71.7
38	22.7	31.4	49.6	4.5	39.3	69.8
39	----	33.4	----	3.9	28.4	53.3
40	15.6	24.2	37.0	2.8	23.5	57.0
41	32.4	38.8	48.5	1.5	36.9	89.5
41b	----	39.3	----	0.7	43.4	89.5
42	37.0	35.4	55.4	2.3	42.4	80.6
43	----	35.6	----	0.0	31.5	75.2
44	28.1	36.4	45.3	3.4	29.7	76.5
45	31.9	38.3	46.1	3.9	35.6	73.0
46	21.0	28.6	37.1	3.3	29.2	55.8
47	20.4	30.5	36.6	3.6	29.5	79.6
48	23.0	34.0	48.3	13.0	45.1	78.4
49	7.0	21.8	72.6	16.5	40.7	57.8
50	23.9	33.7	40.4	9.5	35.2	64.8
51	19.5	28.9	37.9	1.8	38.5	85.1
52	25.5	35.1	43.5	16.3	47.1	83.5
53	7.1	16.7	73.9	17.0	42.4	62.1
54	27.5	30.0	41.3	9.3	37.2	70.4

further nitrogen type analyses. Again, all losses are attributed to the soluble portion of the SRC product. Adjusted results of these experiments are also summarized in Table A-5.

CHEMICAL ANALYSIS

A. Grinding

The coal sample as received has a size range from approximately 1/2 to 2 inches. The coal is ground in an air atmosphere by first reducing the size to less than 1/16" by using a jaw and roll crusher. A 6 1/2 inch McCoal pulverizer is used for the final size reduction on samples. After pulverization, the samples are split with a portion being air dried for screening and ultimate analysis. The remainder is stored in sealed glass jars until charging to the reactor.

B. Proximate Analysis

Standard ASTM procedures are followed in the determination of ash, moisture, volatile matter and fixed carbon in coal.

C. Ultimate Analysis

1. Nitrogen: The analysis of all liquid and solid samples (decant oils, SRC, feed solvents coal, residue, benzene insoluble residue) is by the macro Kjeldahl nitrogen method (ASTM 3179). Elemental mercury is used as the catalyst in the digestion step which converts the nitrogen to ammonium salts. The ammonia produced when the caustic NaOH solution is added to the ammonium salt solution is collected in a 5% boric acid solution and titrated with .1 N HCl to the endpoint.

2. Carbon-Hydrogen: The sample is placed in an unglazed zircon combustion boat, covered with dried alumina and slowly pushed into a globar furnace where it is burned in a closed system of oxygen. The H_2O and CO_2 formed by the combustion of the sample are absorbed on anhydrane (magnesium perchlorate, anhydrous) and ascarite (NaOH on asbestos). The hydrogen and carbon in the sample is determined by the increase in weight of the Nesbitt absorption bulbs. A silver plug is placed in the combustion tube before the absorbers to purify the gas stream of sulfur and halogens

The temperature of the hot zone and the size of the sample is dependent on the type of sample. For Wyodak coal a temperature of 1250°C is used for a .2g sample. For SRC a maximum temperature of 1000°C is used for a .2g sample. Due to their explosiveness, the oil samples (.05g) are placed in a quartz tube packed with acid washed asbestos and burned at 850°C.

3. Sulfur:

(a) The ASTM procedure for the sulfur determination by the Eschka method is used in determining the total sulfur in the coal and SRC samples.

(b) Sulfur types in coal are analyzed using ASTM procedures.

(c) A Leco sulfur analyzer (Laboratory Equipement Corporation) is used for the determination of sulfur in the oils, centrifuge residues and ashes.

4. Oxygen: This quantity is obtained by difference.

D. Nitrogen Type Analysis

A procedure which involves non-aqueous titrations in three solvents and infrared analysis was successfully employed by Wang (2) in the determination of nitrogen types in shale oils. The same procedure has been used in determining the weight fraction of quinoline, indole, amine, and amide-type nitrogen compounds in coal oils.

The procedure consists of titrating the sample in three solvents--acetic acid, acetic anhydride, and a mixed solvent consisting of a .1M solution of acetic anhydride in acetic acid to obtain the weight fraction for all but the indole-type compounds. The five member ring heterocyclics such as carbazoles and indoles are too weakly basic to be titrated quantitatively. Infrared analysis is used to estimate the content of this class of compound. Table A-6 shows the chemical types which are titratable in the various solvents and Table A-7 gives the procedures for obtaining the weight fraction of the various nitrogen types.

Non-aqueous titrations

All titrations are run on a Precision-Dow Recordomatic Titrometer using the millivolt mode. The electrode system consists of a Beckman calomel electrode (NO. 39400) with a saturated solution of KCl in methanol and a Beckman glass reference electrode (NO. 39301).

1. Reagents:

(a) .1 N perchloric acid in purified dioxane solution is used as the titrant in all the solvent systems. Benzene is used as co-solvent to facilitate the dissolution of the sample. The acetic acid and acetic anhydride solutions are made by mixing 30 ml. of the reagent with 15 ml. of benzene. The mixed solution is prepared by adding 5 ml. of benzene to 50 ml. of a .1 M acetic anhydride in acetic acid solution.

(b) Procedure: The electrodes are preconditioned by soaking them in the particular solvent used in the titration for at least an hour. A .3 gram sample of process solvent or a 10-20 ml. sample of the benzene soluble SRC oil is placed in a 100 ml. beaker and dissolved in the freshly prepared solvent. For the mixed solvent titration the solution is stirred for an hour prior to titration. The acetic acid and acetic anhydride solutions are titrated immediately. The titration curve is recorded automatically with the endpoint of the titration being determined from the inflection of the curve indicating the maximum change in potential. The distance between the starting

TABLE A-6

BASIC NITROGEN TYPES BY TITRATION

Solvent	Chemical Types Titratable
Acetic Anhydride	Strong base: Quinolines, 3° amines
	Weak base: 1, 2, 3, 4--Tetrahydroquinoline 1° and 2° amines, amides, some indoles
Acetic Acid	Strong base: Quinolines, 1, 2, 3, 4--Tetrahydroquinolines, 1°, 2°, 3° amines
Mixed Solvent	Strong base: Quinolines, 1°, 2°, 3° amines

TABLE A-7

NITROGEN CLASSES FROM TITRATION RESULTS

(1) Quinolines = Strong base nitrogen in acetic anhydride

(2) Indoles = IR determined nitrogen

(3) Aryl amines = Acetic Acid - Mixed Solvent

(4) 1°, 2° amines = Mixed - Strong base nitrogen in acetic anhydride

(5) Amides = Total Titratable Nitrogen (TTN) in acetic anhydride - acetic acid - 0.5 (Indoles)

and endpoints are measured and corrected by running a blank by titrating a sample of quinoline. The weight percent of the various nitrogen types is determined by the following relationships:

$$\text{(i)}\quad \frac{\text{grams of nitrogen}}{\text{cm. of chart}} = \frac{\text{wt. of quinoline}}{\text{cm. of chart}} \times \frac{14\ (\text{M.W. of nitrogen})}{129.15\ (\text{M.W. of quinoline})}$$

(ii) Wt. % of nitrogen in sample

$$= \frac{\text{corrected cm. of chart}}{\text{weight of sample}} \times \frac{\text{grams of nitrogen}}{\text{cm. of chart}} \times 100$$

In order to determine the two potential breaks in the curve for the acetic anhydride titration it is necessary to dope the sample with approximately .003 grams of n, n-dimethyl formamide ($HCON(CH_3)$). This is necessary to spread the distance between the endpoint of the total titratable nitrogen and the strongly basic nitrogen so that they are easier to detect. The chart distance corresponding to the weight of doping agent used is subtracted from the second endpoint (total titratable) to obtain the weight percent of TTN attributed to the oil sample.

To obtain the weight of oil present in the benzene soluble SRC samples, the total volume of the solution obtained from the soxhlet extraction was measured. Knowing the weight of SRC which is soluble, it is then possible to obtain a density of oil in the soxhlet solution. Using this density it is then possible to determine the weight of soluble oil in a 20 ml. sample of the soxhlet solution. The total nitrogen in the soluble oil is obtained by difference. A Kjeldahl nitrogen determination is made on the insoluble SRC and the total SRC. The nitrogen in the soluble oil is given by:

% nitrogen in soluble SRC =

$$\frac{\%\ \text{N in SRC} - (\%\ \text{N in insoluble SRC})(\text{fraction insolubles})}{(1 - \text{fraction insolubles})}$$

There is a possibility that the large fraction of miscellaneous nitrogen that is unaccounted for may be due to the temperature of the nitrogen analysis being lower than the boiling point of benzene. Some of the nitrogen compounds which are soluble at the temperature of the soxhlet extraction may not be soluble at room temperature where the analysis is performed. Further, any small errors in the total nitrogen analysis of the SRC and in the nitrogen analysis of the benzene insoluble SRC could lead to a larger error in the total predicted total nitrogen in the benzene soluble SRC.

Infrared Analysis

A Beckman ACTA MIV spectrophotometer is used for this analysis. The sample is dissolved in reagent grade CCl_4 (5 to 10 gms/l) and scanned in the region of 3600 to 3200 cm^{-1}. A 1.0 cm quartz cell is used in the reference and sample beam. It is assumed that the molal absorptivity of the NH group is the same in all the molecules containing pyrrole rings.

The average absorptivity for the NH stretch of the five-member ring is taken as 16.85/gmN/l/cm. The wt % of nitrogen contained in a five-member ring is calculated from the absorption at 3480 cm^{-1}.

wt % indole-type nitrogen =

$$\frac{\text{absorbance of peak at 3480 cm}^{-1}\text{ measured from base line}}{.1685 \times \text{conc. (gm/l)} \times \text{cell path (cm)}}$$

A summary of the experimantal results on nitrogen classes is presented in Table A-8 and A-9.

E. Aliphatic to Aromatic Hydrogen Ratio Analysis

A Beckman IR 10 spectrometer is used to determine the aliphatic to aromatic hydrogen ratios of the solvents using infrared absorption ratios. Two to four drops of oil are placed between Econo-Cell, number 0026-011, NaCl plates, obtained from Barnes Infrared Analytical Accessories. These plates are four mm thick by twenty mm in diameter.

The oils are scanned from 4000 to 2500 cm^{-1} and the aromatic peak is at 3060 cm^{-1} while the aliphatic peak is at 2940 cm^{-1}. The measured infrared transmittances are then converted to absorbance using the relationship

$$\text{absorbance} = -\log\ (\text{transmittance})$$

where transmittance is a decimal fraction. In order to check the precision of this method, a sample that had been analyzed at the Merriam Laboratories of Pittsburgh and Midway Coal Mining Company was reanalyzed. The Merriam labs reported an absorbance ratio of 2.96 compared to an absorbance ratio of 3.10 obrained in this laboratory.

TABLE A-8

TITRATION RESULTS FOR COAL SOLVENTS

wt. % titrated

Solvent	Infrared	Mixed	Acetic Acid	Acetic TTN	Anhydride SBN	Total N
F1	.081	.372	.408	.455	.310	.49
F1 LT	.030	.170	.181	.196	.170	.23
F1 HV	.099	.417	.454	.534	.407	.70
F2	.082	.248	.326	.380	.186	.45
F2 LT	.021	.144	.187	.204	.118	.22
F2 HV	.115	.295	.421	.494	.245	.60
F3	.079	.118	.295	.316	.109	.34
F3 LT	.033	.050	.234	.232	.040	.25
F3 HV	.111	.163	.226	.352	.161	.46

TABLE A-9

TITRATION RESULTS FOR SOLUBLE SRC

wt. % titrated

Run	Infrared	Mixed	Acetic Acid	Acetic TTN	Anhydride SBN	Total N
28	.333	.558	.556	.851	.535	1.53
29	.385	.556	.556	.879	.551	1.07
30	.359	.662	.666	.946	.558	1.16
31	.360	.663	.678	1.010	.567	1.41
32	lost sample					
32b	.192	.375	.417	.572	.345	1.38
32c	.136	.412	.428	.617	.409	.74
33	.343	.520	.526	.877	.505	1.12
34	.410	.541	.561	.695	.490	1.31
35	.172	.550	.630	.772	.419	1.39
36	.126	.525	.607	.716	.406	1.12
37	.109	.549	.624	.783	.473	1.36
38	.218	.521	.548	.671	.480	1.43
39	.168	.585	.624	.671	.404	1.18
40	.147	.436	.562	.600	.356	1.00
41	.147	.565	.645	.743	.446	.92
41b	.191	.548	.614	.674	.422	.94

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