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EFFECTS OF SOLVENT CHARACTERISTICS ON WYODAK COAL LIQUEFACTION

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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 first year of this project.

During the past year, three different solvents have been prepared for use in this study. Solvent F-1 was produced from recycle SRC operation of Wyodak coal at Wilsonville, Alabama. Because hydrogen donor capacity seems to be an important solvent property, solvent F-2 was prepared by hydrogenating the F-1 solvent over a Co-Mo catalyst under mild reaction conditions, and solvent F-3 was prepared using severe hydrogenation conditions. The tetralin content of F-1, as measured using procedures developed in this work, was increased from 2.3 wt% to 2.7 wt% in F-2 and 6.1 wt% in F-3.

Several preliminary coal-solvent runs were performed in order to establish reaction conditions which would produce results comparable to the results obtained in flow reactor studies of Wyodak coal at Wilsonville and at HRI. This work indicates that mass transfer of hydrogen from the gas phase to the solid-liquid phase may be a rate limiting step.

Batch reactor runs in which Wyodak coal and solvent under a cold reactor pressure of 2000 psig were heated to 850°F and held at this temperature for 40 minutes gave a conversion of 91.7 wt%. This conversion is comparable to a conversion at 850°F of 93 wt% obtained by HRI. However, as there was a net solvent loss of 7.9 wt%, based on MF coal charged, reaction conditions were reduced to 0 minutes at 825°F. Under these conditions, a conversion of 79.8 wt% was obtained which is somewhat lower than the 83% conversion obtained at 824°F in flow reactor studies at Wilsonville. Even though a net solvent loss of 7.5 wt%, based on MF coal, was observed at these conditions compared to a net solvent gain of 13.4 wt% at Wilsonville, these latter reaction conditions have been selected as the basis for further studies.

In single runs using F-1, F-2 and F-3 solvents under the same reaction conditions, little, if any, difference was seen in the extent of Wyodak coal liquefaction, asphaltene production or nitrogen removal. F-3 solvent did produce more hexane soluble oil than the other two solvents.

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.

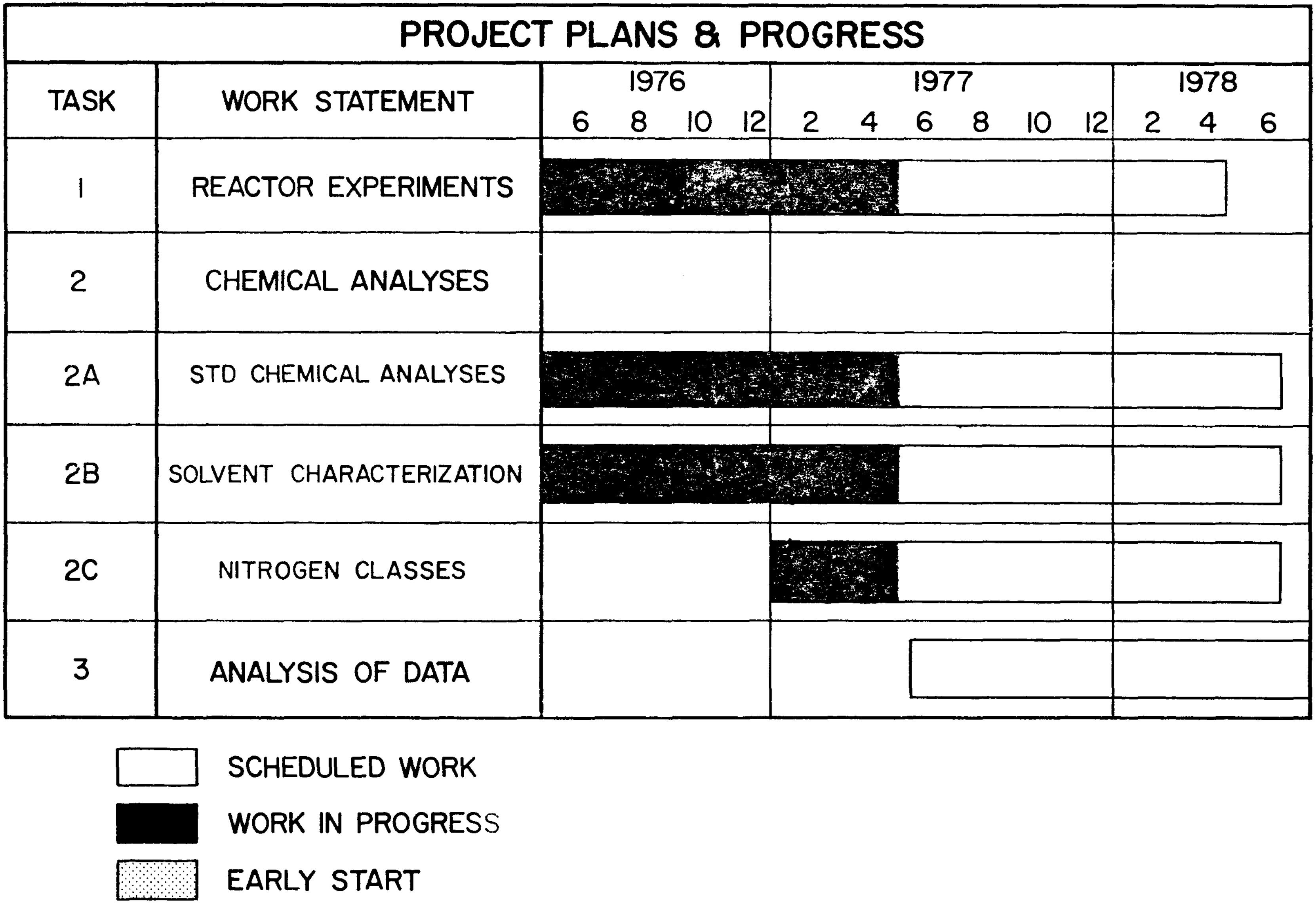
2. Chemical Analyses
   a. Standard Chemical Analyses
      Use of accepted analytical procedures to evaluate both chemical and physical properties of both the reactants and products from the reactor.

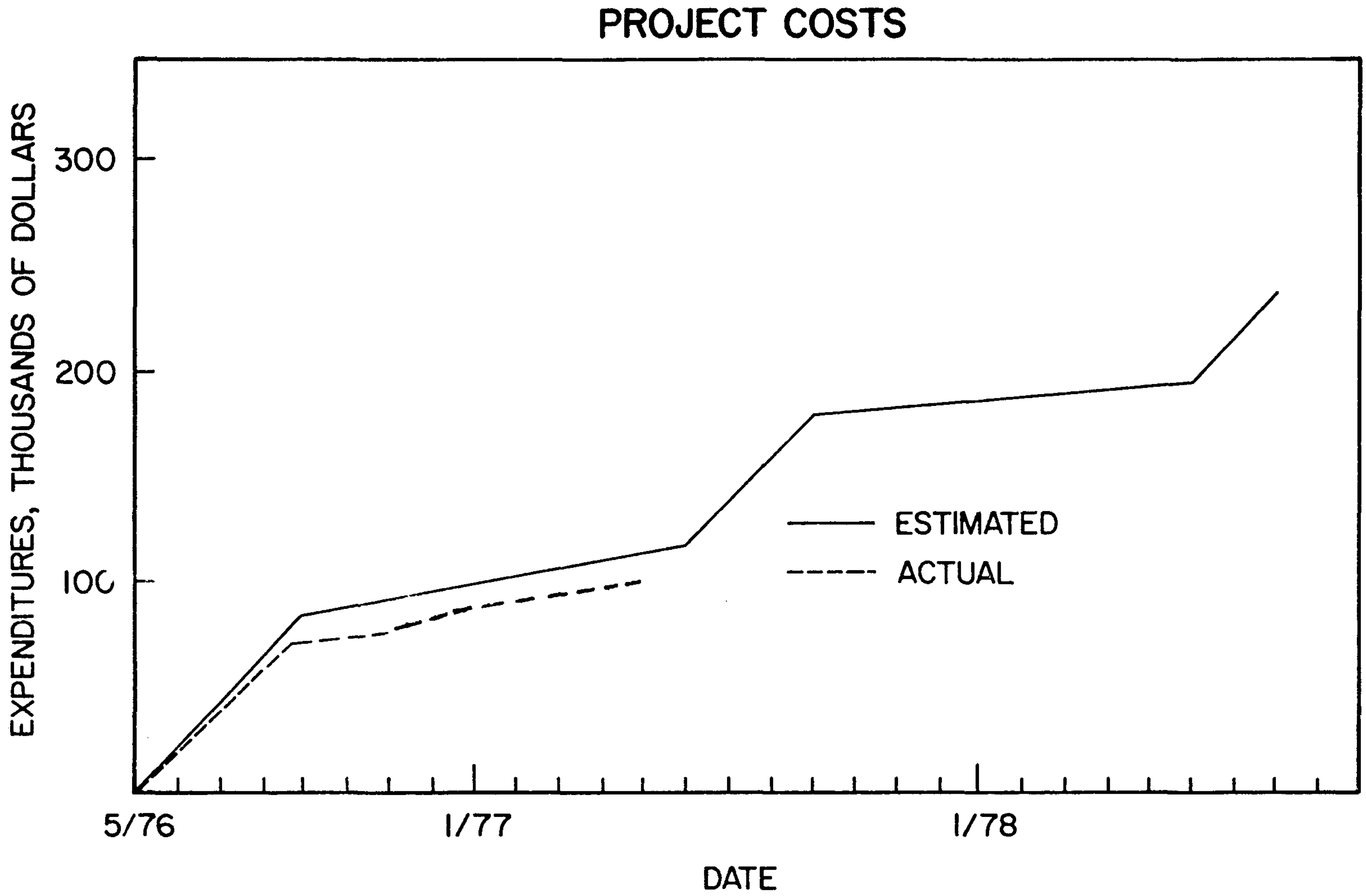
   b. Solvent Characterization
      Measurement of changes in the chemical characteristics of the solvents and the relative concentrations of aromatic, hydroaromatic, and aliphatic hydrocarbons in the solvents.

   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
ESTIMATED
ACTUAL
5/76
1/77
1/78
DATE

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 gage, 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.

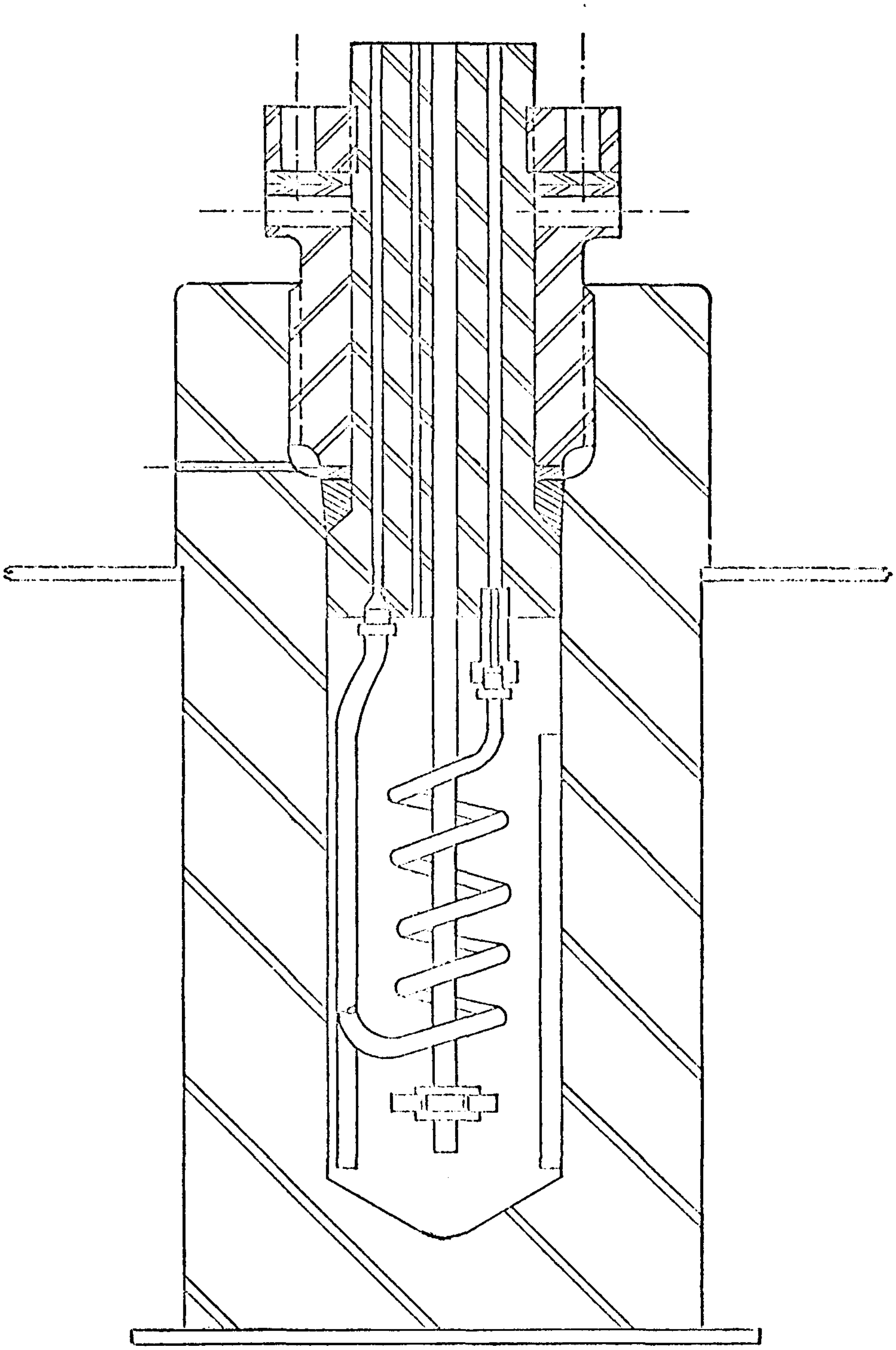
The magnedrive reactor is provided with ceramic heater wired in three equally dispersed 220 volt, 60 cycle single phase circuits of 1.7 kw each. Two circuits are provided with on-off control, and the third circuit is provided with a variable transformer control.

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, Inc. 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 underground 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

ANALYSIS OF WYODAK COAL

	C-1	C-2	C-3
PROXIMATE ANALYSIS WT% (MF BASIS)			
Volatile Matter	43.0	42.4	42.5
Fixed Carbon	49.3	49.5	49.5
Ash	7.7	8.1	8.0
ULTIMATE ANALYSIS WT% (MF BASIS)			
Carbon	68.9	68.8	68.7
Hydrogen	5.0	5.0	5.0
Sulfur	0.5	0.4	0.4
Nitrogen	1.0	1.0	1.0
Oxygen (by difference)	16.9	16.7	16.9
Ash	7.7	8.1	8.0
SCREEN SIZE (TYLER), WT%			
+65	0	0	34.9
65/100	15.2	5.7	13.5
100/150	17.2	12.1	9.6
150/200	16.1	19.5	9.2
200/325	20.4	15.0	7.4
325/PAN	31.1	52.7	25.4
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 primary solvent used in this phase of the work is the recycle solvent derived from the liquefaction of Wyodak coal at the Southern Services Inc. SRC plant in Wilsonville, Alabama, in 1975. This solvent, designated F-1, was supplied in a 55 gallon drum by Catalytic, Inc. Properties of the solvent, based on accepted analytical procedures, are presented in Table II. For comparison purposes, the analyses of a different sample representing this same solvent and analyzed by Galbraith Laboratories, Inc., Knoxville, Tennessee, for the Wilsonville SRC plant is also included. In addition, an analysis of a solvent derived from Wyodak coal in the operation of a flow reactor at the Hydrocarbon Research, Inc. (HRI) laboratories in Trenton, N.J., is also included in Table II. The HRI solvent is not an exact duplicate of the Wilsonville solvent.

TABLE II

WYODAK RECYCLE SOLVENT ANALYSES

	UW (F-1)	Wilsonville	HRI
GRAVITY, °API	6.8	7.1	4.3
ELEMENTAL ANALYSIS, WT%			
C	87.14	86.54	88.40
H	7.94	8.08	7.47
N	0.49	0.49	0.40
S	0.13	0.12	0.21
Unaccounted	4.30	4.79	3.52
DISTILLATION (D-1160), °F			
Vol % Over			
0/5	325/385	340/	378/390
10/30	435/470		406/450
50	520		505
70/90	590/715		577/633
95/100	770/---	/838	700/---
EP, °F	800		761
Vol % Over at EP	97		99

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

TABLE III

PROPERTIES OF HYDROGEN

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

TABLE IV

PROPERTIES OF CATALYST

Catalyst Designation	Nalcomo 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. Component analyses for runs 1-23 were performed using standard Burrell Gas Analysis Apparatus, called an Orsat. The Orsat consists of four glass bubblers and two catalytic combustion tubes connected in series by a glass manifold. The first bubbler contains a saturated solution of lead acetate in dilute acetic acid for the removal of hydrogen sulfide. Experiment showed that any ammonia present in the gas sample would also be absorbed in this bubbler. The second bubbler contains a 35 weight percent potassium hydroxide solution for removal of carbon dioxide. The third bubbler contains "Lusorbant" for removal of unsaturated hydrocarbons. The fourth bubbler contains "Oxsorbent" for the removal of oxygen. The two catalytic combustion tubes contain cupric oxide maintained at 560° to 570°F. Hydrogen and carbon monoxide are oxidized to water and carbon dioxide in these tubes. After correcting for nitrogen, any unadsorbed gas remaining in these tubes was assumed to be methane.

In runs 24-31, a Hewlett Packard HP 5840A chromatograph was 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 atmospheric condenser and receiver. A toluene cut and a decant oil cut at 350°F, corrected to 760 mm of Hg, are then made in this modified ASTM D-86 apparatus.

At this point, the distillation residue is cooled and vacuum of approximately 5 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 Characterization

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 of 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 naphthalene 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 naphthalene 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 than 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 naphthalene. 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 10 μl 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 measured and "normalized" to the peak height of the only other predominant chromatographic peak in Fraction 1 which has been identified as 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 plotting 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).

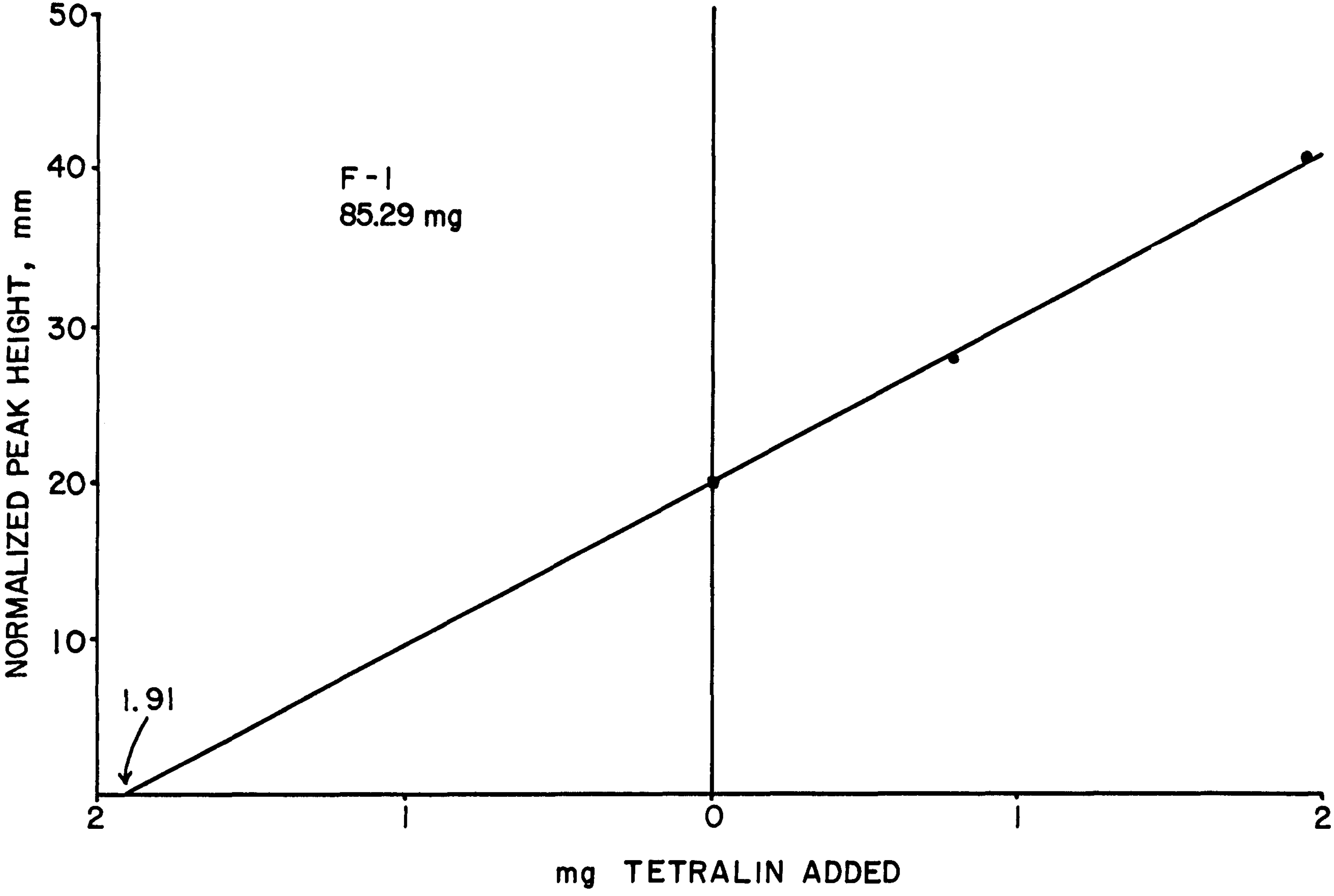
Injections of 10 μl at 0.1 absorbance units have been used for the determination of naphthalene. Peak heights are normalized to the predominant peak at 18.4 ml elution volume, which is believed to be composed mainly of biphenyl and 2-methylnaphthalene. The percentage naphthalene is calculated in the same manner as 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 (1), 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.

FIGURE 2



Standard addition curve for determination of tetralin

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 to 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 accross 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.

Before initiating the coal liquefaction runs, a series of hydrogenation runs were made to modify the Wilsonville solvent F-1. As hydrogen donor capacity is believed to be an important chracteristic of coal liquefaction solvents, the hydrogen donor capacity of the Wyodak coal-derived solvent, F-1, was increased by first hydrogenating this solvent in a series of runs 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 thermoactivated at 1000°F for 2 hours in a muffle furnace. The product from these runs was designated F-2. A second series of runs in which F-1 solvent was hydrogenated under an initial hydrogen pressure of 3000 psig at 800°F for one hour over the same Co-Mo on Al_2O_3 catalyst resulted in a product designated F-3. As a result of hydrogenation and cracking reactions taking place during the runs, the F-2 solvent boiled approximately 15-20°F below the F-1 solvent at the same distillation volume percent recovered while the F-3 solvent boiled 50-60°F below the F-1 solvent at the same distillation volume percent recovered. In order to increase the boiling range of the F-3 solvent, the front end of this product was partially removed by atmospheric distillation. The properties of the F-1 solvent as well as the properties of the F-2 and F-3 solvents as prepared for coal liquefaction experiments are presented in Table V.

As a cross-check on the distillation results, both the F-1 solvent and an anthracene oil supplied by U.S. Steel were analyzed by simulated distillation at the Laramie Energy Research Center by Dr. Lawrence Wojdoc. A comparison of the vacuum distillation and simulated distillation results is presented in Table VI.

During the solvent preparation runs, a few prelimianry coal liquefaction runs (6-11) were made to develop experimental procedures. Nonreproducibility of the products from these preliminary runs was found to be a result of sample inhomogeneity. That is, it was virtually impossible to obtain two different samples with the same solids content. This led to the procedure in which all of the reactor product is centrifuged to separate liquids from solids, not merely a sample of the reactor product.

Once a reasonable procedure for sampling reactor product had been developed, a second series of coal liquefaction runs was initiated to determine reactor operating conditions to be used in this work. At the conclusion of these efforts, initial runs were made to compare the liquefaction effectiveness of the F-1, F-2, and F-3 solvents.

TABLE V

SOLVENT PROPERTIES

Solvent	F-1	F-2	F-3
Description	As received from Wilsonville	F-1 Hydrogenated @ 700°F, 2000 psig and 1 hr over Co-Mo (Runs 1-5)	F-1 Hydrogenated @ 800°F, 3000 psig and 1 hr over Co-Mc (Runs 12-16, 18)
Specific Gravity (60/60)	1.023	1.015	0.991
Distillation, °F (1, 2)			
Vol % Distilled			
0/5	325/385	200/350	200/300
10/30	435/470	420/460	415/450
50	520	515	490
70/90	590/715	575/670	540/630
95/100	770/	755/	700/
E.P. (Vol %)	97	97	98
T (°F) @ E.P.	800	800	755
Wt % Distilled			
350°F-	2.1	3.6	6.0
350°-500°F	41.0	37.8	46.7
500°-650°F	37.9	40.6	36.7
650°-800°F	14.5	13.9	9.3
800°F+	4.5	4.1	1.3
Ultimate Analysis			
C	87.14	86.81	85.83
H	7.94	8.54	9.99
N	0.49	0.45	0.34
S	0.13	0.12	0.04
O (by diff.)	4.30	4.08	3.80
Wt % Tetralin	2.27	2.74	6.12
Wt % Naphthalene	7.30	7.06	6.36

Notes:

[1] Atmospheric distillation to 350°F, vacuum distillation @ 5 mm to E.P.

[2] Front end of F-3 partially removed by atmospheric distillation.

TABLE VI

COMPARISON OF SOLVENT DISTILLATION RESULTS

RECYCLE SOLVENT, F-1

Vacuum Distillation, °F Vol % Over		Simulated Distillation, °F Wt % Over	
0/5	265/425	0/5	325/355
10/30	435/470	10/30	395/475
50	520	50	505
70/90	590/715	70/90	550/655
95/100	770/	95/100	750/1000
EP (Vol %)	97	EP (Wt %)	100
EP (°F)	800	EP (°F)	1000

ANTHRACENE OIL (U.S. Steel)

Vacuum Distillation, °F Vol % Over		Simulated Distillation, °F Wt % Over	
0/5	500/505	0/5	425/500
10/30	515/525	10/30	530/577
50	545	50	610
70/90	575/655	70/90	645/740
95/100	750/	95/100	795/
EP (Vol %)	98	EP (Wt %)	98
EP (°F)	800	EP (°F)	900

Table VII includes 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. 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

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 was 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 (2). 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 VII.

In addition to the standard ultimate analysis of the SRC product presented in Table VII, 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 VIII.

TABLE VII

SUMMARY OF LIQUEFACTION RESULTS

RUN NUMBER	17	19	20	21	22	23	25*	26	27	28	29	30	31
COAL	C-2	C-2	C-2	C-2	C-2	C-2	C-2	C-2	C-2	C-3	C-3	C-3	C-3
SOLVENT	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-2	F-3
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 TIME (°F)	850	850	850	850	850	850	850	850	850	825	825	825	825
TIME AT REACTION T (mins)	5	20	20	40	40	60	40	40	0	0	0	0	0
INITIAL P(H_2) (psig)	1000	1000	1500	1500	2000	2000	2000	1500	2000	2000	2000	2000	2000
MAXIMUM PRESSURE (psig)	2450	2375	3200	3250	3900	4000	4225	3175	3950	4100	3950	3825	4975
YIELDS (WT% MF COAL)													
H_2-Free Gas	18.8	22.6	25.7	28.6	19.1	27.3	23.9	26.6	16.1	13.5	13.2	14.7	12.9
Water	(3.4)	2.2	5.5	5.0	2.2	.9	8.9	5.1	14.1	6.7	8.7	39.0	24.3
-350°F	6.8	7.7	8.0	9.6	10.2	15.9	22.8	35.2	9.9	32.2	12.3	14.7	10.1
350-500°F	2.0	(9.4)	(7.4)	(13.6)	(5.6)	(14.9)	(0.5)	(10.1)	(9.6)	(24.7)	(5.0)	(7.5)	(8.4)
500-650°F	(7.3)	(11.4)	(12.1)	(2.0)	8.7	13.4	(4.3)	(14.4)	(.2)	(4.3)	(12.2)	(25.0)	(11.2)
650-800°F	1.4	(2.2)	5.1	3.4	(1.7)	(2.4)	(3.1)	0.8	5.5	4.6	9.7	6.2	12.7
+800°F	31.1	43.8	40.3	37.6	46.0	37.3	38.9	33.1	47.1	43.7	48.1	37.2	39.2
Solids	53.2	49.3	37.7	35.1	28.1	26.8	17.2	27.0	20.1	30.3	27.4	23.6	21.7
TOTAL	102.6	102.6	102.8	103.7	107.0	104.3	103.8	103.3	103.0	102.0	102.2	102.9	101.3
H_2 CONSUMPTION (WT% MF COAL)	2.8	2.6	2.8	3.7	7.1	4.3	3.4	3.3	2.9	1.9	2.1	2.9	.9
LIQUID PRODUCT DENSITY (°API)	0.1	3.5	3.7	3.7	3.7	4.8	4.8	4.1	3.1	3.0	3.0	4.0	6.7
ULTIMATE ANALYSIS OF SRC (WT%)													
Hydrogen	6.05	5.57	5.65	5.58	5.71	5.57	5.88	5.54	5.84	5.98	6.12	6.01	6.36
Carbon	87.62	88.98	88.78	89.64	89.37	89.96	89.13	88.18	87.30	84.58	86.69	85.68	85.86
Nitrogen	1.42	1.26	1.20	1.51	1.33	1.48	1.55	1.35	1.41	1.50	1.29	1.36	1.42
Sulfur	.16	.22	.17	.15	.13	.15	.10	.08	.14	.22	.18	.15	.12
Oxygen	4.75	3.97	4.20	3.12	3.46	2.84	3.34	4.85	5.31	7.72	5.73	6.80	6.24
BENZENE INSOLUBLE CONV.	55.6	60.6	70.8	73.0	80.2	82.1	90.8	79.0	87.9	75.8	78.9	83.0	85.1
BENZENE INSOLUBLE CENTRIFUGE RESIDUES	17-1 17-2												
Wt% Ash	31.1 13.2	15.41	20.39	22.30	29.10	28.10	41.68	27.60	32.75	22.62	24.43	25.52	29.14
Wt% S in Ash	2.64 3.56	2.80	2.98	2.80	2.64	2.88	2.39	3.52	3.34	3.42	3.14	3.13	3.02
WT% LIQUEFACTION	51.8	67.3	75.8	78.3	85.8	83.9	91.7	83.7	87.9	78.0	79.8	79.7	82.2

*Changed reactor impeller from 3 cm to 5 cm for this and subsequent runs.

TABLE VIII

SRC SOLUBILITY ANALYSES

RUN	WT% UNREACTED COAL AND PREASPHALTENES	WT% ASPHALTENES	WT% OILS
17	15.3	58.6	26.1
19	49.0	41.8	9.2
20	46.2	34.0	19.8
21	34.0	49.4	16.6
22	33.6	49.8	16.6
23	29.8	51.6	18.6
25	27.3	55.8	16.9
26	46.3	44.8	8.9
27	37.2	57.1	5.7
28	40.4	49.2	10.4
29	42.6	42.6	14.8
30	38.5	46.6	14.9
31	30.8	49.2	20.0

Solvent Characterization

Initial work with infrared spectroscopy of recycle solvents F-1 and F-2 shows that both solvents have the same infrared spectra except for the relative heights of some of the peaks. The following groups are suggested by the infrared spectra: O-H, N-H, C-O, and Ar-O. Also, several alkyl and aromatic skeletal vibrations are indicated. There was no indication of the presence of a C=O group. 'Hnmr spectra have been obtained from samples of F-1 and F-2. The relative amounts of non-aromatic and aromatic protons have been determined semi-quantitatively by 'Hnmr spectroscopy. F-1 contains 46.0% aromatic protons and 54.0% non-aromatic protons. F-2 contains 41.1% aromatic protons and 58.9% non-aromatic protons. F-3 contains 36.6% aromatic protons and 63.4% non-aromatic protons.

Thin-layer chromatography (TLC) has been used to separate polycyclic aromatic hydrocarbons (PAH) in F-1. Some PAH have been identified by obtaining their fluorescence emission spectra directly from the surface of the chromatoplates with a Schoeffel spectrodensitometer. Pyrene, fluoranthene, and benzo [a] pyrene have been identified in F-1. F-2 and F-3 showed similar but less intense fluorescent spots. The spectrodensitometer has also been used to obtain fluorescent profiles of the components in F-1, F-2, and F-3 separated on chromatoplates. The F-1, F-2, and F-3 fluorescent profiles are all similar except for relative fluorescence intensity. It is planned to expand the fluorescent profile approach in future work because it is a rapid way to obtain general information on samples. Preliminary work with several phenols involved recrystallization of the phenols and development of TLC systems for their separation.

During the past year, time has been spent in isolating PAH and hydroaromatics from F-1, F-2, and F-3 using TLC and high performance liquid chromatography (HPLC), and in developing a quantitative method for tetralin and naphthalene in F-1, F-2, and F-3. Fluorescence excitation and emission spectra have been obtained to identify separated components corresponding to chromatographic peaks from HPLC. The results of the work will be presented at the American Chemical Society meeting Division of Fuel Chemistry in Chicago, August 1977. A discussion of the work is to appear in Preprints of Division of Fuel Chemistry for the August meeting.

The quantitative method for tetralin and naphthalene involves initial separation of the recycle solvent (F-1, F-2 or F-3) into two fractions by aluminum oxide n-hexane column chromatography. The first fraction contains tetralin, and the second fraction contains naphthalene. Each fraction is further separated by HPLC with a μ-bondapak C_{18} column and methanol:water (65:35) mobile phase. Tetralin and naphthalene have been quantitated with the aid of an ultraviolet detector. The amounts of tetralin found in F-1, F-2, and F-3 are 2.27%, 2.74%, and 6.13%, respectively. The amounts of naphthalene found in F-1, F-2, and F-3 are 7.30%, 7.06%, and 6.35%, respectively. The detection limits of the method are 0.2% for tetralin and 0.1% for naphthalene. Table IX gives the results of the precision of the method, Table X gives results of a variation of sample size study, and Tables XI and XII give percentage recovery in spiked samples. Figures 3 and 4 are examples of fluorescence excitation and emission spectra.

R_f values on aluminum oxide chromatoplates with n-hexane as a mobile phase have been obtained for several hydroaromatic and polycyclic aromatic hydrocarbons. The results show generally, as other researchers have found, that these compounds separated according to ring size with larger ring compounds retained more strongly on the aluminum oxide. Retention volumes of the same compounds have been determined by HPLC using a μ-bondapak C_{18} column and methanol:water (65:35) mobile phase. The results indicate generally that compounds are more strongly retained the greater the number of carbons in the alkyl substituent bonded to an aromatic ring. The R_f and retention volume data suggest the possiblity of developing general separation schemes for aromatic and hydroaromatic hydrocarbons in coal liquid samples. This is presently under investigation, and a further discussion of this aspect will be in a manuscript to be submitted to Analytical Chemistry. The R_f values and retention volumes obtained in this work are presented in Table XIII.

TABLE IX

PRECISION OF THE METHOD WITH F-3

Sample Weight, mg	Tetralin, %w/w	Naphthalene, %w/w
97.92	6.08	6.36
97.92	6.13	6.40
97.92	6.10	6.38
96.67	6.10	6.31
96.67	6.14	6.34
	$\bar{x}$ = 6.11	$\bar{x}$ = 6.36
	s = 0.024	s = 0.035

95% confidence level

tetralin: 6.11 ± 0.030%

naphthalene: 6.36 ± 0.043%

TABLE X

VARIATION OF SAMPLE SIZE

Sample	Weight, mg	Tetralin, %w/w	Average	Naphthalene, %w/w	Average
F-3	96.67	6.10		6.31	
	96.67	6.14	6.12	6.34	6.32
	48.93	6.13		6.40	
	48.93	6.15	6.14	6.36	6.38
F-2	81.20	2.71		7.09	
	81.20	2.73	2.72	7.03	7.06
	43.61	2.77		7.08	
	43.61	2.73	2.75	7.04	7.06
F-1	85.29	2.24		7.27	
	85.29	2.32	2.28	7.33	7.30
	44.24	2.24		7.28	
	44.24	2.28	2.26	7.32	7.30

TABLE XI

PERCENTAGE TETRALIN RECOVERY IN SPIKED SAMPLES

Sample	Weight, mg	Tetralin[a] Present, mg	Tetralin Added, mg	Tetralin[b] Found, mg	Recovery, %
F-3	95.79	5.86	0.96	0.96	100
	95.79	5.86	0.96	1.01	105
	96.67	5.92	2.41	2.33	97
	96.67	5.92	2.41	2.46	102
					$\bar{x}$ = 101
F-2	86.32	2.36	0.77	0.77	100
	86.32	2.36	0.77	0.74	96
	84.60	2.32	1.93	1.98	102
	84.60	2.32	1.93	1.91	99
					$\bar{x}$ = 99
F-1	84.98	1.93	0.78	0.72	92
	84.98	1.93	0.78	0.73	94
	81.02	1.84	1.95	1.92	98
	81.02	1.84	1.95	1.89	97
					$\bar{x}$ = 95

[a] Results obtained from the standard addition method.

[b] Results corrected for original tetralin content present in the sample.

TABLE XII

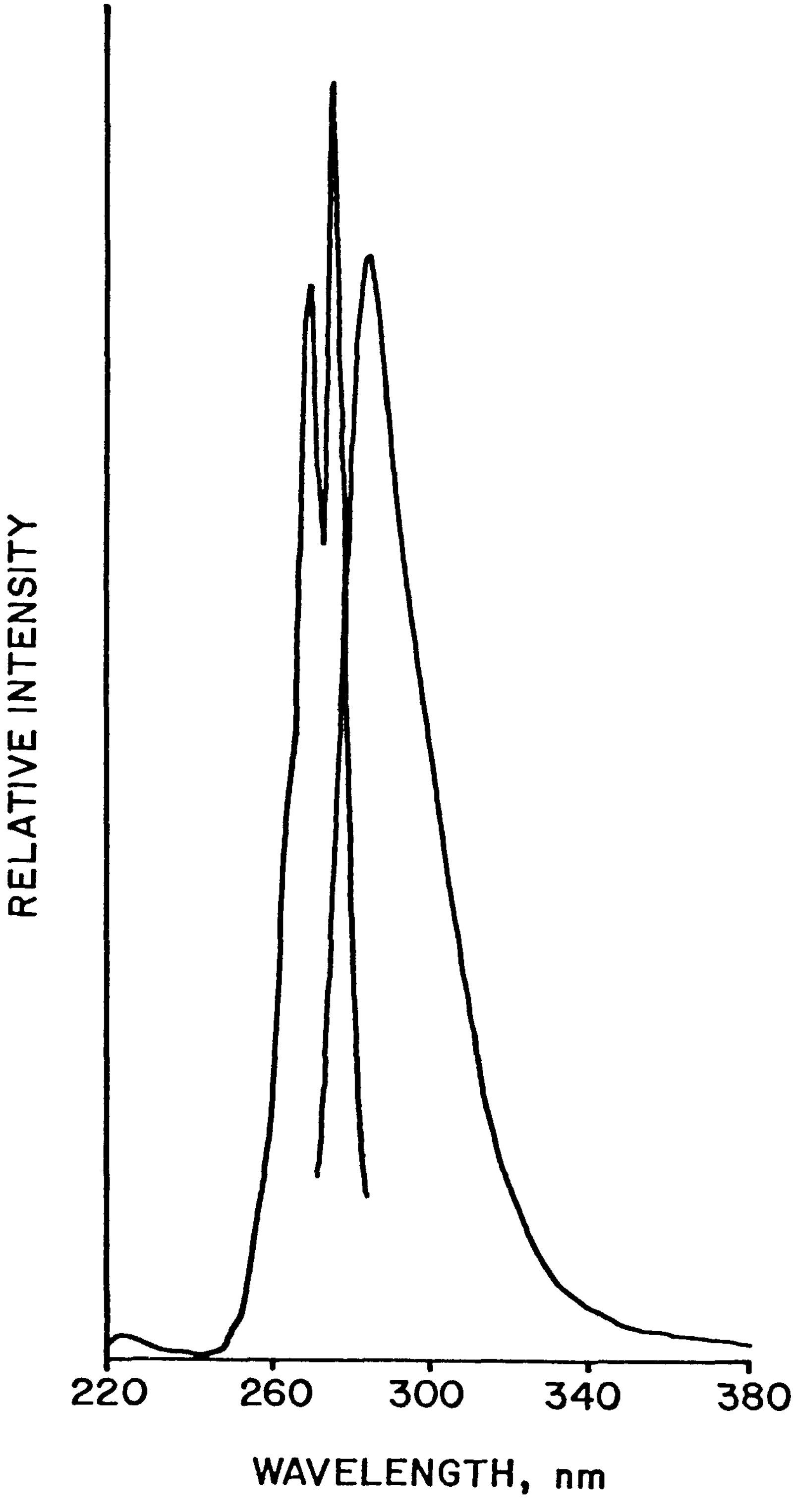
PERCENTAGE NAPHTHALENE RECOVERY IN SPIKED SAMPLES

Sample	Weight, mg	Naphthalene[a] Present, mg	Naphthalene Added, mg	Naphthalene[b] Found, mg	Recovery, %
F-3	95.79	6.09	0.87	0.85	98
	95.79	6.09	0.87	0.83	95
	96.67	6.15	2.18	1.98	91
	96.67	6.15	2.18	2.02	93
				average	94
F-2	86.32	6.09	0.70	0.65	93
	86.32	6.09	0.70	0.71	101
	84.60	5.97	1.75	1.81	103
	84.60	5.97	1.75	1.80	103
				average	100
F-1	84.98	6.20	0.69	0.68	99
	84.98	6.20	0.69	0.66	96
	81.02	5.91	1.73	1.66	96
	81.02	5.91	1.73	1.69	98
				average	97

[a] Results obtained from standard addition method.

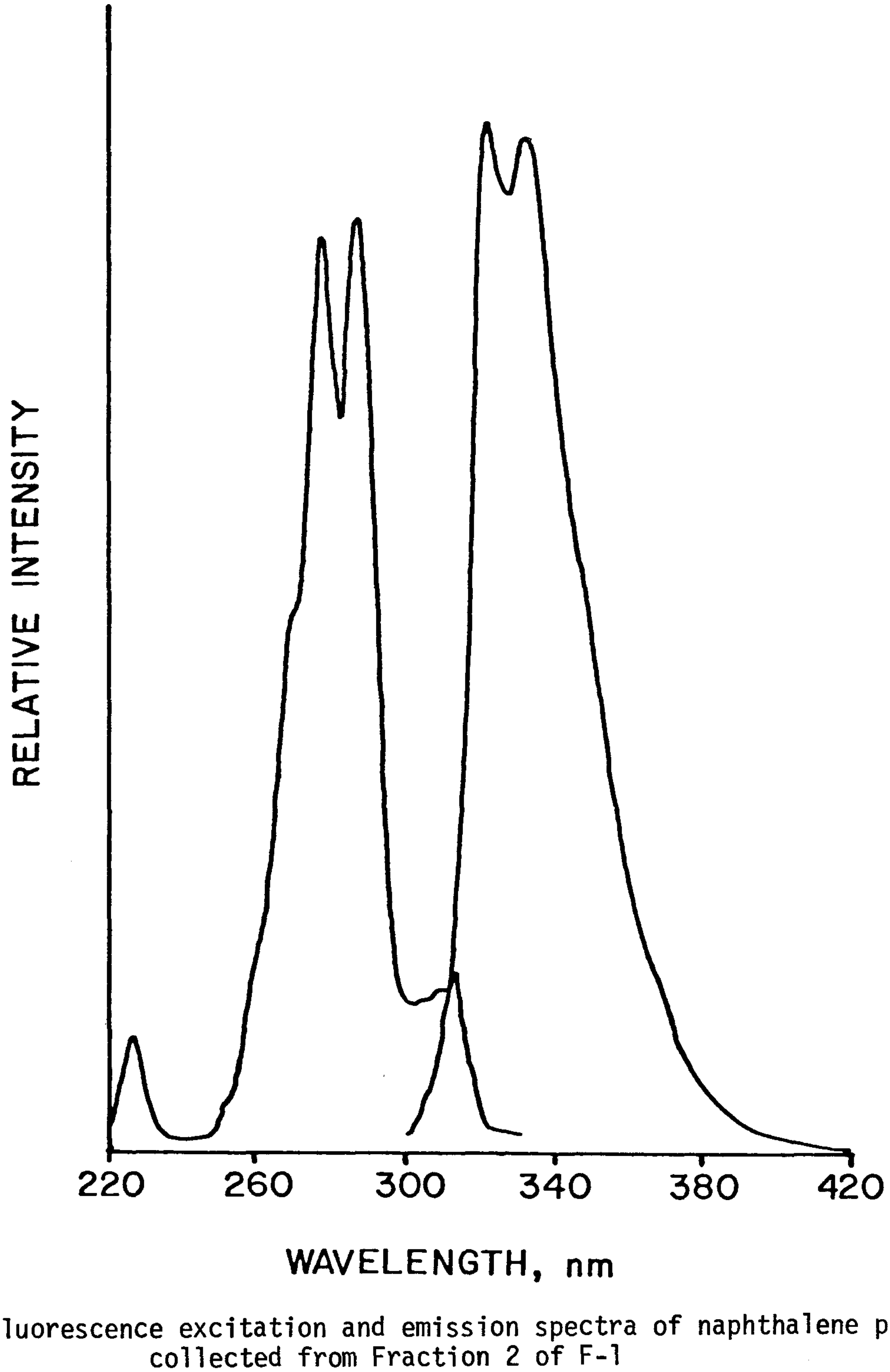
[b] Results corrected for original naphthalene content present in the sample.

FIGURE 3



Fluorescence excitation and emission spectra of tetralin peak collected from Fraction 1 of F-1.

FIGURE 4



Fluorescence excitation and emission spectra of naphthalene peak collected from Fraction 2 of F-1

TABLE XIII

R_f VALUES AND RETENTION VOLUMES[a] OF HYDROAROMATIC AND POLYCYCLIC AROMATIC HYDROCARBONS

	Compound	R_f Value	Retention Volume, ml
1)	benzene	-----	6.3
2)	1, 2, 4-trimethylbenzene	-----	19.5
3)	1-phenyldodecane	-----	No indication of elution
4)	tetralin	0.74	21.5
5)	indan	-----	14.8
6)	5-methyltetralin	-----	33.0
7)	indene	0.55	10.5
8)	naphthalene	0.50	11.7
9)	acenaphthene	0.44	21.5
10)	1, 5-dimethylnaphthalene	0.43	26.8
11)	1-methylnaphthalene	0.43	17.6
12)	biphenyl	0.43	18.3
13)	2-methylnaphthalene	0.42	18.4
14)	2, 3-dimethylnaphthalene	0.40	27.3
15)	1-phenyl-3, 4-dihydronaphthalene	0.38	55.2
16)	9, 10-dihydroanthracene	0.34	26.1
17)	acenaphthylene	0.32	14.6
18)	9, 10-dihydrophenanthrene	0.27	30.3
19)	[2.2] paracyclophane	0.24	32.8
20)	fluorene	0.20	25.2
21)	anthracene	0.14	28.0
22)	phenanthrene	0.13	25.0
23)	pyrene	0.069	39.6
24)	fluoranthene	0.056	36.9
25)	chrysene	0.054	62.1

[a] One μ-bondapak C_{18} column with methanol:water (65:35) at 1 ml/min.

Nitrogen Classes

The procedures used to determine classes of nitrogen compounds in coal liquids are discussed in the appendix. Analysis of the data presented in the appendix is summaried in Table XIV below.

TABLE XIV

WT % NITROGEN TYPE

	Quinoline	Indoles	Aryl Amines	Primary and Secondary Alkyl Amines	Amides	Unident.
Solvents						
F-1	.310	.081	.036	.062	----	----
F-2	.182	.082	.078	.066	----	----
F-3	.109	.079	.177	.009	----	----
SRC (Bz sol)						
Run 25	.633	.096	.121	.014	.081	.435
Run 26	.405	.044	.029	.006	.106	.540
Run 27	.408	.066	.017	.009	.144	.265

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.

DISCUSSION OF RESULTS

Liquefaction Experiments and Standard Chemical Analyses

One of the first objectives of this work has been to attempt to establish constant volume batch reaction conditions which would produce liquefaction results representative of constant pressure SRC flow reaction results. Flow reactor results of 83 wt% cresol insoluble conversion for Wyodak coal obtained at Wilsonville and 93 wt% liquefaction of Wyodak coal obtained at HRI have been used as a basis of comparison.

Since the coal and solvent are essentially the same in this work and the flow reactor work, reaction temperature, time and pressure were varied in this study. Reaction temperatures of 825°F and 850°F used in the flow reactor studies essentially set the reaction temperatures to be used in the batch studies. Reaction times, however are not so readily related.

The space time in flow units of 21 to 32 lbm coal/hr ft^3 of reactor used to define reactor conditions in the flow reactors can be related to the actual residence time in the flow reactor only if the relative quantities and densities of the gas and the solid-liquid phases as well as the vertical flow patterns of these phases are known or can be estimated with reasonable certainty. On the other hand, reactions begin to take place in the batch reactor at temperatures above 600-700°F, the devolatilization temperature of the coal. Therefore, the actual reaction time in a batch reactor not only includes the time at reaction temperature, but also time for heat-up and cool-down periods. Consequently, equivalent reaction times between the batch and flow reactor systems is most readily determined by experiment.

Initial studies of the effect of time were made in runs 17 and 19 under conditions in which the pressure at reaction conditions in the batch reactor closely approximated the pressure at reaction conditions in the flow reactors. The results of these runs, presented in Table XV, indicated that more severe operating conditions would be required to reach the levels of conversion obtained in the flow reactor systems. Therefore, a series of runs were made in which both time and pressure were varied.

As shown in Table XV, pressure appears to have a greater effect on the extent of Wyodak coal liquefaction in a batch reactor than time at reaction temperature. It was necessary to double the reaction pressure used at Wilsonville and HRI in the batch reactor for runs 22 and 23 to obtain comparable liquefaction results. This suggested the possiblity of mass transfer limitations between hydrogen in the gas phase and hydrogen dissolved in the liquid-solid phase, where

$$r_{H_2} \approxeq k_g a \, P_{H_2}$$

TABLE XV

EFFECT OF BATCH REACTION CONDITIONS

RUN NUMBER	17	19	20	21	22	23
Temp (°F)	850	850	850	850	850	850
Time at Temp (mins)	5	20	20	40	40	60
Initial H_2 Pressure (psig)	1000	1000	1500	1500	2000	2000
Agitator Impeller Diam (cm)	3	3	3	3	3	3
Wt% Liquefaction	51.8	67.3	75.8	78.3	85.8	83.9

In order to check this hypothesis, the reactor agitator impeller diameter was increased from 3 to 5 cm to increase the mass transfer coefficient k_ga. As shown in Table XVI, this increase in impeller diameter appears to be nearly as effective as increasing the initial hydrogen pressure in the batch reactor by 500 psig. Thus, it can be concluded that mass transfer from the gas to the liquid-solid phase is an important variable in the coal liquefaction reaction.

Although batch reactor weight percent liquefaction yields comparable to HRI flow reactor weight percent liquefaction yields were obtained at 2000 psig initial hydrogen pressure at a 40 minute time at reaction temperature, there was a net loss of solvent in the batch reactor as compared to a net gain of solvent in the flow reactor. In an attempt to decrease solvent loss, the time at reaction temperature was first decreased to 0 minutes. As shown in Table XVI, this only decreased the weight percent liquefaction from 91.7 wt% at 40 minutes to 87.9 wt% at 0 minutes.

TABLE XVI

EFFECT OF IMPELLER DIAMETER
ON LIQUEFACTION RESULTS

RUN NUMBER	21	26	22	25	27
Temp (°F)	850	850	850	850	850
Time at Temp (mins)	40	40	40	40	0
Initial H_2 Pressure (psig)	1500	1500	2000	2000	2000
Agitator Impeller Diam (cm)	3	5	3	5	5
Wt% Liquefaction	78.3	83.7	85.8	91.7	87.9

However, there was still a net loss of solvent. Thus, the reaction temperature was lowered from 850°F to 825°F. Even at 0 minutes at 825°F reaction temperature, there is a net solvent loss as shown in the results for run 29 in Table XVII.

TABLE XVII

COMPARISON OF BATCH AND FLOW REACTOR RESULTS

RUN	HRI 177-115-4	UW 25	UW 27	Wilsonville 21-22 Dec, '75	UW 29
TEMP (°F)	850	850	850	824	825
TIME AT TEMP (mins)		40	0		0
P (psig)	2510			2470	
P_{H_2} (charge) (psig)		2000	2000		2000
P (max) (psig)		4225	3950		3950
SOLVENT/COAL	2.0	2.0	2.0	4.0	2.0
YIELDS (WT% MF COAL)					
H_2-Free Gas	17.8	23.9	16.1	13.4	13.2
H_2O (liquid)	10.4	8.9	14.1	7.3	8.7
Oil					
350°F-	5.2	22.8	9.9	3.2	12.3
350-500°F	5.5	(0.5)	(9.6)	7.7	(5.0)
500-650°F	7.0	(4.3)	(0.2)	4.0	(12.2)
650-800°F	9.7	(3.1)	5.5	1.7	9.7
800°F+ (SRC)	37.6	38.9	47.1	44.9	48.1
Solids	10.4	17.2	20.1	20.0	27.4
TOTAL	103.6	103.8	103.0	102.2	102.2
WT% LIQUEFACTION	93.3	91.7	87.9	83.0*	79.8
SRC N (WT%)	1.24	1.55	1.41	1.51	1.29
SRC S (WT%)	0.22	0.10	0.14	0.22	0.18

*cresol insoluble conversion

Even so, these reaction conditions have been selected as most representative of conditions which would be comparable to those used in the flow reactor studies.

Using these reaction conditions, initial runs have been made comparing the effectiveness of F-1, F-2, and F-3 solvents. These results are summarized in Table XVIII.

TABLE XVIII

COMPARISON OF SOLVENTS

RUN	29	30	31
SOLVENT	F-1	F-2	F-3
COAL	C-3	C-3	C-3
SOLVENT/COAL (WT/WT)	2.0	2.0	2.0
TEMP (°F)	825	825	825
TIME AT TEMP (mins)	0	0	0
INITIAL P_{H_2} (psig)	2000	2000	2000
MAXIMUM P (psig)	3950	3825	4975
YIELDS (WT% MF COAL)			
H_2-Free Gas	13.2	14.7	12.9
H_2O (liquid)	8.7	39.0	24.3
Oil			
350°F-	12.3	14.7	10.1
350-500°F	(5.0)	(7.5)	(8.4)
500-650°F	(12.2)	(25.0)	(11.2)
650-800°F	9.7	6.2	12.7
800°F+ (SRC)	48.1	37.2	39.2
Solids	27.4	23.6	21.7
TOTAL	102.2	102.9	101.3
WT% LIQUEFACTION	79.8	79.7	82.2
SRC N (WT%)	1.29	1.36	1.42
SRC S (WT%)	.18	.15	.12
SRC			
Unconverted coal and preasphaltenes (Wt%)	42.6	38.5	30.8
Asphaltenes (Wt%)	42.6	46.6	49.2
Oils (Wt%)	14.8	14.9	20.0

Although no conclusions should be drawn from these unduplicated results, it appears that all three solvents may be equally effective at the reaction conditions used. This preliminary result appears to be in agreement with results reported for the Exxon Donor Solvent process which showed no improvement in the extent of coal liquefaction at a fixed set of reaction conditions for solvents with a proprietary solvent quality index above a certain minimum.(3) On the other hand, results of Mobil work show a direct correlation between increasing tetralin content and increasing liquefaction not observed here.(4) This would indicate F-3 should be the best solvent. Results of work on the Arthur D. Little extractive coking process indicate that there appears to be an optimum solvent hydrogen content of 8.1 to 8.7 percent H.(5) Above or below this range, the conversion of coal to gases and liquids is reported to be significantly lower. This would indicate that F-2 would be a good solvent while F-1 and F-3 would be poorer solvents. All of these results suggest the importance of the coal studied as well as the reaction conditions used.

Nitrogen Classes

Nitrogen compounds found in coal-derived liquids are an impediment to further refining steps using existing petroleum technology. The basic nitrogen compounds strongly poison the acidic components of petroleum catalysts.

In addition, these nitrogen compounds contribute to NO_x emission from combustion processes. As it appears that NO_x emission standards have been set on the basis of the combustion characteristics of essentially nitrogen free petroleum stocks, it may be necessary to substantially reduce the nitrogen content of coal-derived liquids.

No definite correlation between total nitrogen removal and solvent characteristics has been observed in the work performed thus far. However, it has been shown that the nitrogen compounds in the solvents and in the SRC can be classified as to type. These results show that the nitrogen types are primarily aromatic and will be difficult to remove from the product. As the program progresses, this type of information will be valuable in determining the direction in which the reaction conditions must be modified to reduce the nitrogen content of the products.

SUMMARY AND CONCLUSIONS

Solvents of varying hydrogen donor capacity have been prepared and batch reaction conditions which give results reasonably similar to results obtained in flow systems processing Wyodak coal have been selected. Mass transfer of hydrogen from the gas phase to the liquid-solid phase has been shown to be a possible rate limiting step in the reaction.

A quantitative method has been developed for determining tetralin and naphthalene in solvent boiling range coal liquids. Some polycyclic aromatic hydrocarbons have been identified using fluorescence emission spectra directly from the surface of chromatoplates with a Schoeffel spectrodensitometer. Preliminary work has been initiated on the separation of phenols.

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.

Preliminary results also indicate little if any difference in the effect of the solvents studied on the extent of Wyodak coal liquefaction, asphaltene production or nitrogen removal, despite significant differences in the tetralin content of these solvents.

Future liquefaction work will be directed toward determining the reproducibility of the results already obtained and in evaluating a wider range of solvents for correlation purposes. Future solvent characterization work will center around 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, F-1, was used directly as received and as modified by hydrogenation in a batch autoclave. In the solvent modification runs, preweighed amounts of recycle solvent and a Co-Mo catalyst (Nalcomo 471) was added to the reactor. In the coal liquefaction runs, preweighed amounts of Wyodak coal and solvent were added to the reactor. The reactor was 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 was 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 was made for the hydrogen which dissolved in the solvent when the magnetic stirrer was initially activated at room temperature.

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

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

The products removed from the reactor consisted of gases, liquids, called decant oil, and solids. Gases were first vented from the reactor through a manifold into successive gas sample tanks which had been pre-evacuated to approximately 22 in. of Hg vacuum until a vacuum was attained in the reactor. This was done to minimize the quantity of gases which could flash into the atmosphere when the reactor was opened. Next, the gases in the sample tanks were allowed to mix through the manifold so that there would be sufficient pressure in all tanks to permit gas samples to be withdrawn. The quantity of gases collected in the sample tanks was then calculated from the ideal gas law using measurements of the pressure, temperature and volume of the gas collection system and a molecular weight determined gravimetrically.

After the gases had been recovered, the reactor was opened and the liquid was siphoned out. Solids adhering to the reactor walls were scrapped out and added to the recovered liquid. The total recovered liquid and solid mixture was then weighed. In the initial coal liquefaction runs, a sample of the liquid-solid product was centrifuged to separate the solids from the liquids. Non-reproducibility of results led to a change in procedure at run 17 in which all of the liquid-solid product recovered from the reactor was centrifuged. The solid-free liquid was then weighed and its specific gravity was measured with an API hydrometer.

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

The experimental material balance was 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 were attributed to the gases. Rather, all losses were attributed to the liquid product from the catalytic runs and were divided proportionally between the liquid and solid products in the coal liquefaction runs. However, the gas yield was adjusted to account for the ammonia and hydrogen sulfide which remained in solution in the liquid. The total grams of hydrogen sulfide produced were estimated from a sulfur balance and the grams of ammonnia produced were 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.

TABLE A-1

OPERATING RESULTS

RUN NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
OPERATING CONDITIONS															
Charge															
Coal						C-1	C-1	C-1	C-1	C-1	C-1				
Solvent	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1
Catalyst	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	850	850	700	825	850	825	800	800	800	800
Time at Temperature, mins	60	60	60	60	60	5	5	180	10	5	10	60	60	60	60
Initial Hydrogen Pressure, psi	2000	2000	2000	2000	2000	1000	1000	1000	1000	1000	1000	3000	3000	3000	3000
Maximum Reactor Pressure, psi	3325	3500	3425	3375	3325	2800	2475	2175	2300	2500	2300	5275	5175	5025	5000
OPERATING RESULTS															
Charge, gms															
Hydrogen	9.8	10.3	10.3	10.2	10.1	8.6	8.7	8.9	8.5	8.9	8.4	14.7	14.6	14.5	14.5
Solvent	1000.2	1000.5	998.2	1000.2	999.8	298.6	302.3	300.1	399.5	300.7	401.4	1000.5	1000.2	999.4	999.8
Coal						150.0	150.0	150.0	100.0	150.0	100.0				
Catalyst	60.0	60.0	60.0	60.0	60.0							60.0	60.0	60.0	60.0
TOTAL	1070.0	1070.8	1068.5	1070.4	1069.9	457.2	461.0	459.0	508.0	459.6	509.8	1075.2	1074.8	1073.9	1074.3
Product (Raw Data), gms															
Hydrogen	8.2	7.7	10.9	11.7	8.7	4.7	4.7	4.8	5.2	5.9	5.4	4.0	4.0	3.9	3.4
H_2-Free Gases	3.6	4.1	3.7	0.5	1.8	27.1	28.8	18.3	19.7	27.4	21.0	11.8	10.2	12.3	10.2
Water						5.3	1.7	11.1	9.2	11.3	8.8				
Decant Oil + Solids	1051.2	1054.0	1046.2	1051.6	1029.7	408.3	416.5	410.8	462.5	392.9	459.6	1030.3	1037.9	1040.3	1035.6
Catalyst															
Losses	7.0	5.0	7.7	6.6	29.7	11.8	9.3	14.0	11.4	22.1	15.0	29.1	22.7	17.4	25.1
TOTAL	1070.0	1070.8	1068.5	1070.4	1069.9	457.2	461.0	459.0	508.0	459.6	509.8	1075.2	1074.8	1073.9	1074.3
Product (Adjusted Data), gms															
Hydrogen	8.2	7.7	10.9	11.7	8.7	4.7	4.7	4.8	5.2	5.9	5.4	4.0	4.0	3.9	3.4
H_2-Free Gases	3.6	4.1	3.7	0.6	1.8	27.1	28.8	18.3	19.7	27.4	21.0	11.8	10.2	12.3	10.2
Water	0.0	0.0	0.0			5.4	1.7	11.5	9.4	11.9	9.1				
Decant Oil	998.2	999.0	993.9	998.1	999.4	420.0	425.8	424.4	473.7	414.4	474.3	999.4	1000.6	997.7	1000.7
Solid Residue															
Catalyst	60.0	60.0	60.0	60.0	60.0							60.0	60.0	60.0	60.0
TOTAL	1070.0	1070.8	1068.5	1070.4	1069.9	457.2	461.0	459.0	508.0	459.6	509.8	1075.2	1074.8	1073.9	1074.3
WT% Recovered	99.4	99.5	99.3	99.4	97.2	97.4	98.0	96.9	97.8	95.2	97.1	97.3	97.9	98.4	97.7

TABLE A-1 (Continued)

OPERATING RESULTS

RUN NUMBER	16	17	18	19	20	21	22	23	24*	25	26	27	28	29	30	31
OPERATING CONDITIONS																
Charge																
Coal		C-2		C-2	C-2	C-2	C-2	C-2	C-2	C-2	C-2	C-2	C-3	C-3	C-3	C-3
Solvent	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-1	F-2	F-3
Catalyst	Co-Mo		Co-Mo													
Operating Temperature, °F	800	850	800	850	850	850	850	850	850	850	850	850	825	825	825	825
Time at Temperature, mins	60	5	60	20	20	40	40	60	40	40	40	0	0	0	0	0
Initial Hydrogen Pressure, psi	3000	1000	3000	1000	1500	1500	2000	2000	1500	2000	1500	2000	2000	2000	2000	2000
Maximum Reactor Pressure, psi	5100	2450	5200	2375	3200	3250	3900	4000	2850	4225	3175	3950	4100	3950	3825	4975
OPERATING RESULTS																
Charge, gms																
Hydrogen	14.4	9.2	14.9	8.6	12.7	12.8	16.8	16.8	13.1	17.1	13.1	16.7	16.7	16.8	16.8	16.1
Solvent	999.7	300.0	1000.2	300.2	299.7	300.5	299.9	300.0	300.1	300.5	300.0	300.1	300.3	300.0	300.4	300.0
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	150.0
Catalyst	60.0		60.0													
TOTAL	1074.1	459.2	1075.1	458.8	462.4	463.3	466.7	466.8	463.2	467.6	463.1	466.8	467.0	466.8	467.2	466.6
Product (Raw Data), gms																
Hydrogen	3.1	5.2	4.6	4.9	8.7	7.5	6.7	10.7	8.2	11.8	8.4	12.5	14.3	13.7	12.6	14.8
H -Free Gases	10.2	26.9	12.2	32.3	36.8	40.9	27.3	39.0	33.6	33.4	37.7	22.5	16.0	18.1	20.1	18.4
Water		2.1		9.4	14.2	13.6	9.6	7.7	0.0	20.0	14.1	26.8	30.0	17.1	60.9	37.6
Decant Oil + Solids	1037.6	405.7	1045.0	384.6	385.6	388.2	406.9	383.2	407.4	391.2	392.5	393.0	395.7	413.5	363.7	381.0
Catalyst																
Losses	23.2	19.3	13.3	27.6	17.1	13.1	16.2	26.2	14.0	11.2	10.4	12.0	11.0	4.4	9.9	14.8
TOTAL	1074.1	459.2	1075.1	458.8	462.4	463.3	466.7	466.8	463.2	467.6	463.1	466.8	467.0	466.8	467.2	466.6
Product (Adjusted Data), gms																
Hydrogen	3.1	5.2	4.6	4.9	8.7	7.5	6.7	10.7	8.2	11.8	8.4	12.5	14.3	13.7	12.6	14.8
H -Free Gases	10.2	26.9	12.2	32.3	36.8	40.9	27.3	39.0	33.6	34.2	38.0	23.0	17.4	19.3	21.4	19.0
Water		2.1		10.0	14.8	14.0	10.0	8.2	0.0	19.7	14.2	27.1	29.4	16.1	61.0	38.3
Decant Oil	1000.8	348.7	998.3	341.0	348.2	350.6	382.5	370.5	381.6	377.3	363.8	375.5	366.8	377.5	337.8	362.5
Solid Residue		76.3		70.6	53.9	50.3	40.2	38.4	39.8	24.6	38.7	28.7	39.1	40.2	34.4	32.0
Catalyst	60.0		60.0													
TOTAL	1074.1	459.2	1075.1	458.8	462.4	463.3	466.7	466.8	463.2	467.6	463.1	466.8	467.0	466.8	467.2	466.6
WT% Recovered	97.8	95.8	98.8	94.0	96.3	97.2	96.5	94.4	97.0	97.6	97.8	97.4	97.6	99.1	97.9	96.8

*Changed reactor impeller diameter from 3 cm to 5 cm for this and subsequent runs.

The molecular weight of the gas is determined by weighing the glass balloons filled with the gas sample. Air standards were 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.

The gas composition was determined by use of a Burrell Orsat for runs 1-23. The Orsat consists of four bubblers and two catalytic combustion tubes connected in series by a glass manifold. It operates on the principle of selective absorbtion of various components and catalytic combustion of the hydrogen and carbon monoxide components.

A 100 ml. sample of gas was admitted directly to the Orsat measuring buret from the gas sample tank. Hydrogen sulfide, carbon dioxide, unsaturated hydrocarbons and oxygen were absorbed in lead acetate solution, potassium hydroxide solution, "Lubsorbant" and "Oxsorbant" respectively. Any unsaturated hydrocarbons found were assumed to be ethylene. The amount of gas absorbed in each bubbler was assumed to represent the mole percent of each componenet. The unabsorbed hydrogen, carbon monoxide and saturated hydrocarbons were then passed through cupric oxide catalytic combustion tubes at a temperature between 560° and 570°F. This oxidized the hydrogen to water and the carbon monoxide to carbon dioxide. The volume decrease attained by passing the gas through the combustion tubes was taken to represent hydrogen that had been oxidized to water. Carbon dioxide formed from carbon monoxide was determined by rebubbling the gas through the potassium hydroxide solution. Any unabsorbed gas after this step was assumed to be methane and nitrogen. Since all oxygen found using "Oxsorbant" was assumed to be introduced from the atmosphere, nitrogen in the unabsorbed gases was estimated to be four times the volume percent of oxygen in the gas sample. Any ammonia formed in the reaction would have been absorbed with the hydrogen sulfide in the lead acetate solution.

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 sulfur and nitrogen contents of the coals and solvents charged and the sulfur and nitrogen content of the oil covered centrifuge residues and the centrifuge decant oil was assumed to be due to H_2S plus NH_3 in the gaseous product. The nitrogen and sulfur analyses of the wet centrifuge residue and the centrifuge decant oils is presented in Table A-2.

Upon delivery and calibration of a Hewlett-Packard Model 5840A gas chromatograph, Orsat analyses were discontinued. The chromatograph was used for runs 24-31. A Matheson high purity mixture was used to calibrate the machine monthly. A 12 ft. Porapak QS 50-80 mesh column was used for all runs. Gases quantitatively analyzed were hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and propane. A temperature program was used to achieve satisfactory separation. Liquid nitrogen was used to cool the chromatograph oven at the starting temperature of -40°C. This

TABLE A-2

CENTRIFUGE PRODUCT CHEMICAL ANALYSIS

Run Number	Decant Oils (WT%)		Centrifuge Residues (WT%)	
	Nitrogen	Sulfur	Nitrogen	Sulfur
17	.57	.10	.5	.5
19	.56	.12	.6	.4
20	.58	.06	.5	.5
21	.66	.08	.3	.4
22	.60	.04	.5	.5
23	.58	.06	.5	.5
25	.62	.07	.5	.76
26	.65	.08	.83	.52
27	.61	.10	.75	.39
28	.58	.08	.57	.27
29	.54	.10	.74	.33
30	.44	.05	.65	.27
31	.49	.04	.61	.23

temperature was held for 4 minutes. The oven was then heated at 10°C/min to 125°C. This temperature was held for 4 minutes to complete the run. Each run lasted approximately 25 minutes. Gases were injected into the column using a six port valve (HP 18815A) connected directly to the gas sample tank. Sample size was 17μl.

Although the odor of H_2S and NH_3 could be detected from the reactor product, neither H_2S nor NH_3 showed up on the chromatograms of gases sampled from the reactor. When H_2S or NH_3 was injected into the gas products, the chromatogram indicated the presence of these gases. Therefore, it was assumed that essentially all the H_2S and NH_3 had been adsorbed in the water produced during the liquefaction reaction.

For runs made in which the gaseous products were analyzed primarily in an Orsat, the calculated grams of hydrogen sulfide and ammonia were arbitrarily distributed into the total gas produced because of the uncertainty in the gas composition. However, for runs made in which the gaseous product was analyzed on the Hewlett-Packard 5840A chromatograph, more confidence was placed in the gas composition analyzed so the calculated grams of hydrogen sulfide and ammonia not found in the gases were 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. For runs in which the gaseous products were analyzed using the chromatograph, the 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 distillation head open to the atmosphere, a thermometer, a condenser, and a receiving cylinder. The magnetic stirrer is started and the power to the heating mantle is turned to 30-35 percent of full capacity.

TABLE A-3

GAS ANALYSES

RUN NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
RAW DATA, gms																
Hydrogen	8.2	7.7	10.9	11.7	8.7	4.7	4.7	4.8	5.2	5.9	5.4	4.0	4.0	3.9	3.4	3.1
Hydrogen Sulfide	.3	.2	1.9	0.2	.2	1.8	1.8	1.8	1.5	3.3	2.1	0.2	0.1	0.1		0.1
Carbon Monoxide						2.2	4.6									
Carbon Dioxide			1.7		1.1	5.1	4.9	2.7	2.9	3.8	3.3	0.2	0.2	0.1	0.1	0.1
Methane	3.3	3.9				17.5	16.8	13.5	15.0	19.9	15.4	11.4	9.9	12.0	10.0	9.9
Ethylene			0.1	0.3	0.5	0.5	0.7	0.3	0.3	0.4	0.2			0.1	0.1	0.1
Ethane																
Propane																
TOTAL	11.8	11.8	14.6	12.2	10.6	31.8	33.5	23.1	24.9	33.3	26.4	15.8	14.2	16.2	13.6	13.3
ADJUSTED DATA, gms																
Hydrogen	8.2	7.7	10.9	11.7	8.7							4.0	4.0	3.9	3.4	3.1
Hydrogen Sulfide	0.1	0.1	0.1	0.1	0.1							1.0	1.0	1.0	1.0	1.0
Ammonia	0.5	0.5	0.5	0.5	0.5							1.8	1.8	1.8	1.8	1.8
Carbon Monoxide																
Carbon Dioxide			3.0		0.7							0.2	0.2	0.1	0.1	0.1
Methane	3.0	3.5				Not analyzed for H_2S or NH_3.						8.8	7.2	9.3	7.2	7.2
Ethylene			0.1		0.5									0.1	0.1	0.1
Propane																
TOTAL	11.8	11.8	14.6	12.3	10.6							15.8	14.2	16.2	13.6	13.3
MOLECULAR WEIGHT																
Component Analysis, Unadjusted	2.72	2.89	2.64	2.08	2.39	8.54	8.89	6.90	6.79	7.60	6.97	5.76	5.39	5.98	5.80	6.07
Density Measurements	2.58	2.60	3.21	2.71	2.44	7.73	7.36	5.24	5.45	6.99	5.78	4.93	4.49	5.49	4.89	4.80

TABLE A-3 (Continued)

GAS ANALYSES*

RUN NUMBER	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
RAW DATA, gms															
Hydrogen	5.2	4.6	4.9	8.7	7.5	6.7	10.7	8.2	11.8	8.4	12.5	14.3	13.7	12.6	14.8
Hydrogen Sulfide	2.1	0.2	2.3	3.7	4.7	2.3	4.0								
Carbon Monoxide	0.2		3.0	3.0	6.9	3.2	3.5	1.9	2.6	2.2	1.3	0.8	1.3	1.6	1.5
Carbon Dioxide	5.1	0.2	6.1	8.9	6.7	4.9	6.3	15.5	10.9	13.0	10.5	10.8	10.6	11.4	11.3
Methane	19.3	11.7	20.7	20.8	22.4	16.5	24.8	7.2	8.7	10.0	4.1	2.0	2.6	2.6	2.2
Ethylene	0.2	0.1	0.2	0.4	0.2	0.4	0.4								
Ethane								5.0	6.0	6.8	2.9	1.4	1.9	2.2	1.6
Propane								4.0	5.2	5.7	3.7	1.0	1.7	2.3	1.8
TOTAL	32.1	16.8	37.2	45.5	48.4	34.0	49.7	41.8	45.2	46.1	35.0	30.3	31.8	32.7	33.2
ADJUSTED DATA, gms															
Hydrogen	5.2	4.6	4.9	8.7	7.5	6.7	10.7		11.8	8.4	12.5	14.3	13.7	12.6	14.8
Hydrogen Sulfide	0.3	1.0	0.6	0.2	0.8	0.8	0.9		0.6	0.3	0.4	.9	.8	.5	0.3
Ammonia	0.8	1.8	0.7	0.7	0.7	0.7	0.8		0.2	0.0	0.1	.5	.4	.8	0.3
Carbon Monoxide	0.2		3.0	3.0	6.9	3.2	3.5		2.6	2.2	1.3	0.8	1.3	1.6	1.5
Carbon Dioxide	6.1	0.2	7.1	11.7	9.9	5.7	8.6		10.9	13.0	10.5	10.8	10.6	11.4	11.3
Methane	19.3	9.1	20.7	20.8	22.4	16.5	24.8		8.7	10.0	4.1	2.0	2.6	2.6	2.2
Ethylene	0.2	0.1	0.2	0.4	0.2	0.4	0.4								
Ethane									6.0	6.8	2.9	1.4	1.9	2.2	1.6
Propane									5.2	5.7	3.7	1.0	1.7	2.3	1.8
TOTAL	32.1	16.8	37.2	45.5	48.4	34.0	49.7		46.0	46.4	35.5	31.7	33.0	34.0	33.8
MOLECULAR WEIGHT															
Component Analysis, Unadjusted	8.03	5.54	9.13	7.46	8.53	7.27	6.80	7.99	6.35	8.27	5.01	4.10	4.59	4.87	3.65
Density Measurements	7.73	5.66	8.93	7.71	8.45	7.81	7.41	8.34	6.48	8.89	5.05	4.10	4.59	4.87	3.65

*Orsat used for runs 1 through 23; chromatograph used for runs 24 through 31.

Vapor temperatures and volumes distilled over into a receiving 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 the distilling flask weighed again. All weights are recorded for material balance calculations. All vapor temperatures are corrected to 760 millimeters of mercury.

The 500 ml. distilling flask containing the residue from the atmospheric distillation is again placed in the heating mantle and fitted with a distillation head, a thermometer, a condenser, and a receiving cylinder. Three receiving cylinders are attached to a three-way distillation udder so that low boiling liquid product weights can be measured directly. The apparatus 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 manetic 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 5 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 was 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

Beginning with run 17, the total liquid-solid product from the reactor was 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 were 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 were arbitrarily assigned to the soluble portion of

TABLE A-4

DISTILLATION DATA

RUN NUMBER	6	7	8	9	10	11	17	19	20	21
DEAN STARK										
Charge (gms)										
Toluene	49.5	38.1	49.4	50.2	50.5	47.8	154.0	50.4	48.4	50.2
Decant Oil	70.5	31.1	102.8	102.7	100.3	75.8	131.2	122.0	125.1	119.8
TOTAL	120.0	69.2	152.2	152.9	150.8	123.6	285.2	172.4	173.5	170.0
Product										
Toluene	22.2	22.9	22.7	21.0	17.0	21.2	22.2	20.6	22.5	18.7
Water	0.9	0.2	2.7	2.0	2.8	1.9	0.8	3.5	5.1	4.6
Decant Oil + Toluene	64.3	32.2	118.1	126.2	125.3	97.4	210.3	148.3	144.7	145.5
Losses	32.6	13.9	8.7	3.7	5.7	3.1	51.9	0.0	1.2	1.2
TOTAL	120.0	69.2	152.2	152.9	150.8	123.6	285.2	172.4	173.5	170.0
WT% Recovery	72.8	79.9	94.3	97.6	96.2	97.5	81.8	100.0	99.3	99.3
ATMOSPHERIC DISTILLATION										
Charge (gms)	64.3	32.2	118.1	126.2	125.3	97.4	210.3	148.3	144.7	145.5
Product (gms)										
Toluene			17.3	25.5	27.8	22.6	79.3	29.8	24.7	30.3
350°F-		1.7		3.8	5.6	1.8	4.6	3.5	4.4	5.0
350°F+	64.2	29.2	100.2	96.0	90.1	72.1	125.3	114.0	114.5	109.3
Losses	0.1	1.3	0.6	0.9	1.8	0.9	1.1	1.0	1.1	0.9
TOTAL	64.3	32.2	118.1	126.2	125.3	97.4	210.3	148.3	144.7	145.5
WT% Recovery	99.8	96.0	99.5	99.3	98.6	99.1	99.5	99.3	99.2	99.4

TABLE A-4 (Continued)

DISTILLATION DATA

RUN NUMBER	6	7	8	9	10	11	17	19	20	21
VACUUM DISTILLATION										
Charge (gms)	64.2	29.2	100.2	96.0	90.1	72.1	125.3	114.0	114.5	109.3
Product (gms)										
350-500°F	27.3	10.0	34.6	38.1	29.6	25.8	47.1	38.1	38.7	34.1
500-650°F	19.3	8.1	25.8	24.5	19.2	23.3	38.6	33.9	33.2	36.5
650-800°F	(17.4	5.3	3.9	10.9	13.0	11.3	17.0	14.0	17.5	15.9
800°F+		5.7	34.2	20.6	27.8	11.5	21.7	26.5	24.5	22.1
Losses	0.2	0.1	1.7	1.9	0.5	0.2	0.9	1.5	0.6	0.7
TOTAL	64.2	29.2	100.2	96.0	90.1	72.1	125.3	114.0	114.5	109.3
WT% Recovery	99.7	99.7	98.3	98.0	99.4	99.7	99.3	98.7	99.5	99.4
ADJUSTED MATERIAL BALANCE										
Charge (gms)	70.5	31.1	102.8	102.7	100.3	75.8	131.2	122.0	125.1	119.8
Product (gms)										
H_2O (ℓ) + Dissolved NH_3+ H_2S	0.9	0.2	2.7	2.0	2.8	1.9	0.8	3.5	5.1	4.6
350°F-	5.6	1.8	(36.2	4.7	7.4	2.0	6.0	6.0	6.1	6.6
350-500°F	27.3	10.0		40.0	30.1	25.8	47.1	38.1	38.7	34.1
500-650°F	19.3	8.1	25.8	24.5	19.2	23.3	38.6	33.9	33.2	36.5
650-800°F	(17.4	5.3	3.9	10.9	13.0	11.3	17.0	14.0	17.5	15.9
800°F+		5.7	34.2	20.6	27.8	11.5	21.7	26.5	24.5	22.1
TOTAL	70.5	31.1	102.8	102.7	100.3	75.8	131.2	122.0	125.1	119.8

TABLE A-4 (Continued)

DISTILLATION DATA

RUN NUMBER	22	23	24	25	26	27	28	29	30	31
DEAN STARK			Not Analyzed							
Charge (gms)										
Toluene	50.0	50.2		49.8	51.0	54.3	51.0	50.0	50.7	50.9
Decant Oil	122.2	125.1		129.0	128.9	137.5	95.5	107.2	101.5	100.0
TOTAL	172.2	175.3		178.8	179.9	191.8	146.5	157.7	152.2	150.9
Product										
Toluene	20.5	20.1		15.4	17.1	13.4	14.9	16.1	8.1	12.4
Water	3.1	2.7		6.7	5.0	9.4	7.4	4.7	15.8	9.7
Decant Oil + Toluene	147.2	151.1		148.2	156.5	167.3	122.4	134.9	126.9	128.1
Losses	1.4	1.4		8.5	1.3	1.7	1.8	1.5	1.4	0.7
TOTAL	172.2	175.3		178.8	179.9	191.8	146.5	157.2	152.2	150.9
WT% Recovery	99.2	99.2		95.2	99.3	99.1	98.8	99.0	99.1	99.5
ATMOSPHERIC DISTILLATION										
Charge (gms)	147.2	151.1		148.2	156.5	167.3	122.4	134.9	126.9	128.1
Product (gms)										
Toluene	28.1	28.7		23.8	26.2	11.7	33.1	31.1	40.9	37.1
350°F-	4.0	5.8		4.0	3.2	33.9	12.4	7.8	7.9	8.5
350°F+	113.2	113.4		110.0	104.9	121.4	76.6	96.4	77.9	82.2
Losses	1.9	3.2		10.4	22.2	0.3	0.3	(0.4)	0.2	0.3
TOTAL	147.2	151.1		148.2	156.5	167.3	122.4	134.9	126.9	128.1
WT% Recovery	98.7	97.9		93.0	85.8	99.8	99.8	100.3	99.8	99.8

TABLE A-4 (Continued)

DISTILLATION DATA

RUN NUMBER	22	23	24	25	26	27	28	29	30	31
VACUUM DISTILLATION										
Charge (gms)	113.2	113.4	Not Analyzed	110.0	104.9	121.4	76.6	96.4	77.9	82.2
Product (gms)										
350-500°F	35.8	33.6		39.7	37.0	37.3	21.9	31.5	26.0	31.8
500-650°F	39.3	43.9		34.9	31.7	38.7	26.0	26.1	21.7	23.3
650-800°F	12.8	13.2		12.7	15.2	17.5	11.9	15.8	12.9	11.6
800°F+	24.7	22.1		22.4	20.7	27.6	16.8	22.8	16.9	15.4
Losses	0.6	0.6		0.3	0.3	0.3	0.0	0.2	0.4	0.1
TOTAL	113.2	113.4		110.0	104.9	121.4	76.6	96.4	77.9	82.2
WT% Recovery	99.5	99.5		99.7	99.7	99.8	100.0	99.8	99.5	99.9
ADJUSTED MATERIAL BALANCE										
Charge (gms)	122.2	125.1		129.0	128.9	137.5	95.5	107.2	101.5	100.0
Product (gms)										
H_2O (ℓ) + Dissolved NH_3+ H_2S	3.1	2.7		6.7	5.0	9.4	7.4	4.7	15.8	9.7
350°F-	6.5	9.6		12.6	19.3	7.0	11.5	6.6	8.2	8.2
350-500°F	35.8	33.6		39.7	37.0	37.3	21.9	31.4	26.0	31.8
500-650°F	39.3	43.9		34.9	31.7	38.7	26.0	26.0	21.7	23.3
650-800°F	12.8	13.2		12.7	15.2	17.5	11.9	15.7	12.9	11.6
800°F+	24.7	22.1		22.4	20.7	27.6	16.8	22.8	16.9	15.4
TOTAL	122.2	125.1		129.0	128.9	137.5	95.5	107.2	101.5	100.0

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 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 cone pulverizer is used for the final size reduction on samples C-2 and C-3. The final reduction in size on coal sample C-1 is accomplished with a Bico Type VA plate pulverizer with 10 inch plates. 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.

A micro apparatus was tried with little success. The results obtained for oils, SRC, and residues were much lower than those using the macro method. In future analyses the macro method will be used.

2. Carbon-Hydrogen: The sample is placed in an unglazed zircon combustion boat, covered with dried alumina and slowly pushed into a globar furance 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

TABLE A-5

WEIGHT % INSOLUBLES

	Centrifuge Residue			SRC (800°F+)		
Run	Pyridine	Benzene	n-Hexane	Pyridine	Benzene	n-Hexane
17	27.1%	33.9%	45.3%	2.6%	15.3%	73.9%
18	--	--	--	--	--	--
19	37.4	41.3	43.7	0.2	49.1	90.8
20	36.3	43.6	44.4	0.2	46.2	80.2
21	32.4	38.0	42.8	0.7	34.1	83.4
22	39.4	39.3	46.1	0.5	33.6	83.4
23	35.2	37.4	43.8	0.7	29.8	81.4
24	--	--	--	--	--	--
25	39.3	39.1	48.1	1.2	27.3	83.2
26	38.0	44.2	48.6	1.8	46.3	91.2
27	30.0	33.5	41.1	0.7	37.3	94.3
28	18.8	26.7	30.9	1.2	40.4	89.6
29	24.8	32.6	40.2	2.0	42.6	85.3
30	19.1	27.0	33.3	--	38.5	85.1
31	16.6	27.1	36.2	--	30.8	80.0

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 Equipment 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 (1) in the determination of nitrogen types in shale oils. The same procedure will be 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

TABLE A-6

BASIC NITROGEN TYPES BY TITRATION

Solvent	Chemical Types Titratable
Acetic Anhydride	Strong base: Quinolines, 3° amines, 1,2,3,4 tetrahydroquinoline
	Weak base: 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: Quinoline, 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 - .7 (Indoles)

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

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

(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.

E. 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}. One 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 experimental results on nitrogen classes is presented in Table A-8.

TABLE A-8

NITROGEN TYPES

Wt % Titrated

	IR	Mixed	Acetic Acid	Acetic Anhydride	
				TTN	SBN
F-1	.081	.372	.408	.455	.310
F-2	.082	.248	.326	.380	.182
F-3	.079	.118	.295	.316	.109
SRC solubles					
25	.096	.647	.768	.916	.633
26	.044	.414	.443	.580	.408
27	.060	.423	.440	.623	.414

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