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CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS

Quarterly Report for the Period
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CATALYSTS FOR UPGRADING COAL-DERIVED LIQUIDS
(FE 2011-2)

ABSTRACT

Work continued on assessment of catalysts for sulfur and nitrogen removal from coal liquids. A 150 hour activity test was performed on Nalco 474 Sphericat catalyst using an FMC oil at 700F (371C), 1500 psig and 3 hours space time. The resultant sulfur removal was 94% with no signs of activity loss over the 150 hours. Denitrogenation activity showed a marked decay with an initial removal of 60% and a final value of 40%. Four other experimental runs were conducted using catalysts made from Ketjen support material and processing raw anthracene oil. These results are not yet available.

Nearly all equipment items have been received for construction of the catalyst test unit and a data acquisition system has been ordered. Estimated construction is about 30% completed.

The field ionization source for the CEC 21-110B double focusing mass spectrometer is now routinely operational. Its performance was assessed in part using known samples of compounds which are structurally related to those in coal liquids. Approaches to the semiquantitative analysis of coal type mixtures have been explored using the known samples. The techniques used were gas chromatography and field ionization and low-voltage electron - impact ion abundances. The consequences of sensitivity data on the analytical results have been considered. Although including sensitivity corrections enhances the accuracy of the analyses, reasonable sample composition estimates can be obtained without using the corrections.

OBJECTIVE AND SCOPE OF WORK

The objective of this program is to investigate catalysts for upgrading liquids from coal-to-oil processes to remove sulfur, nitrogen and, possibly, other heteroatoms.

The present trickle-flow reactors in the School of Chemical Engineering, Oklahoma State University, shall be revamped and used for upgrading coal-derived liquids under high hydrogen pressures. Catalysts with supports of various pore sizes and pore size distributions shall be tested to seek optimum pore properties for such upgrading processes. The liquids used will mainly include those from ERDA sponsored coal-to-oil processes. Catalysts tested will also include those with various active-metals contents.

At least three trickle-flow reactors will be designed and constructed for testing catalysts life. Preliminary tests in this catalyst life test unit shall be performed in the second year. At the same time, catalyst degeneration or activity decay mechanisms shall be investigated.

Based upon the above studies, catalyst or catalysts shall be recommended for up-grading coal-derived liquids under hydrogen pressure to remove certain heteroatoms.

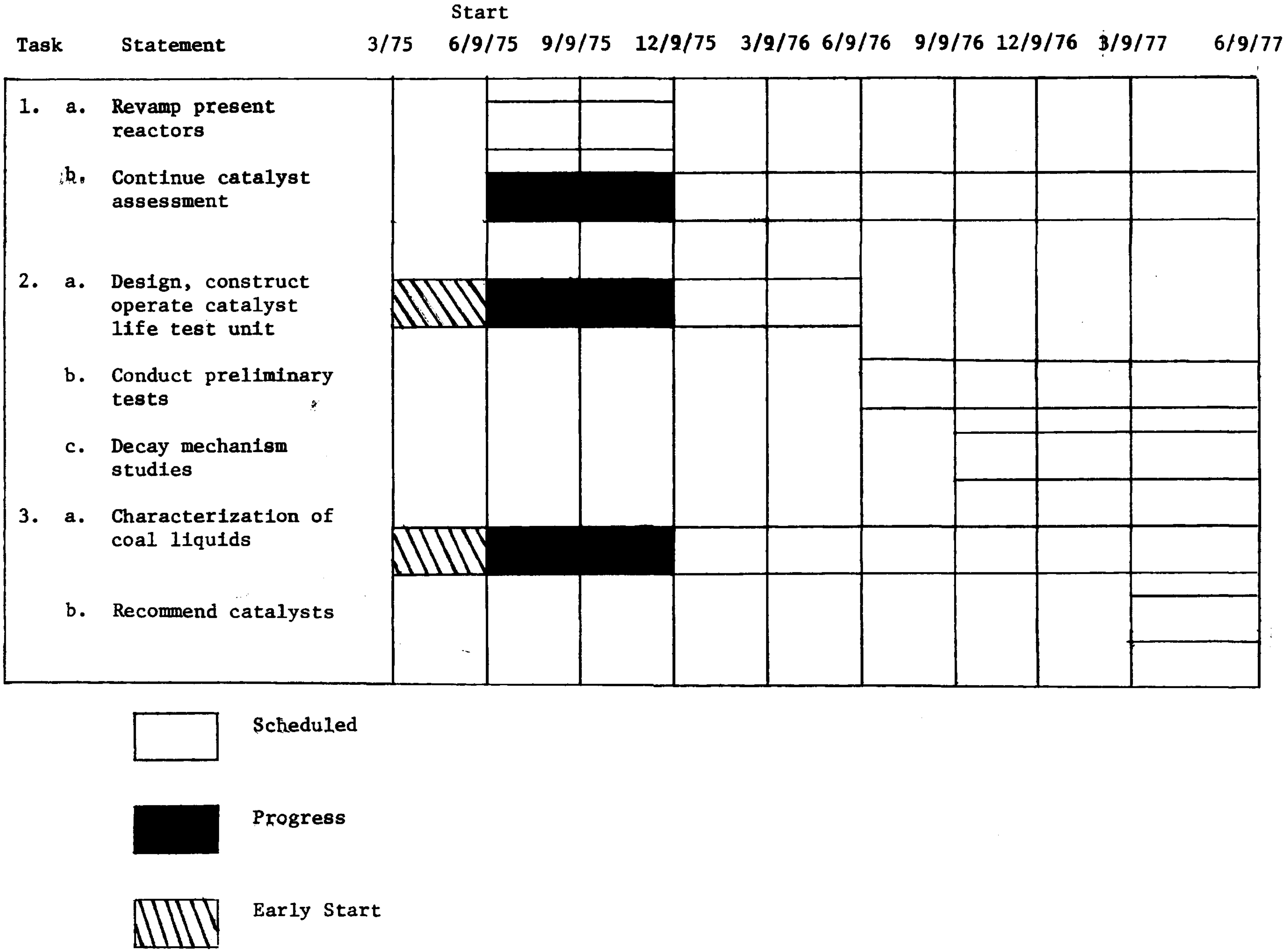
SUMMARY OF PROGRESS TO DATE

The following chart summarizes the progress to date. Because we are continuing portions of a program initiated from a previous project, Tasks 2a and 3a show an early progress achievement. The revamp of our present reactors (Task 1a) has not begun because we are using these reactors to continue our regular catalyst assessments. The revamping will be scheduled at convenient times to allow continued catalyst testing.

The three major thrusts of Tasks 1b, 2a, and 3a are well underway and on schedule, if not somewhat ahead.

As of December 1, 1975, 54% of the first year's budget($69,838 of $130,400) and 32% of the total budget($69,838 of $214,890) has been spent. This is within the expected rate of expenditures.

PROGRESS SUMMARY AS OF DECEMBER 9, 1975



DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1 - Continued Catalyst Testing and Revamp of Present Reactors

Four experimental runs were conducted in Reactor II during this quarter. The results from sample analyses are not yet available. One experimental run was a repeat of a run made earlier to check operational consistency and reproducibility. The three other experimental runs were made using a reference oil, raw anthracene oil,(properties given in Quarterly Report FE 2011-1) doctored with a nitrogen containing compound, quinoline. The objective of these doctored feed studies is to introduce nitrogen containing compounds and to trace their removal patterns, thereby giving additional details about the catalyst intrinsic activities and pore functions.

The product oil samples and feedstocks will be distilled into eight fractions and these will then be analyzed for their nitrogen contents. A profile of the doctored compound, the easily removed and difficult to remove compounds can be obtained from these distillations. The ASTM vacuum distillation unit was redesigned to provide for continuous sample collection with out disturbance or loss of vacuum.

The model doctor compound, quinoline, was chosen as representative of a coal type, nitrogen containing compound, and for its solubility in the anthracene oil feedstock. The first choice was that of carbazole, a three ring, difficult-to-hydrogenate compound. However, several attempts to obtain suitable concentration levels of carbazole in anthracene oil failed without use of additional preheating lines on the reactor and pump.

The experimental run conditions are summarized in Table 1. Analytical results from these runs will be reported in the next quarterly report.

Run Series SC-E

The objective of this experimental run series was to assess the rate of catalyst desulfurization-denitrogenation activity decay using a Nalco 474, Sphericat catalyst with a heavier feedstock, FMC oil (properties given in quarterly report FE 2011-1). The sulfur and nitrogen levels of the feed oil are 0.35 wt% and 1.13 wt%, respectively. The experimental run conditions were as follows:

Run Series	SC-E
Catalyst	Nalco 474 Sphericat
Feedstock	FMC oil
Temperature	700F (371C)
Pressure Total	1500 psig
Space Time (Vol. Hrly.)	2.99 hrs.
Hydrogen Flow (nominal)	7700 SCF/Bbl (sℓ/ℓ)*
Run Duration	150 hrs.

Properties of the Nalco 474 Sphericat catalyst are listed below. This catalyst is commericially available and has a bimodal pore distribution and is produced with a spherical shape.

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*Standard cubic feet of gas per barrel of oil or liter of gas at standard temperature and pressure per liter of oil.

TABLE 1
EXPERIMENTAL CONDITIONS

Run Series	Objectives	Catalyst	Feedstock	Run Conditions
KER	Repeat of previous run for reproducibility check	Ketjen support 007-1.5E impregnated with Co and Mo	Raw anthracene oil	650, 700, 750F (343, 371, 398C) 1500 psig total pressure 0.46, 0.92, 1.84 vol. hrly space time
KDC	Assess time, temperature response of a catalyst using doctored oil	Same as above	Quinoline doctored raw anthracene oil	Same as above
KDT	Same as above	Ketjen support 007-1.5E with ten hour steam treatment then impregnated with Co and Mo	Same as above	Same as above
KDP	Same as above	Ketjen support 000-3P impregnated with Co and Mo	Same as above	Same as above

Nalco 474 Sphericat

CoO Wt%	3.5
MoO_3 Wt%	12.5
Support	Alumina
Pore Volume	0.997
Surface Area M^2/g	286
Pore Radii (most frequent)	30Å micro, 860Å macro

The results from product oil sample analyses are given in Table 2 and shown in Figure 1. The experiment was conducted at a fixed set of operational conditions and all samples were taken within one startup and operational period of 150 hours of oil-on-catalyst. As seen in Table 2, the sulfur levels in all of the product oil samples were at 0.02 wt%S (94% removal). This is at the lower limit of the analytical instrument (Leco Sulfur Analyzer) used to determine total sulfur. No desulfurization activity decay could be distinguished. Figure 1 reveals appreciable denitrogenation activity decay over the 150 hours of operation. Initial removal levels of 60% fell to only 40% after about 120 hours of operation. Again, in this experiment as in others, sulfur removal is easily achieved; whereas,nitrogen removal is much more difficult. The bimodal properties revealed,within the limited range of this experiment, no particular advantage.

Work Forecast

During the next quarter the product oil samples from those outstanding experimental runs will be analyzed. These data will be assessed to obtain some insight into the intrinsic activity of the tested catalysts. Based on these studies, additional experimental runs will be conducted. If the scheduling is appropriate, some revamping of the two reactor systems will be made.

Task 2 - Construct Catalyst Life Test Unit and Study Catalyst Decay Mechanisms.

The primary objective under this task is to design, construct and operate a three reactor unit to assess the long-time activity life of catalysts. The unit will be used to gather data to study the catalyst decay mechanisms for coal derived liquids.

Construction on the Catalyst Life Test Unit (CLTU) continued during this quarter. Details and flow diagrams were given in the previous quarterly report (FE 2011-1). Approximately 98% of the equipment needed to construct the CLTU has been received. Most of the temperature and other controllers have been mounted and their corresponding power sources wired in. Construction of the control panel station is complete except for the sensor signals and final check out. The safety shutdown system, including telephone dialer, has been mounted and connected, except for the master electric shutdown switch and a few sensor signals. When these have been installed, all that will remain will be a final check out for the safety system to be operational. Within the high pressure cell, approximately 30% of the work has been completed. Required installations within the cell include those of the feed pump, hydrogen feed system, mounting reactors, associated gauges, valves, transducers and others.

The data acquisition and control computer has been ordered, and the quoted delivery time is the first week of January, 1976 (hopefully).

During the next quarter, installation and checkout of all systems will be completed. Our goal is to have all but the computer system operational.

TABLE 2

RESULTS FROM REACTOR I WITH NALCO 474 SPHERICAT (8/10 MESH), FMC OIL (COLORADO BEAR MINE) FEEDSTOCK

Run Number	Sample Number	Temp[a] (oF)	Pressure (psig)	Space Time[b] (Volume hrly)	Hydrogen (SCF/BBL)	Hours[c] on oil	%S[d]	%S[e] Removal	%N[d]	%N[e] Removal
	Feed						0.47		1.13	
030975	SC-E-1	700	1506	2.99	6792	10	0.02	94	0.450	60
031075	2	700	1509	2.99	7865	20	0.02	94	0.439	61
031075	3	700	1503	2.99	8026	30	0.02	94	0.500	56
031175	4	700	1507	2.99	8233	40	0.02	94	0.508	55
031175	5	700	1506	2.99	8727	50	0.02	94	0.549	51
031175	6	700	1506	2.99	6839	60	0.02	94	NA	-
031275	7	700	1508	2.99	8309	70	0.02	94	NA	-
031275	8	700	1507	2.99	7269	80	0.02	94	0.573	49
031375	9	700	1506	2.99	7163	90	0.02	94	0.554	51
031375	10	700	1510	2.99	8338	100	0.02	94	0.617	45
031375	11	700	1507	2.99	8669	110	0.02	94	0.646	43
031475	12	700	1505	2.99	7060	120	0.02	94	0.690	39
031475	13	700	1502	2.99	6976	130	0.02	94	0.668	40
031575	14	700	1506	2.99	7854	140	0.02	94	0.688	39
031575	15	700	1500	2.99	7606	150	0.02	94	0.654	42

a. Nominal Reactor Temperature

b. This is a volume hourly space time (volume of catalyst/volume of oil per hour)

c. Total hours which the catalyst has been contacted with oil at reaction conditions

d. Percent of sulfur or nitrogen in liquid product

e. % Removal = (fraction in feed less fraction in product)/(fraction in feed)

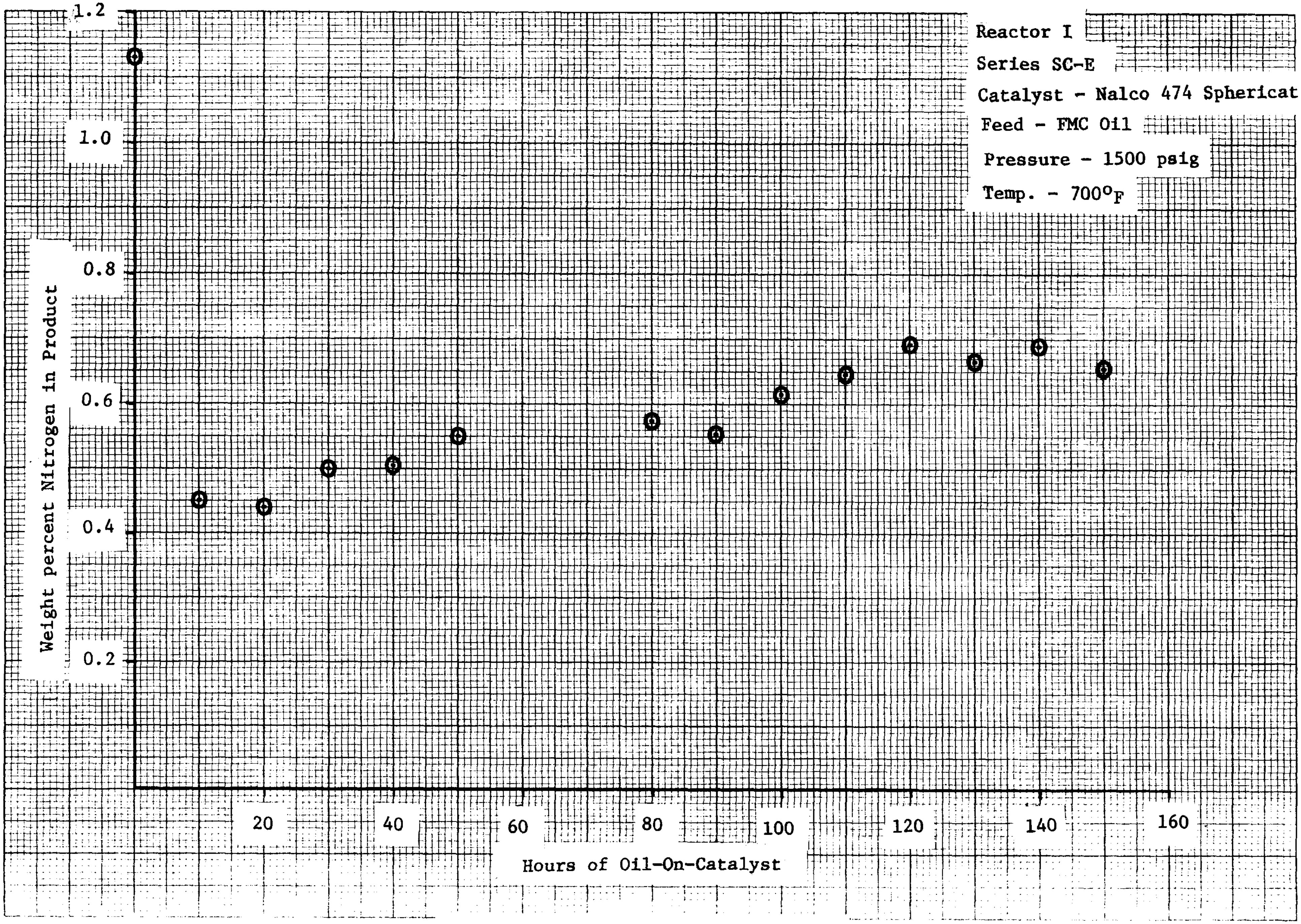


Figure 1. Catalyst Activity Decay

Task 3 - Final Catalysts Recommendation and Liquids Characterization

This task should, in fact, be the final conclusion resulting after Tasks 1 and 2 are completed. However, incorporated under this heading is work in the Oklahoma State University Chemistry Department under Professor S. E. Scheppele and Mr. G. J. Greenwood. This work is directed toward much more detailed analysis and characterization of our coal liquid feedstocks and product oils. Our goal is to achieve a better understanding of the coal liquids to be processed and those compound types that may be limiting satisfactory upgrading of coal liquids. Also, synthesis of model coal compounds could result from this work. Much of the effort thus far has been given to the development of detailed analytical techniques.

Technique of Field Ionization

The field ionization (FI) source for the CEC 21-110B mass spectrometer (1) has been made routinely operational. The principal difficulty encountered in obtaining ions by the field-ionization technique was associated with the materials used for emitters. By process of elimination, it was discovered that satisfactory emitters could be obtained from uncoated Personna-74 stainless-steel blades. A series of detailed tests confirmed that modification of the ion-source to produce FI spectra did not affect its performance in the electron-impact (EI) mode. A number of studies were made to check on the reproducibility of the FI spectra from one emitter to another and as a function of time, age of a given emitter, alignment of the emitter with respect to the slit in the field ionization electrode, and various operating voltages of the mass spectrometer. Tables 3 and 4 present typical relative abundance data for a hydrocarbon + ether fraction obtained from separation of a sample of hydrogenated anthracene oil (Reactor Sample 1, see reference 2) and percent total ionization for a fraction obtained from a Synthoil sample by gel permeation chromatography (3), respectively. The reproducibility of the relative ion abundances and percent total ionization as a function of instrumental parameters is seen to be quite satisfactory. For all ions, the average percent standard deviation a) in the relative ion abundances is 9.48% from four spectra of Reactor Sample 1 and b) in the percent total ionizations is 8.90% from three spectra of the Synthoil fraction. It is thus encouraging to note that the reproducibility of the FI relative ion abundances compares well with the reproducibility of the EI relative abundances we have obtained from the CEC 21-110B and CEC 21-103(4) mass spectrometer.

For the anthracene oil hydrocarbon + ether fraction (2) Figures 2, 3, and 4 present 70 volt EI, 10 volt EI and FI spectra, respectively. The contrast between the spectra in Figures 3 and 4 with the one in Figure 2 is marked. Since the technique of field ionization is known to produce largely fragment-ion free mass spectra, the FI spectrum confirms the previous conclusions (1) drawn from the 10-V EI spectrum concerning the compound types present in the hydrocarbon + ether fraction. In terms of the absence of fragment ions, the observed correspondence between the FI and low-voltage EI spectra is not expected to be a general phenomenon. In this instance the agreement undoubtedly reflects the fact that the sample is largely composed of polynuclear aromatic hydrocarbons. Since for such compounds the appearance potentials for the least energetic fragmentation reactions of the internally excited molecular ion are *ca.* several electron volts above the threshold for ionization, the 10-volt EI spectrum should not be characterized by the presence of fragment ions. Indeed for the Synthoil sample, whose composition is significantly different, the FI spectrum exhibits fewer ions than does the low voltage EI spectrum.

TABLE 3

FI RELATIVE ION ABUNDANCES FOR REACTOR SAMPLE 1

	Relative Ion Abundances for Emitter Number				
m/e(a)	1	2	2 repositioned		% Std. Dev. in Rel. Abd.
118	9.17	9.60	8.75	8.00	7.68
128	70.83	72.00	70.83	72.00	0.95
132	48.33	48.80	47.50	44.40	4.19
142	33.75	35.20	35.00	34.40	1.89
146	23.33	22.00	19.58	24.00	8.75
154	58.33	54.00	58.33	56.00	3.69
156	27.50	26.40	30.00	24.80	8.04
158	37.08	37.20	40.00	40.80	4.93
166	41.67	42.00	44.58	41.20	3.57
168	55.00	56.00	61.67	56.00	5.32
170	12.08	10.40	14.58	13.60	14.43
172	14.17	12.80	14.58	14.00	5.51
174	10.83	8.00	11.67	10.40	15.40
178	100.00	100.00	100.00	100.00	0.00
180	46.25	52.00	54.17	52.00	6.64
182	62.50	68.00	70.83	72.00	6.20
186	21.67	20.00	20.00	20.00	4.90
190	10.83	11.20	10.83	12.00	4.92
192	26.25	31.20	30.42	33.20	9.66
194	17.50	17.20	18.75	17.60	3.83
196	26.67	25.20	25.83	27.60	3.96
200	7.08	7.20	7.50	9.60	15.08
202	45.00	60.00	46.25	48.00	13.86
204	24.58	22.80	25.00	24.40	3.98
206	39.58	42.00	42.50	43.60	4.05
208	20.42	18.80	20.83	20.00	4.38
210	14.58	8.80	12.50	10.00	22.52
212	15.00	15.60	16.25	17.20	5.88

TABLE 3 (continued)

	Relative Ion Abundances for Emitter Number				
m/e(a)	1	2	2 repositioned		% Std. Dev. in Rel. Abd.
216	7.08	9.60	7.08	6.80	17.19
218	11.25	14.00	10.42	10.80	13.98
220	10.42	10.00	10.42	10.00	2.38
222	8.33	8.40	9.58	10.80	12.57
224	2.92	2.40	4.17	3.60	23.66
226	3.33	2.80	2.92	3.60	11.68
228	2.50	3.20	2.92	2.00	19.70
230	6.67	5.20	5.00	4.40	28.12
232	6.25	8.40	7.50	4.80	23.21
234	5.42	5.20	7.83	4.80	8.09
236	2.50	4.40	4.17	3.20	24.71
					Ave. 9.48

(a) Intensities for isotope peaks are not included for sake of brevity.

TABLE 4

FI RELATIVE ION ABUNDANCES FOR SYNTHOIL SAMPLE 173-21

m/e	Relative Ion Abundances from Scan #1	Scan #2	Scan #3	% Std. Dev. in Rel. Abd.
154	0.40	0.68	0.65	26.7
156	1.81	2.00	2.03	6.1
168	4.30	5.10	5.43	11.8
169	0.76	1.10	0.91	18.5
170	8.16	7.62	8.70	6.6
171	1.53	1.32	1.56	8.9
180	0.51	0.71	0.94	29.9
182	10.71	11.62	12.61	8.2
183	1.98	1.84	1.96	3.9
184	6.49	6.07	6.85	6.0
185	0.99	1.00	1.16	9.1
190	0.96	0.74	0.80	13.6
194	3.29	3.55	4.06	10.8
195	0.91	0.77	0.80	8.9
196	18.86	18.78	20.43	4.8
197	3.74	3.74	3.55	3.0
198	1.42	1.55	1.30	8.8
208	6.51	6.32	6.67	2.7
209	1.08	1.23	1.34	10.7
210	9.18	9.20	9.78	3.6
211	2.10	2.39	1.88	12.0
218	0.68	0.58	0.65	8.1
220	1.25	1.55	1.88	20.2
222	5.61	4.97	5.36	6.1
223	1.19	1.29	1.12	7.1
224	2.10	1.61	1.74	14.0
234	1.59	1.23	1.38	12.9
236	1.93	1.45	2.28	22.1
				Ave. 8.90

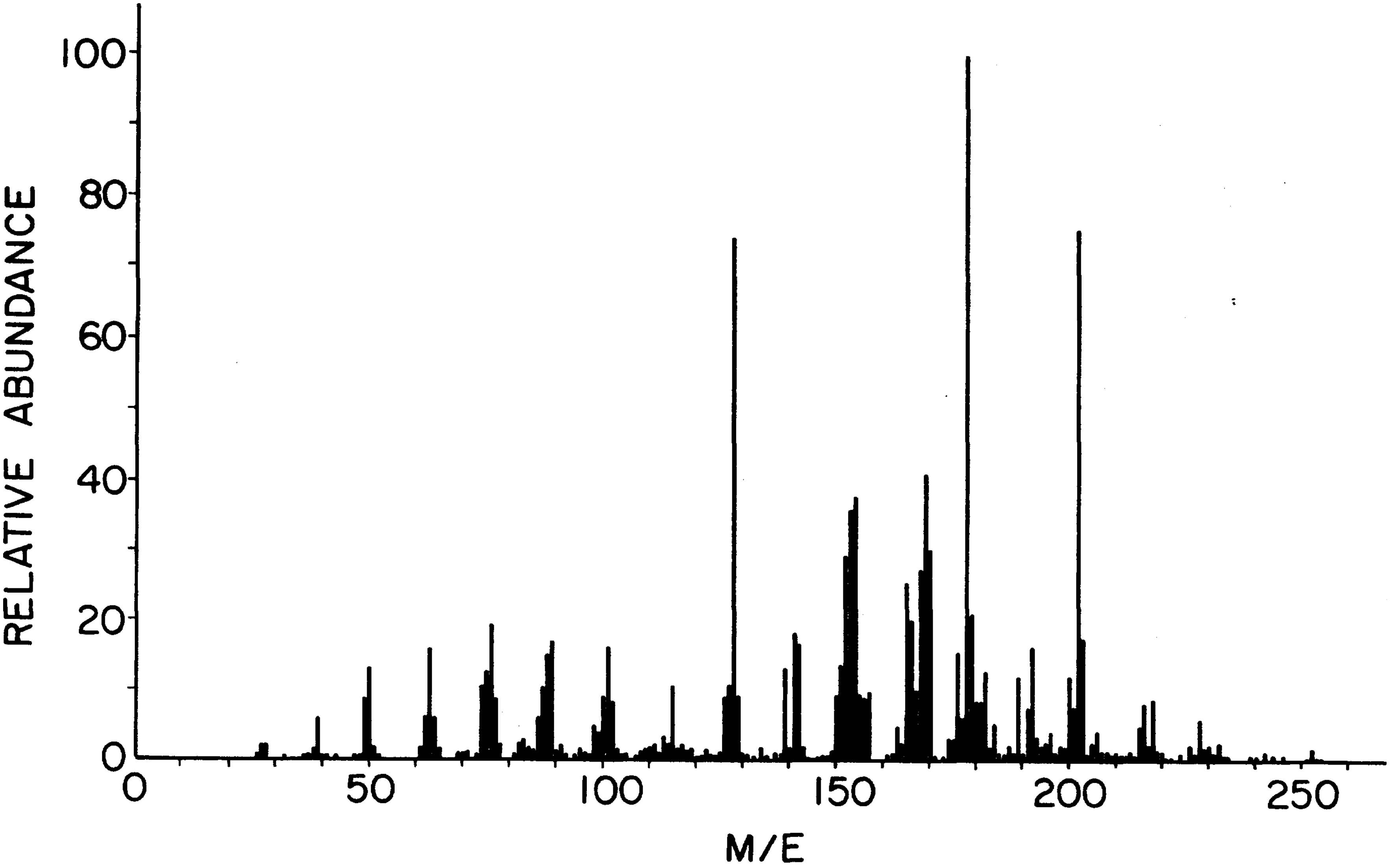


Figure 2. 70 EV Mass Spectrum of Anthracene Oil Hydrocarbon + Ether Fraction

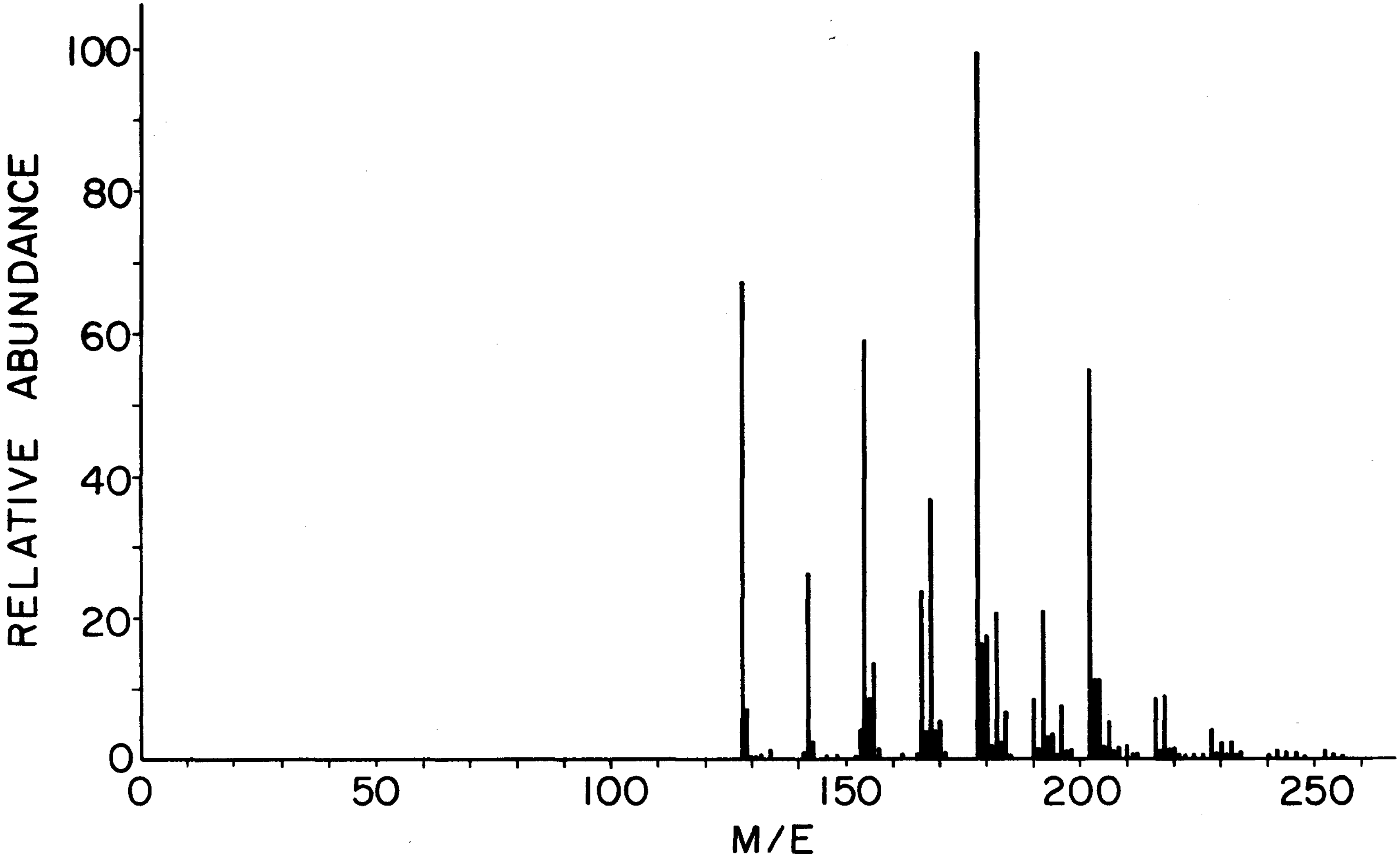


Figure 3. 10 EV Mass Spectrum of Anthracene Oil Hydrocarbon + Ether Fraction

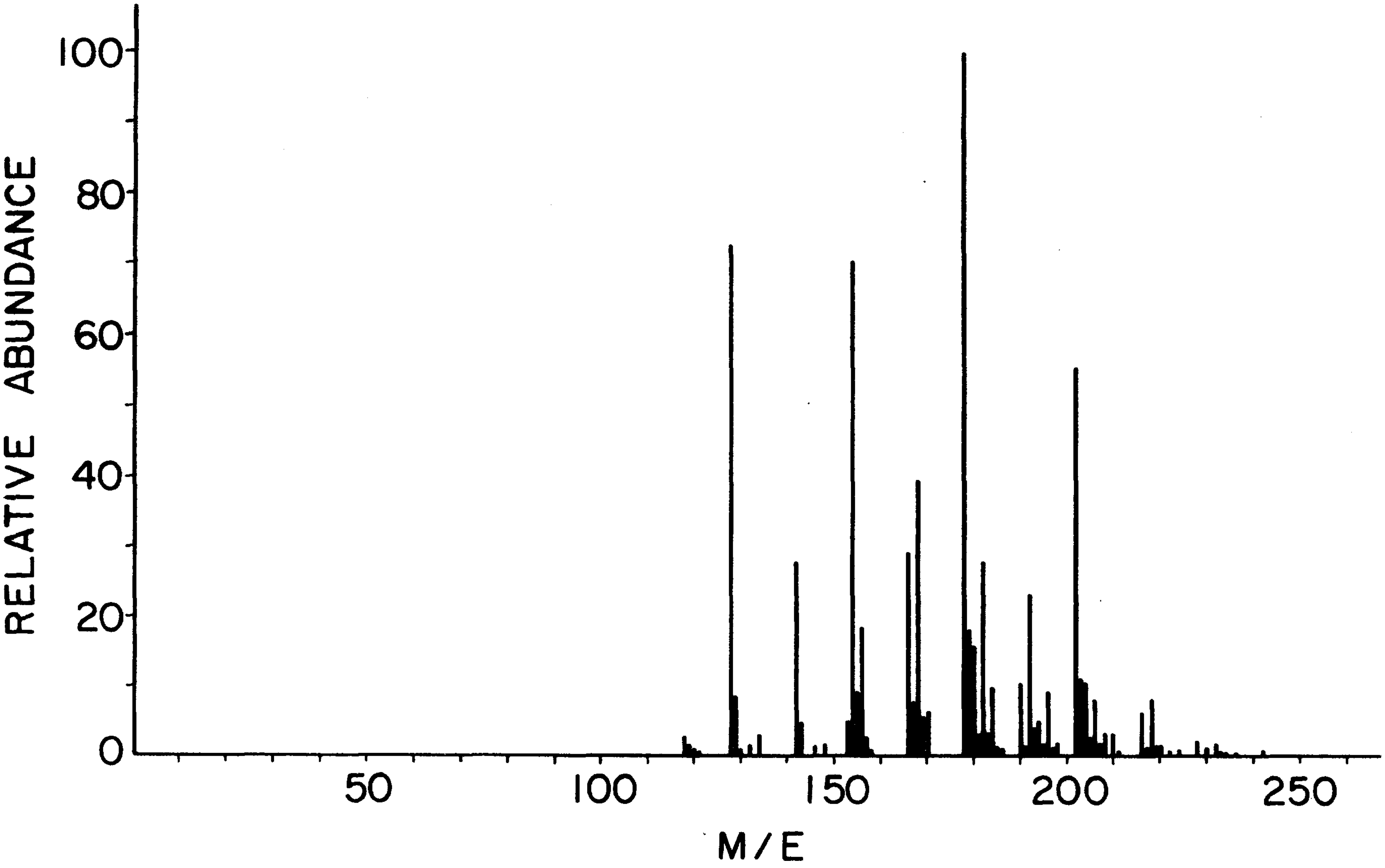


Figure 4. Field Ionization Mass Spectrum of Anthracene Oil Hydrocarbon + Ether Fraction

Finally, from a pragmatic viewpoint it is easier to obtain reproducible FI than low voltage EI spectra, at least on our CEC 21-110B.

Approaches to the Semi-Quantitative Analysis of Samples

Because of the nature of the research, the following discussion and results represent a synthesis of the combined efforts of Mr. G. J. Greenwood on this project and Dr. P. L. Grizzle on ERDA project number E(34-1)-0020. Gas chromatography-mass spectrometry, low-voltage mass spectrometry, and field-ionization mass spectrometry are techniques being used to obtain semi-quantitative estimates of sample composition. Before comparing the results obtained by these various techniques, it is appropriate to briefly consider those factors which relate instrument output to sample composition and their effect on the final analytical data.

Gas Chromatography with Flame Ionization Detection (FID)

Since the detector responds to ions, the area under a peak on a strip-chart recorder is proportional to the moles of ions, N_m^+, detected over the observing window (5). To relate N_m^+ to the moles of neutral, N_n, admitted to the detector requires knowledge of the stoichiometry of the reactions occurring in the flame. Use of authentic compounds constitutes an approach to circumventing this formidable problem. In the present instance this approach is not generally feasible for the following reasons: 1) the required sensitivity data are either not available or cannot be determined because of a lack of authentic compounds and 2) even if the required compounds were available the determination of sensitivities would be extremely time consuming - the time spend should be considered within the framework of the accuracy required in the analysis.

In view of these considerations we proceed as follows. To formulate the approach, Eq 1 expresses the peak area in units proportional to the moles of neutral introduced to the detector; k_{inst} is an instrument constant and C_E is the effective number of carbons in the compounds (5). For a series of hydrocarbons, data indicate

$$A(N)_n = k_{inst} \cdot N_n \cdot C_E \qquad (1)$$

C_E is essentially given by the number of carbons in the molecule (5). For example, based upon propane as a reference with an effective carbon number of 3, C_E values of 1.98, 7.90, 2.58, 6.05 and 6.91 were obtained for ethane, octane, acetylene, benzene, and toluene, respectively (5). The peak area in Eq 1 can be expressed in units proportional to the number of grams of neutral, $A(g)_n$, by using $N_n = g_n/MW_n$; see Eq 2. For the above compounds the quantity C_E/MW_n using nominal molecular

$$A(g)_n = \frac{k_{inst} \cdot g_n \cdot C_E}{MW_n} \qquad (2)$$

molecular weights has the value 0.066, 0.069, 0.099, 0.078, and 0.075, respectively.

Thus, with the exception of acetylene the value of this ratio is seen to be sensibly constant. Consequently, as a first approximation to obtain a semi-quantitative estimate of sample composition, the ratio of C_E/MW_n was assumed to be essentially constant and thus factors out in converting peak areas to weight percents. An attempt has been made to assess the validity of this assumption by analyzing known mixtures of hydrocarbons equivalent or structurally related to those in our samples (6). An alternate approach, which has not yet been explored, would be to determine sensitivities for a representative number of compounds for each homologous series. These values could be plotted as a function of carbon number (7) to obtain estimates of sensitivities for other compounds in the series. The problem associated with this approach is dominated by the availability of pure compounds, the validity of the interpolation or extrapolation, and the accuracy desired in the analysis.

Low-Voltage Mass Spectrometry

Equation 3 gives the weight percent of the *i*-th component in terms of the

$$\%wt_i = \left[\frac{I_i/S_i}{\sum_{i=1}^{n} (I_i/S_i)} \right] \times 100 \qquad (3)$$

relative peak intensities and the sensitivities expressed in divisions per mg (8). Assuming that variation in instrumental parameters associated with obtaining mass spectra is marginally affecting the ion abundances, the accuracy of the analytical data will reflect:

1) contributions to the intensity at the m/e value corresponding to the molecular ion of the *i*-th component from fragmentations of ions at higher mass.
2) the correspondence of the ionizing voltages at which the sensitivity data and the mass spectra were obtained. Since we have used sensitivity data reported in the literature (9), noncorrespondence between ionizing energies could introduce some uncertainty in the analyses.
3) uncertainties associated with sensitivity data obtained by interpolation or extrapolation. At the present time some sensitivity data have been obtained from the correlation (9) of sensitivities for various classes of homologous compounds with the reciprocal of the molecular weight. Even these results do not provide sufficient data to permit a complete sample analysis. Attempts are being made to collect additional compound types for sensitivity determinations.

Field Ionization Mass Spectrometry

The following equations which are derived for a two-component mixture can be generalized to a multi-component mixture. For a mixture of A and B the moles of A, N_A, and of B, N_B, are given by I_A/S_A and I_B/S_B, respectively. Equation 4 expresses the mole fraction of component A in terms of these quantities. Thus by

$$X_A = \frac{I_A}{I_A + \frac{S_A I_B}{S_B}} \qquad (4)$$

Thus be defining the mole sensitivity of component B relative to component A as s_B, Eq 5 is obtained from Eq 4.

$$X_A = \frac{I_A}{I_A + \frac{I_B}{s_B}} \qquad (5)$$

The value of s_B is given by Eq 6. Similarly the relative weight sensitivity

$$s_B = \left(\frac{I_B}{I_A}\right)\left(\frac{X_A}{1 - X_A}\right) \qquad (6)$$

of component B is given by Eq 7 in which w_A is the weight fraction of A defined

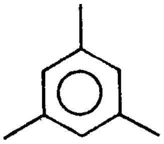
$$s_B' = \left(\frac{I_B}{I_A}\right)\left(\frac{w_A}{1 - w_A}\right) \qquad (7)$$

by $g_A/(g_A + g_B)$. The weight percents are thus obtainable from Eq 3.

In the present instance sensitivities for compounds in known mixtures were obtained relative to naphthalene. Thus in addition to any contributions from instrumental factors, the accuracy of an analysis is determined by the availability of sensitivity data, or parenthetically, the validity of assuming that $S_j/S_1 = 1$ for the j th component and a negligible contribution to the intensity at the m/e value of the j th molecular ion from fragmentations of ions at high mass.

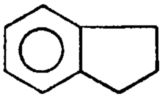
Results Obtained from Analysis of Known Samples

Five hydrocarbon mixtures were prepared using weighed quantities of various of the following compounds. Except for Samples 7, 10, 19 and 20, which were



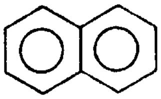
1

Mesitylene



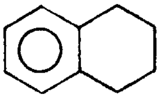
2

Indane



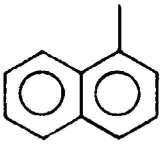
3

Naphthalene



4

Tetralin



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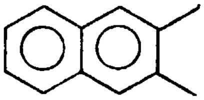
1-Methylnaphthalene



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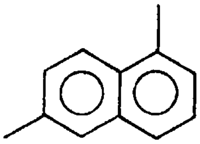

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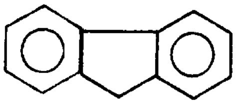
1,6-dimethylnaphthalene



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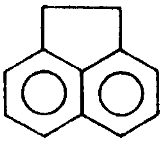
fluorene



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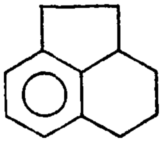
acenaphthene



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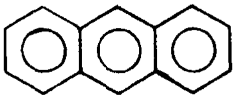
tetrahydroacenaphthene



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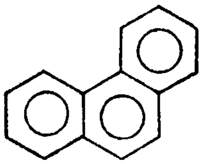
anthracene



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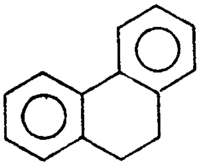
phenanthrene



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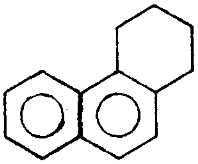
dihydrophenanthrene



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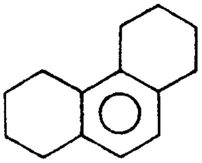

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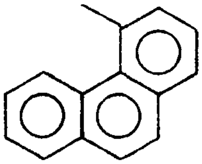
octahydrophenanthrene



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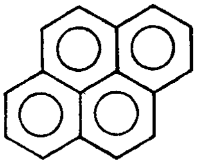
4-methylphenanthrene



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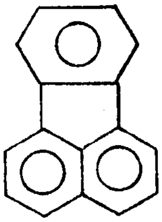
pyrene



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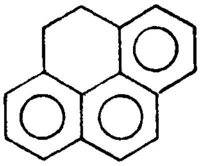
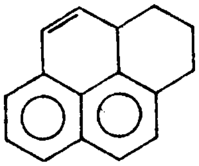
fluoranthene



19a

dihydropyrene



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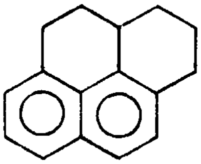
tetrahydropyrene



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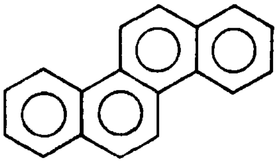
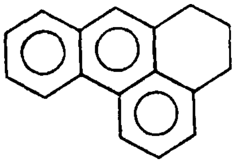
hexhydropyrene



21

chrysene



22

dihydrobenzanthrene

obtained from the Bartlesville Energy Research Center (6), the samples were obtained from either Professor E. J. Eisenbraun (6) or commercial sources. The mixtures were subjected to GC and FI analysis; for Mixture 5, which was chronologically the first one, low-voltage data (4) were also obtained.

For Mixtures 1 through 4 the weights (moles) and FI relative ion abundances were used to obtain weight (mole) sensitivities for each compound relative to the sensitivity for naphthalene. The results are shown in Tables 5 through 8. The minimum purity of samples obtained from Professor Eisenbraun is indicated to 97% or greater. Sample 19 was found to contain two components 19a and 19b. Assuming equal FID sensitivities, the sample is composed of 57.9% of 19a and 42.1% of 19b. Therefore, these weight percents and the total weight of Sample 19 taken were used in calculating the sensitivities for 19a and 19b. GC analysis indicated that Sample 5 was composed of 8.3, 6.8, and 77.6% of 13, 14, and 15, respectively; three additional components which account for 7.3% of the sample were observed but have not yet been identified. The FI spectrum exhibited three ions whose m/e values were not consistent with those for any of the other compounds. Thus as a first approximation these peaks were assigned to the unidentified components present in Sample 15. Compound 13 is seen to be common to Mixtures 1, 2, and 3; compounds 7 and 10 are common to Mixtures 1 and 2. Considering that the samples are not analytically pure, it is gratifying to note that the relative sensitivities for these compounds in the various mixtures agree within the limits of precision calculated from the standard deviations in the ion abundances.

To investigate the neglect of sensitivities on the weight percents obtained by both GC and FI, the analysis of Mixtures 1 through 4 are so constructed in Tables 9 through 12. Finally Mixture 5 was analyzed using GC and both low-voltage and field-ionization mass spectrometry. For the latter data sets the weight-percent composition was calculated including and excluding sensitivities. The results are presented in Table 13. If only a reasonable level of accuracy is required the data in Tables 9 through 13 show that GC peak areas and FI relative ion abundances can be used without sensitivity corrections. The following comments are, however, pertinent. The accuracy of the FI analysis is generally improved by including the sensitivities. Before any real generalizations can be made concerning the neglect of sensitivities on the compositional data, these studies must be expanded to include a wider range in molecular weights and compound types. In Table 13 the compositional data obtained from low-voltage mass spectrometry is seen to be somewhat improved by including sensitivities. In conclusion, for the range of compound types and molecular weights covered in this invesigation, the results suggest that all methods yield a reasonable first approximation to the sample composition.

Other Research Activities

In the previous report (1) the calculation of sample composition from the 70-volt ion abundances using the Swansinger calibration matrix was proposed. However, this approach has been presently abandoned in view of the results obtained from gas chromatography and low-voltage and field-ionization mass spectrometry.

Questions (1) were raised concerning the effectiveness of the proposed method for separating neutral sulfur containing compounds (see Separation Scheme, page 26 in reference 1). Table 14 tabulates weight percent sulfur obtained from combustion of: 1) the anthracene oil and the four reactor samples and 2) the

TABLE 5

RELATIVE FI SENSITIVITIES CALCULATED FROM ANALYTICAL DATA FOR MIXTURE 1

Compound		Relative Sensitivities by	
Number	Name	Weight[a]	Moles[a]
3	Naphthalene	1.00	1.00
5	1-Methylnaphthalene	0.95 ± 0.09	1.06 ± 0.07
7	1,6-Dimethylnaphthalene	1.00 ± 0.11	1.22 ± 0.10
10	Tetrahydroacenaphthene	0.80 ± 0.09	0.99 ± 0.07
12	Phenanthrene	0.94 ± 0.02	1.24 ± 0.09
13	Dihydrophenanthrene	0.88 ± 0.08	1.28 ± 0.06
18	Fluoranthene	0.69 ± 0.03	1.08 ± 0.10
22	Dihydrobenzanthrene	0.60 ± 0.03	1.02 ± 0.10

[a] Average of three determinations; deviations are standard deviations.

TABLE 6

RELATIVE FI SENSITIVITIES CALCULATED FROM ANALYTICAL DATA FOR MIXTURE 2

Compound		Relative Sensitivities by	
Number	Name	Weight[a]	Moles[a]
3	Naphthalene	1.00	1.00
7	1,6-Dimethylnaphthalene	1.03 ± 0.09	1.26 ± 0.04
10	Tetrahydroacenaphthene	0.81 ± 0.08	1.00 ± 0.06
11	Anthracene	1.03 ± 0.04	1.39 ± 0.01
13	Dihydrophenanthrene	0.83 ± 0.08	1.17 ± 0.06
17	Pyrene	0.80 ± 0.03	1.25 ± 0.08
19a	Dihydropyrene	0.90 ± 0.01	1.43 ± 0.09
19b	Tetrahydropyrene	0.83 ± 0.02	1.32 ± 0.08
20	Hexahydropyrene	0.69 ± 0.01	1.12 ± 0.04

[a] Average of three determinations; deviations are standard deviations.

TABLE 7

RELATIVE FI SENSITIVITIES CALCULATED FROM ANALYTICAL DATA FOR MIXTURE 3

	Compound	Relative Sensitivities by	
Number	Name	Weight[a]	Moles[a]
2	Indane	0.90 ± 0.04	0.83 ± 0.02
3	Naphthalene	1.00	1.00
4	Tetralin	0.82 ± 0.06	0.85 ± 0.03
13	Dihydrophenanthrene	0.72 ± 0.12	1.02 ± 0.10
14	Tetrahydrophenanthrene	0.74 ± 0.04	1.05 ± 0.05
15	Octahydrophenanthrene	0.64 ± 0.03	0.93 ± 0.03

[a] Average of three determinations; deviations are standard deviations.

TABLE 8

RELATIVE FI SENSITIVITIES CALCULATED FROM ANALYTICAL DATA FOR MIXTURE 4

Number	Compound Name	Relative Sensitivites by Weight[a]	Relative Sensitivites by Moles[a]
1	Mesitylene	0.99 ± 0.02	0.92 ± 0.02
3	Naphthalene	1.00	1.00
8	Fluorene	0.87 ± 0.04	1.15 ± 0.06
9	Acenaphthene	0.99 ± 0.14	1.19 ± 0.17
16	Methylphenanthrene	0.83 ± 0.13	1.25 ± 0.19
21	Chrysene	0.31 ± 0.01	0.55 ± 0.01

[a] Average of three determinations; deviations are standard deviations.

TABLE 9

WEIGHT PERCENTS OF VARIOUS COMPONENTS IN MIXTURE 1 EXCLUDING SENSITIVITY CORRECTIONS

Compound		Weight Percents Obtained From		
Number	Name	Grams[a]	GLC Peak Areas[b]	FI Abundances (Excluding Sensitivities)
3	Naphthalene	10.61	11.26	9.58
5	1-Methylnaphthalene	18.64	18.79	17.86
7	1,6-Dimethylnaphthalene	16.81	16.40	18.57
10	Tetrahydroacenaphthene	18.49	18.83	16.44
12	Phenanthrene	3.44	3.71	4.00
13	Dihydrophenanthrene	15.10	14.84	16.84
18	Fluoranthene	6.88	6.76	6.81
22	Dihydrobenzanthrene	10.03	9.40	9.90

[a] All samples were weighed to an accuracy of ± 0.0003 on a Mettler balance.

[b] Peak areas determined by using peak height and width at half height.

TABLE 10

WEIGHT PERCENTS OF VARIOUS COMPONENTS IN MIXTURE 2 EXCLUDING SENSITIVITY CORRECTIONS

	Compound	Weight Percents Obtained From		
Number	Name	Grams[a]	GLC Peak Areas[b]	FI Abundances (Excluding Sensitivities)
3	Naphthalene	8.86	8.66	7.61
7	1,6-Dimethylnaphthalene	21.37	20.79	24.29
10	Tetrahydroacenaphthene	22.49	21.76	18.31
11	Anthracene	9.39	14.86	11.53
13	Dihydrophenanthrene	19.65	17.58	19.79
17	Pyrene	7.12	6.72	7.68
19a	Dihydropyrene	5.36	2.54	2.30
19b	Tetrahydropyrene		1.85	2.94
20	Hexahydropyrene	5.77	5.24	5.56

[a] All samples were weighed to an accuracy of ± 0.0003 on a Mettler balance.

[b] Peak areas determined by using peak height and width at half height.

TABLE 11

WEIGHT PERCENTS OF VARIOUS COMPONENTS IN MIXTURE 3 EXCLUDING SENSITIVITY CORRECTIONS

Compound		Weight Percents Obtained From		
Number	Name	Grams[a]	GLC Peak Areas[b]	FI Abundances (Excluding Sensitivities)
2	Indane	15.75	15.45	13.86
3	Naphthalene	8.72	10.47	9.23
4	Tetralin	19.61	21.56	17.60
13	Dihydrophenanthrene	25.30	25.39	27.24
14	Tetrahydrophenanthrene	15.31	12.69	17.05
15	Octahydrophenanthrene	15.31	14.28	15.01

[a] All samples were weighed to an accuracy of ± 0.0003 on a Mettler balance.

[b] Peak areas determined by using peak height and width at half height.

TABLE 12

WEIGHT PERCENTS OF VARIOUS COMPONENTS IN MIXTURE 4 EXCLUDING SENSITIVITY CORRECTIONS

Compound		Weight Percents Obtained From		
Number	Name	Grams[a]	GLC Peak Areas[b]	FI Abundances (Excluding Sensitivities)
1	Mesitylene	34.32	34.13	31.37
3	Naphthalene	19.33	19.62	19.12
8	Fluorene	17.54	18.07	20.08
9	Acenaphthene	15.44	15.50	18.17
16	Methylphenanthrene	5.92	6.14	7.17
21	Chrysene	7.46	6.54	4.09

[a] All samples were weighed to an accuracy of ± 0.0003 on a Mettler balance.

[b] Peak areas determined by using peak height and width at half height.

TABLE 13

WEIGHT PERCENT OF VARIOUS COMPONENTS IN MIXTURE 5

				Low Voltage Mass Spectrometry		Field Ionization Mass Spectrometry	
Number	Compound	Grams	GLC Peak Areas	without sensitivity corrections	with sensitivity corrections	without sensitivity corrections	with sensitivity corrections
3	Naphthalene	5.02	5.26	3.45	5.41	4.56	5.14
5	1-Methylnaphthalene	21.78	23.07	17.29	19.74	19.73	21.12
6	2,3-dimethylnaphthalene	3.55	3.92	3.86	3.93	5.97	5.53
8	Fluorene	4.56	4.85	4.36	5.57	5.30	5.31
11,12	Anthracene, Phenanthrene	5.06[a]	4.12	8.40	6.66	5.98	4.90[c]
13	Dihydrophenanthrene	28.40	28.45	28.15	28.05	27.58	25.13
14	Tetrahydrophenanthrene	22.18	21.16	21.66	22.01	22.15	23.75
16	4-Methylphenanthrene	1.54	1.65	2.13	1.66	1.63	1.47
17	Pyrene	3.82	3.57	8.05[b]	5.06[b]	6.24[b]	5.95[b,c]
18	Fluoranthene	2.15	2.20				
21	Chrysene	1.94	1.75	2.63	1.90	0.84	1.71

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[a] Total consists of 63.2 and 36.8 percent by weight phenanthrene and anthracene, respectively.

[b] Compounds 10 and 11 have the same exact mass.

[c] Sensitivity used is average wt. % sensitivity.

TABLE 14

WEIGHT PERCENT SULFUR FROM SAMPLE COMBUSTION

	Weight Percent Sulfur in	
Sample	Unseparated Fraction[a]	Hydrocarbon + Ether Fraction[b]
Anthracene oil	0.47 (0.51[b])	0.49
Reactor Sample 1	0.11	0.13
Reactor Sample 2	0.07	0.18
Reactor Sample 3	0.02	0.07
Reactor Sample 4	0.04	0.06

[a] Data obtained in Department of Chemical Engineering.

[b] Data obtained at Bartlesville Energy Research Center, Bartlesville, Oklahoma.

five hydrocarbon + ether fractions obtained from separation of these five samples. For the unseparated anthracene oil the weight percents of sulfur obtained by the two laboratories are in good agreement. Comparison of the data in columns 2 and 3 indicate that the proposed method for removal of the neutral sulfur containing compounds is ineffective. The material recovered from this step in the separation scheme is being analyzed. It is conceivable that the quantity of recovered material reflects the presence of organic-bound mercury. In an attempt to determine what classes of neutral sulfur-containing compounds are present, the high resolution data for the hydrocarbon + ether fractions are being reexamined. Also the fraction obtained from subjecting a second anthracene-oil sample to the first three steps in the Separation Scheme will be analyzed by high resolution mass spectrometry.

Work Forecast

During the following quarter we will:

1) obtain high resolution data by field-ionization mass spectrometry.
2) obtain FI mass spectra for the heteroatom containing components for the above mentioned five samples. Proceed with the qualitative and semi-quantitative analysis of these fractions.
3) proceed with the separation of at least 1 additional coal liquid.
4) finalize analysis of the "hydrocarbon" fractions from the anthracene oil and four reactor samples.
5) draft manuscript for publication based upon the results and conclusions obtained in 4 and the data obtained from the semi-quantitative analysis of known hydrocarbon mixtures by the various techniques.

References

1) The design and construction of the combined FI/EI source was commented on in the quarterly report FE 2011-1, Dist. Category UC 90d for the period June 9, 1975 - September 9, 1975.

2) The relevant EI data for the hydrocarbon + ether fractions obtained from separation of the anthracene oil and from four samples obtained from its hydrogenation-hydrogenolysis can be found in reference 1. Where data are presented for these samples in this report, the designation of samples follows that given in reference 1.

3) Results obtained by S. E. Scheppele and P. L. Grizzle under ERDA contract number E(34-1)-0020.

4) These data were obtained using the CEC 21-103 mass spectrometer at the Bartlesville Energy Research Center, Bartlesville, Oklahoma.

5) D. J. David, "Gas Chromatographic Detectors", John Wiley and Sons, New York, N. Y., 1974, Chapter 3.

6) We thank Professor E. J. Eisenbraun and his colleagues for graciously supplying us standard reference compounds. Some samples were kindly provided by Mr. J. E. Dooley at the Bartlesville Energy Research Center, Bartlesville, Oklahoma.

7) L. S. Ettre, J. Chromatog., <u>8</u>, 525 (1962).

8) V. H. Dibeler, in "Mass Spectrometry" ed. by C. A. McDowell, McGraw-Hill Book Co., Inc., 1963, Chapter 9.

9) H. E. Lumpkin and T. Aczel, Anal. Chem., <u>36</u>, 181 (1964).

CONCLUSIONS

The following conclusions are drawn from the results and progress of this project during the quarter, September 9 - December 8, 1975:

1. Results from experimental run series SC-E have shown that Nalco 474 Sphericat catalyst achieved at least 94% desulfurization while processing a raw anthracene oil at 700F (371C), 1500 psig and at 3 hours space time. No loss in desulfurization activity was noted over 150 hours of continuous operation.
2. Denitrogenation of the same feedstock under the same conditions showed a marked decay over 150 hours, with initial removal of 60% falling to only 40%.
3. The installation of the Catalyst Life Test Unit is now about 30% completed, and a data acquisition computer has been ordered.
4. The field ionization source has been made routinely operational.
5. Various approaches to the semiquantitative analysis have been assessed and found to be satisfactory for routine characterization of coal liquids and related mixtures.