

STANNOUS CHLORIDE AND COBALT MOLYBDATE-ALUMINA CATALYSTS  
IN HYDROGENOLYSIS OF SOLVENT REFINED COAL

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Abstract

The relative effectiveness of  $\text{SnCl}_2$  and  $\text{Co/Mo/Al}_2\text{O}_3$  (silica-stabilized) for the hydrogenolysis of solvent-refined coal was studied in a batch autoclave with tetralin as solvent.  $\text{SnCl}_2$  was exceptional in higher  $\text{H}_2$  consumption, higher liquefaction, and higher ratio of low molecular weight products in the oil fraction than either  $\text{Co/Mo/Al}_2\text{O}_3$  or in catalyst-free tests. Discrimination between catalysts with respect to  $\text{S}$  elimination was difficult because of the low  $\text{S}$  content of SRC; however, the effectiveness with respect to both  $\text{N}$  and  $\text{O}$  elimination decreased in the order  $\text{SnCl}_2 > \text{No Catalyst} > \text{Co/Mo/Al}_2\text{O}_3$ . Oil production was also lower with  $\text{Co/Mo/Al}_2\text{O}_3$  than with no catalyst, an effect which may be due to the  $\text{SiO}_2$  present as a stabilizer in the support  $\text{Al}_2\text{O}_3$ . The results are consistent with the concept that coal ash catalyzes the difficult step of converting asphaltene to oil.

Introduction

One of the intriguing aspects of catalytic coal liquefaction-hydrodesulfurization is that multifunctional catalysts are desirable, as is also true in the well-known cases of naphtha reforming and of hydrocracking in petroleum refining. Most of the individual catalysts best studied in coal processing are at least bifunctional, although this aspect has not received much explicit attention. The role of  $\text{SnCl}_2$  (or  $\text{Sn} + \text{HCl}$ , or  $\text{Sn} + \text{NH}_4\text{Cl}$ ) in coal liquefaction is still not understood after some decades of study, but clearly the catalyst exercises cracking as well as hydrogenative functions. The catalysts consisting of "cobalt molybdate" supported on silica-stabilized alumina are acidic, whatever their detailed action may be in the hydrodesulfurization of coal or coal-derived liquids.

It is an interesting fact that the best catalyst for liquefaction of coal is not best for hydrodesulfurization. The comprehensive catalyst survey of Kawa et al. (1974) provides a recent illustration. Supported  $\text{SnCl}_2$ , even in small concentration, was outstanding in its ability to promote both total liquefaction and the production of benzene-soluble oil, but not in desulfurization. Supported "cobalt molybdate" was equally outstanding in giving products of low  $\text{S}$  content, but not in liquefaction.

The study of catalysts for coal hydrogenolysis is essential, but the catalytic effects of coal ash itself may confound the interpretation of the effects of added catalysts. There is some advantage, therefore, in studying

added catalysts for the hydrogenolysis of solvent-refined coal (SRC) rather than of coal itself. SRC is essentially ash-free.

The present limited study was intended to explore what seem to be extreme cases of catalytic action, with the use of SRC as feed. The study is a comparison of (a) no catalyst, (b) unsupported  $\text{SnCl}_2$  at low concentration, and (c) a commercial  $\text{Co/Mo/SiO}_2\text{-Al}_2\text{O}_3$  at low concentration. In some ways SRC is a reasonable "model compound" with which to study the difficult steps in coal-to-oil conversion free of the complication of intrinsic catalyst (ash). The sample of SRC was almost completely soluble in pyridine, in Soxhlet extraction; only 17% soluble in either benzene or toluene; and almost insoluble in n-pentane (< 2%). The difficult steps of converting pyridine-solubles to "asphaltene" and "oil", as well as of hydrodesulfurization, may therefore be followed conveniently with SRC as feed.

## Experimental

### Equipment

All autoclave experiments were conducted with the same 1- $\frac{1}{2}$  stirred autoclave (Autoclave Engineers Model MB-1005 Magnedash) used in the work of Yen et al. (1976). As in the earlier studies, a glass liner was used in the autoclave to eliminate possible catalyst "memory effects". The following changes were made in equipment used for product analyses:

1. At the conclusion of a run, after cooldown, autoclave gas was passed through 2N zinc acetate solution (rather than caustic) in the scrubbing bottles, to remove  $\text{H}_2\text{S}$  and permit subsequent analysis of  $\text{H}_2\text{S}$  by an iodometric method.
2. After the scrubbing bottles, the autoclave gas was passed through an on-line gas chromatograph (Perkin-Elmer Model 810) for analysis of light hydrocarbons. The column was 7 ft. x 1/8 inch Porapak Q, operated at 80°C.; flow rate of the He carrier was 45 ml./min.
3. Analysis of the "oil" samples was performed with a Varian Aerograph gas chromatograph, Model 1420, equipped with 5 ft. x 1/8 inch columns packed with 1.5% OV-101 on 100/120 Chromosorb G-H.P., with a helium carrier flow rate of 25 ml./min. The column was operated isothermally at 125°C. for the first 3 minutes after sample injection, after which the column temperature was increased from 125°C. to (a maximum of) 270°C. at the programmed rate of 15°C./min. The G.C. data were processed with a Varian CDS-111 Data System and visually displayed on a Leeds and Northrup Azar recorder.

### Materials

The solvent-refined coal used in this work was obtained, through the courtesy of Mr. E.L. Hoffman, from the pilot plant operated in Wilsonville, Alabama by Southern Services, Inc. Our material, said to have been made from

Kentucky No. 14 coal, has the following elemental analysis: 86.77% C, 6.0% H, 1.3% N, 0.7% S, and 5.3% O (by difference). These values are close to, but differ slightly from, "typical values" reported for the Wilsonville plant. Ash was about 0.2%.

The tin chloride used as catalyst was ACS grade  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , obtained from Fisher Scientific Co. The  $\text{Co/Mo/Al}_2\text{O}_3$  catalyst was Harshaw Type 0402T, containing approximately 15 wt.%  $\text{MoO}_3$  and 3 wt.%  $\text{CoO}$  on silica-stabilized alumina (5%  $\text{SiO}_2$ ). Its properties are given in greater detail in Yen et al. (1976).

### Procedures

Procedures for the autoclave experiments were essentially the same as those used by Yen et al. (1976), except for the addition of a solid-state temperature controller (Barber-Colman Model 520) for the 2 kw. furnace. Internal temperatures were monitored by a chromel-alumel couple, inserted in the autoclave thermowell, connected to a millivolt potentiometer. Initial (cold)  $\text{H}_2$  pressure was 1000 psig in all experiments. The autoclave "dasher" was operated during heatup and the reaction period of 1 hr. at 450°C. ( $\pm 5^\circ\text{C}$ .) at the constant frequency of 180 strokes per minute.

The procedures for analyzing the letdown gases at the conclusion of a run have been described above. A series of eight gas samples was taken during the letdown period for G.C. analysis; the analyses for any single run were integrated to obtain total gas composition.

After the autoclave was unsealed, the glass liner with its contents was removed for analysis. Some material, found outside the liner in the bottom of the autoclave, was removed by aspiration, collected, and weighed; it was denoted as "autoclave residue". Although the average amount of "autoclave residue" was approximately 14 wt.% of the total initial charge (75g. SRC + 300g. tetralin), it was not included in the mass balance or in the product separation scheme because of possible catalytic effects of the metal autoclave walls.

The separation scheme used for liquid and solid products is summarized in Figure 1. Distillations in Run 1 (see Table I) were performed at atmospheric pressure, as was done by Furlani et al. (1976). In all other runs, the distillations were generally conducted at 30-35 Torr. under a  $\text{N}_2$  atmosphere. Separation of "asphalts" (toluene-insoluble, pyridine-soluble material) was effected in only a few runs; the results are therefore not included in this paper. Occasionally naphthalene was observed to be condensing during the tetralin distillation. When this occurred, the vacuum distillation was carried to a vapor temperature somewhat in excess of 105°C., cooling water was drained from the condenser, and a heat gun was employed to drive the naphthalene into the tetralin distillate. The pot temperature was always kept below 250°C. in this distillation. Further details of the separation scheme are to be found in Lovetro (1977).

Analyses for C, H, and N were performed with a Perkin-Elmer Model 240 Analyzer in the Department of Chemistry of this university. Analyses for S were very kindly provided through the courtesy of the Hooker Chemical Co.

### Results and Discussion

The catalysts used in the various autoclave runs are summarized in Table I. Also shown are the weights of H<sub>2</sub> consumed in each run, calculated by difference, and the weights of H<sub>2</sub>S absorbed in the zinc acetate scrubbers.

Table I  
Autoclave Tests: H<sub>2</sub> Consumed and H<sub>2</sub>S Discharged\*

Run No.	Catalyst	Hydrogen (g.)			H <sub>2</sub> S
		Charged	Discharged	Consumed**	Discharged (g.)
1	None	3.56	2.43	1.13	0.0154
1A	None	4.44	3.42	1.02	0.0528
2	SnCl <sub>2</sub> ***	4.45	Not detnd.	Not detnd.	0.0139
2A	SnCl <sub>2</sub>	4.53	2.78	1.75	0.0219
2B	SnCl <sub>2</sub>	4.53	2.71	1.82	0.0416
3	Co/Mo/Al <sub>2</sub> O <sub>3</sub> ****	4.43	3.43	1.00	0.0487
3A	Co/Mo/Al <sub>2</sub> O <sub>3</sub>	4.49	3.31	1.18	0.0416

\*75g. SRC + 300g. tetralin charged to glass liner.

\*\*H<sub>2</sub> consumption by difference.

\*\*\*1g. SnCl<sub>2</sub> · 2H<sub>2</sub>O charged.

\*\*\*\*1g. Harsshaw 0402T (Co/Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) charged as 40-60 mesh particles.

There was considerable scatter in the H<sub>2</sub>S data. However, the S measured as H<sub>2</sub>S was in all cases less than 10% of that charged in the 75g. of SRC. Substantially more elimination of S actually occurred, based on the analyses of asphaltene and oil shown in Table II. Sulfur analyses of the toluene and tetralin distillates show the presence of small amounts of low-boiling sulfur compounds, and the "missing" S is probably to be accounted for in these cuts.

Of particular interest is the H<sub>2</sub> consumption in the run with SnCl<sub>2</sub> catalyst (Series 2). It was much higher than in the blank runs (Series 1) or in the runs with Co/Mo/Al<sub>2</sub>O<sub>3</sub> (Series 3). This result may be correlated with the relatively poor material balances in the SnCl<sub>2</sub> runs (cf. Table IV, below) and with the relatively rich content of low-boiling constituents in the "oil" fraction from the SnCl<sub>2</sub> runs (cf. Figure 2, below).

The difference between average values for H<sub>2</sub>S discharged, for the blank runs and for those with SnCl<sub>2</sub> or Co/Mo/Al<sub>2</sub>O<sub>3</sub>, was found by application of the "t" test to be significant only at the 80% level. Values for the weight of CH<sub>4</sub> discharged are not shown in Table I. These showed almost no variation, run to run, and the average value for CH<sub>4</sub> produced was about 1.7g. This corresponds to a conversion to CH<sub>4</sub> of about 2% of the carbon in the 75g. of SRC charged.

Table II contains the elemental analyses for the oil and asphaltene fractions from each run.

Table II  
Elemental Analyses

Run No.	Product	Atom Ratio (H/C)	Wt. % C	Wt. % H	Wt. % N	Wt. % S	Wt. % O (by dif.)
Feed	--	0.83	86.66	5.99	1.33	0.70	5.32
SRC							
1	Oil	1.20	87.57	8.74	0.05	0.09	3.55
	Asphaltene	0.77	89.62	5.77	1.82	0.38	2.41
1A	Oil	1.11	88.32	8.20	0.24	0.27	2.97
	Asphaltene	0.87	88.28	6.38	1.82	0.41	3.11
2	Oil	1.10	88.58	8.10	0.63	0.26	2.43
	Asphaltene	0.87	89.87	6.52	0.73	0.37	2.51
2A	Oil	1.12	89.22	8.30	0.81	0.24	1.43
	Asphaltene	0.86	89.69	6.46	1.32	0.39	2.14
2B	Oil	1.08	88.97	8.02	2.38	< 0.15	~ 0.48
	Asphaltene	0.87	89.35	6.47	1.13	0.37	2.68
3	Oil	1.12	87.49	8.20	0.15	< 0.15	~ 4.01
	Asphaltene	0.88	88.28	6.49	1.70	0.40	3.13
3A	Oil	1.18	83.70	8.26	0.37	0.23	7.44
	Asphaltene	0.87	87.96	6.38	1.49	0.46	3.71

With the exception of Run 1, which involved distillations at atmospheric pressure, the H/C atom ratios were almost the same for all of the oil samples, and almost the same for all of the asphaltene samples. The S contents of all fractions were lower than that of the SRC feed, which occasions no surprise. Furthermore, within the limitations of the lower bound for the S analyses, all oil samples had approximately the same S content, as was also true for all asphaltene samples.

The interesting features of the elemental analyses relate to the questions of N elimination and of O elimination from the SRC as a function of catalyst. The average N elimination for Series 1 (blank) was 9%; for Series 2 ( $\text{SnCl}_2$ ), 38%; and for Series 3 ( $\text{Co/Mo/Al}_2\text{O}_3$ ), 1%. The rank ordering, therefore was  $\text{SnCl}_2 >> \text{No catalyst} > \text{Co/Mo/Al}_2\text{O}_3$  for effectiveness in N elimination. The average O elimination for Series 1 was 57%; for Series 2, 69%; and for Series 3, 42%. Again the rank ordering is  $\text{SnCl}_2 > \text{No catalyst} > \text{Co/Mo/Al}_2\text{O}_3$ .

Table III compares results reported by Yen et al. (1976) for the hydrogenolysis of Kentucky coal with those obtained in the present studies for the hydrogenolysis of SRC made from Kentucky coal. The same autoclave (Magedash) and conditions were used in both studies; tetralin was used as solvent in both cases; and the  $\text{Co/Mo/Al}_2\text{O}_3$  catalyst was the same batch of Harshaw 0402T in both cases.

Table III  
Comparison of Coal and SRC

Quantity	Coal*		SRC**	
	Blank Run	Co/Mo/Al <sub>2</sub> O <sub>3</sub>	Blank Run	Co/Mo/Al <sub>2</sub> O <sub>3</sub>
% S in Oil	0.25	0.21	0.18	<0.19
% S in Asphaltene	0.27	0.47	0.40	0.43
( $\frac{\text{Oil}}{\text{Oil} + \text{Asphaltene}}$ )	34	49	19	5

\*Data from Yen et al. (1976). "Blank Run" = Run T-3; "Co/Mo/Al<sub>2</sub>O<sub>3</sub>" = Run T-4.

\*\*Present work. Data given are average values for Runs 1 and 1A for "blank", Runs 3 and 3A for "Co/Mo/Al<sub>2</sub>O<sub>3</sub>"; see Table IV.

The S contents in both the oil and the asphaltene fractions were slightly lower in the SRC runs than in the corresponding fractions from whole coal. This is not surprising, of course, since the organic S of the coal is already significantly reduced in the process of making SRC. It is surprising that (1) the oil production in the SRC runs (cf. Table IV) was exceptionally low relative to the runs with whole coal, and (2) the oil production from SRC was even lower in the presence of Co/Mo/Al<sub>2</sub>O<sub>3</sub> than with no catalyst. Two implications may be suggested:

1. The lower oil production from SRC is consistent with the notion, now generally accepted, that the ash in the coal is catalytically active and its removal is harmful (cf. "SRC I" vs. "SRC II" processes). This result is reminiscent of that reported by Weller and Pelipetz (1951). In the earlier work it was found that under identical experimental conditions with no added catalyst, whole Pittsburgh seam coal showed 50-60% conversion, whereas low-ash (1.4%) hand-picked anthraxylon from the same mine showed only 30% conversion. Since iron pyrite is so important an ash constituent in high-ash coals, this again is not surprising: (a) the commercial development of the Bergius process by I.G. Farbenindustrie included Luxmasse, a high-iron material, in the coal-oil paste; (b) impregnated iron sulfate is known to be an excellent catalyst for coal liquefaction (Weller and Pelipetz, 1951a).
2. The deleterious effect of Harshaw Co/Mo/Al<sub>2</sub>O<sub>3</sub> on oil production from SRC, relative to no added catalyst, may reflect an undesired polymerization of feed or products occurring as a result of the acidic support (silica-stabilized alumina). Variation of the support acidity was not studied in the present work, but it should be examined.

Table IV summarizes the material balances, total "liquefaction", and the oil and asphaltene distributions for the individual runs.

Table IV

## Product Distributions\*

Run No.**	Total Products Recovered (g.)	% Liquefaction***	Oil, % of Total Products	Asphaltene, % of Total Products	$\frac{(\text{Oil}) \times 100}{(\text{Oil} + \text{Asphaltene})}$
1****	61.7	Not detnd.	22.1	77.4	22.2
1A	64.8	93.7	14.0	77.2	15.4
2	50.5	100.0	13.5	86.5	13.5
2A	56.3	99.6	21.8	77.5	22.0
2B	59.8	99.8	20.5	79.1	20.6
3	67.6	94.5	2.7	90.1	2.9
3A	69.9	94.1	5.9	87.2	6.3

\*75g. SRC + 300g. tetralin charged in each run.

\*\*See Table I for identification.

\*\*\*% Liquefaction =  $\frac{75 - \text{Toluene insolubles (including catalyst)}}{75} \times 100$

\*\*\*\*Distillations in Run 1 made at atmospheric pressure. Vacuum distillation (30-35 Torr.) under  $N_2$  used in all other runs.

Two points should be noted:

1. Although the liquefaction is high in all cases, it is highest in the  $SnCl_2$  runs. (Note: Correction for the catalyst in the toluene insolubles would increase the % Liquefaction to 95.8% in Run 3 and 95.5% in Run 3A. The very small amount of toluene insolubles in Runs 2, 2A, and 2B means that the  $SnCl_2$  has been somehow "solubilized"; it is not present in the toluene insolubles.)
2. Although the material balances are low in all cases, they are consistently lower in the  $SnCl_2$  runs. The losses are tentatively attributed to low-boiling liquid products from the SRC which are lost to the overhead during the toluene and tetralin distillations. The particularly high losses in the  $SnCl_2$  runs are consistent with (a) the higher  $H_2$  consumptions observed in these runs (Table I), and (b) the evidence for many low-boiling constituents in the recovered oil fractions (cf. Figures 2 and 3, below). If this interpretation is correct, then the attribution of the "missing" material to distillation of low-boiling fractions of the oil product would mean that all the oil recoveries listed in Table IV may be lower than the true values. This would be particularly true for the  $SnCl_2$  runs.

Figures 2 and 3 are illustrative of the gas chromatograms obtained on the oil fractions. Figure 2 is for the oil from Run 2A ( $SnCl_2$ ); Figure 3 is for the oil from Run 3A ( $Co/Mo/Al_2O_3$ ). In both cases there was some residual

(unstripped) solvent, typically a mixture of tetralin and naphthalene. In both cases there was a major, sharp peak with a retention time of 13.5 minutes (at 270°C.) in this temperature-programmed chromatogram. The identity of this component is unresolved. However, correlations of relative retention time vs. carbon number and vs. normal boiling point were used to predict that the 13.5 minute peak could correspond to a compound analogous to an alkane of carbon number  $C_{20}$ - $C_{21}$  and a normal boiling point of ca. 365°C. The sharpness of the peak and the estimated carbon number make it tempting to attribute the peak to some dimeric (i.e.,  $C_{20}$ , with  $M \approx 260$ ) species originating from the tetralin solvent, and not from the SRC. Our determinations, by vapor-phase osmometry, of the molecular weight of the total oil fractions routinely showed an average molecular weight in the range 250-300. The rich mixture of peaks in the  $SnCl_2$  run (Figure 2) between naphthalene and the "13.5 minute unknown" presumably represents low-boiling products in the oil, derived from the SRC with  $SnCl_2$  catalyst. It is noteworthy that these peaks are almost absent in the  $Co/Mo/Al_2O_3$  run (Figure 3). As pointed out above, the chromatogram shown in Figure 2 is consistent with the high  $H_2$  consumption and the very low material balances when  $SnCl_2$  is used. Oil constituents with retention times longer than 13.5 minutes at 270°C., the highest temperature chosen for use with the OV-101 columns, would not have been detected; the G.C. analysis was terminated at this point.

#### Acknowledgment

The authors are grateful to the Energy Research and Development Administration and to the Hooker Chemical Co. for partial support of this research. D. Elmore and M. LaRosa established the solubility of SRC in various solvents; Miss E. Rabcewicz and C. Orcheski measured the molecular weights of oil and asphaltene samples. P. Ho and J. Scinta provided continuous advice and assistance.

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Illustrations

Figure 1. Analytical Procedure

Figure 2. Chromatogram of Oil Fraction from Run 2A

Figure 3. Chromatogram of Oil Fraction from Run 3A

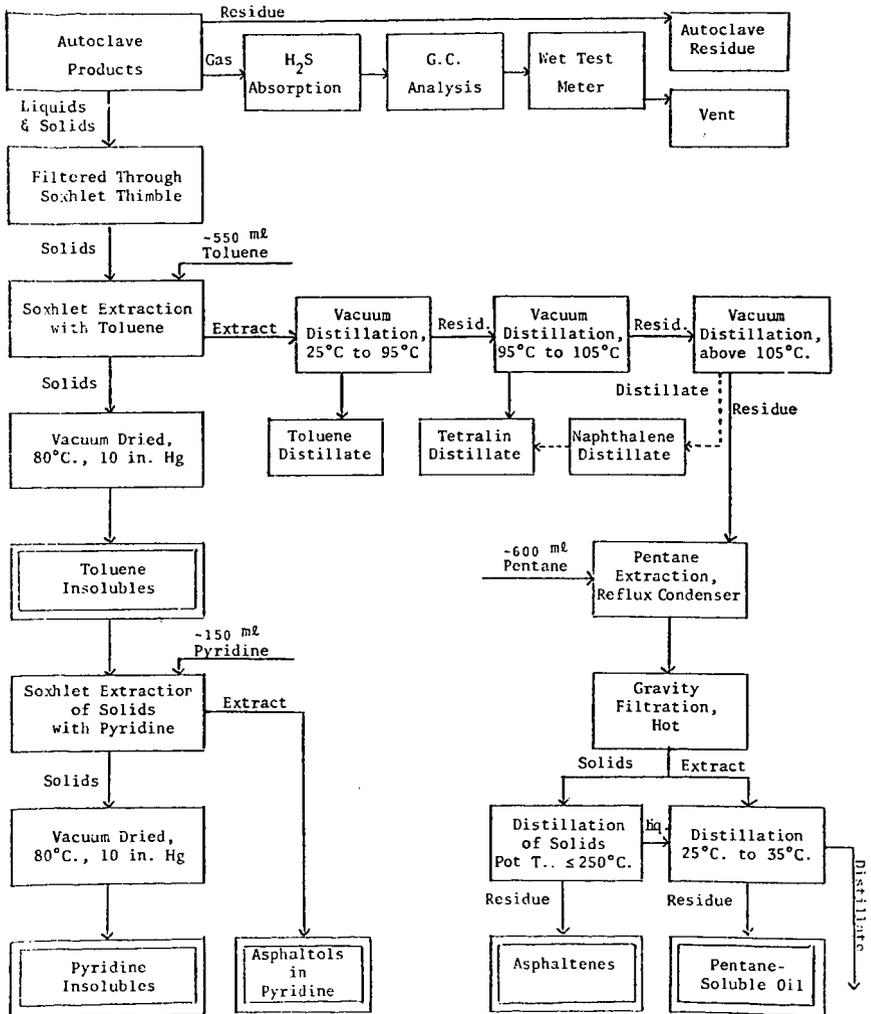


Figure 1. Analytical Procedure

Figure 2  
SRC Run #2A Oil Fraction  
(1 Time Unit = 0.5 Minutes)

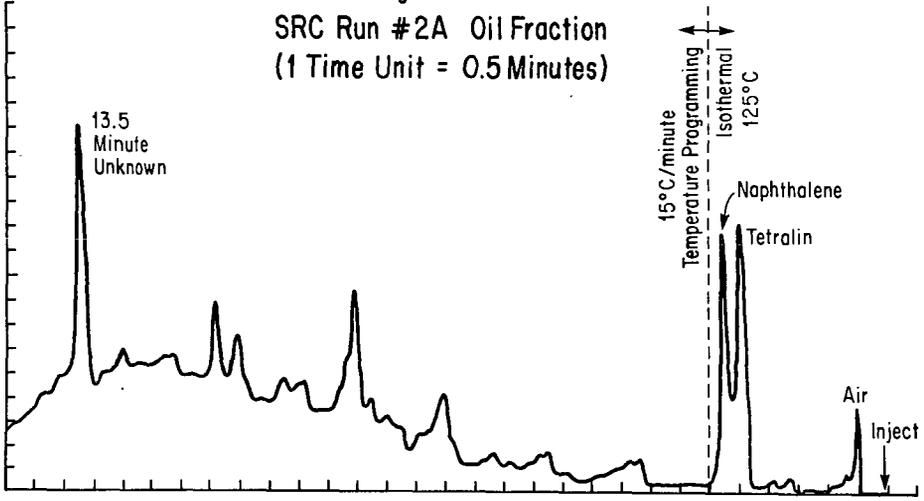


Figure 3  
SRC Run #3A Oil Fraction  
(1 Time Unit = 0.5 Minutes)

