MASTER

SYNTHETIC CRUDE OILS CARCINOGENICITY SCREENING TESTS

QUARTERLY REPORT

Covering the Period October 16, 1978 to February 15, 1979

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ABSTRACT

Four crude oils (Southern Louisiana Crude Petroleum, H. Coal Syncrude, Paraho Crude Shale Oil and Geokinetics in situ Shale Oil) have been distilled into four fractions (naphtha, mid-distillate, gas oil and residue) for analysis and biological (mutagenicity and "carcinogenicity") screening testing. Results of selected analytical tests have been obtained on the original crude oils and the fractions. Ames tests and initiation/promotion tests have been started on the original crude oils and the fractions. Four additional synthetic crude oils (Exxon EDS, SRC II, H Coal Fuel Oil and Occidental In Situ Shale Oil) are being obtained for a second similar series of tests to be started in approximately four months.

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Syncrude Carcinogenicity Screening Tests
Quarterly Technical Progress Report for the Period
October 16 - February 15

INTRODUCTION

This Report is the first Quarterly Technical Progress Report for the U. S. Department of Energy Agreement No. EP-78-C-02-4758.

The objective of this project is to define in a preliminary fashion the carcinogenicity problem to be expected in the production, handling and utilization of synthetic crude oils and distillation fractions derived from them. The study involves conducting a rapid screening series of mutagenicity and tumor initiation promotion tests on original crude oils and common distillation fractions of a crude petroleum control and seven synthetic crude oils derived from coal and oil shale by several processes currently under development. Selected analytical tests are run on the fractions to provide some identification of the nature of the samples. The biological tests [Ames test (1) and Van Duren Initiation-Promotion test (2)] are still developmental in nature, but are well documented and designed to provide on a short term basis an indication of which materials are potentially more hazardous and should be investigated more thoroughly by longer term testing procedures.

The project is being run in two parts; in each part, processing four crude oils. The first four samples were not available until October 16, 1978, and the processing of these samples (S. Louisiana crude petroleum, H Coal Syncrude, Paraho Shale Oil and Geokinetics in situ Shale Oil) began at that time. This Report covers the preparation and distillation of these four crude oils into fractions and the analytical data which has been obtained on the original crude oils and on the distillation fractions.

Three of the four crude oils were received as whole crudes. The Southern Louisiana crude petroleum, Paraho Shale Oil and Geokinetics shale oil were distilled according to the procedure proposed in the contract. The H coal syncrude samples arrived as fractions.

The "atmospheric still overheads" fraction was tested analytically and biologically as the crude oil. It was also distilled to provide the naphtha and light gas oil fractions for testing. The "atmospheric still bottoms" (ASB) and the "vacuum still overhead" (VSOH) fractions were not distilled but were tested as received.

At this writing, the biological testing [mutagenicity (AMES) and carcinogenicity (initiation/promotion)] are in progress. Interim results of these tests will be reported in the next progress report.

Samples are now being obtained for testing the second set of four synthetic crude oils. These are expected to be EDS Exxon coal fluid, SRC II, H Coal fuel oil mode, and Occidental insitu shale oil.

Sample Preparation by Distillation

The first four crude oil samples obtained for this study had large boiling ranges which were to be separated into four distillation fractions. The distillation procedure follows the ASTM D2892-73 (ref. 3). This procedure was modified to minimize any contamination or sample degradation which might influence the biological testing.

The one inch diameter by 27 inch high distillation column with 3 liter still pot used in this study is shown in Figure 1. The 20 Oldershaw plates give sharp distillation end points and also can be easily inspected after cleaning (ref. 4). The glass jacket and external heating tapes maintain process temperature and reduce internal reflux. The pipe flanges with "Teflon®" gaskets eliminated ground joints and grease which could reflux back to the pot. The condensed liquid is split by a timer to return the reflux. The magnetic stirrer with "Teflon®" stirring bar and "Hengar", stone boiling chips, reduced bumping within the pot and overheating. Heat was supplied thru a "Glas-Col" heating mantle controlled by "Variacs". One further modification was necessary, (not shown in the picture); a gooseneck was installed above the receiver to reduce mechanical shocks. The set-up allowed the entire still to "jump" slightly if bumping occurred in the distillation pot.

The details of running the distillation are not significantly different from ASTM 2892. Control of the pressure is by the system shown in Figure 2 with nitrogen bled in to maintain accurate vacuum. Control of the temperatures and boil up rate was by hand using "Variacs" and "Thermocouples" attached to a multipoint recorder. The distillation cuts were taken at points specified in Table I.

Water in the crude samples is often a problem. In addition to the "bumping" of the pot liquids as the water phase flashes, the steam causes some "steam distillation" to occur. The difficulties associated with this are well known (reference 5). When very little water is present, it will be distilled overhead well before the end of the naphtha cut, appear as a second phase in the naphtha, and can be decanted with no effect. For the samples with much water and little naphtha, the naphtha is contaminated by higher boiling species; then, the organic phase of the naphtha is decanted and returned to the pot and the distillation started over.

Figure 1 -
20 Plate
Oldershaw
Distillation
Column

Figure 2 - Distillation Column Controls

Table I

Desired Laboratory Distillation Fractions*

	Observed Temperature at Reduced Pressure			
	<u>Pressure</u> mm Hg	<u>Initial B.P.</u>	<u>Final B.P.</u>	<u>Expected Max. Pot Temp.</u>
Light Ends	700	Trap Liquids Returned to Naphtha		
Naphtha <350°F	700	50°C	175°C	275°C
LGO Light Gas Oil Mid Distillate (350 to 650°F)	5	50°C	179°C	279°C
MGO Mid Gas Oil (650 to 850°F)	1	145°C	210°C	260 to 290°C
Resid		Pot Residue Pours at 50 to 100°C		

*Temperatures for end points were adjusted using the correlation of Table X, ASTM Std. D2892 and the pressure actually achieved. Table III shows results actually achieved.

Distillation of First Four Samples

The first four samples have been distilled and forwarded for analysis and testing as shown in Table II. The distillation procedure cut points are shown in Table III. The samples were held with nitrogen blanket. Those sealed in glass ampoules were cooled in dry ice/acetone prior to evacuating and sealing. There were differences among the distillations:

1. The South Louisiana Petroleum crude distilled with no problems.

2. The H Coal atmospheric still overhead (ASOH) sample distilled well; however, the pot began to dry out near the end of the LGO cut. The column inventory would have been in the LGO boiling range; however, it was returned to the pot as the distillation was stopped. This resid was not tested. During the early naphtha distillation, water formed in a cloudy dispersion. When all cuts were combined and cooled, the water separated cleanly.

3. The first Paraho distillation was stopped when the vacuum jacket cracked during the pressure change step. This liquid was discarded, the still repaired with no vacuum jacket, and a new distillation begun. Because the vacuum jacket was wrapped with heating tapes, the still was then also wrapped and maintained at distillation temperatures. Some slight water content was stripped over in the naphtha cut; it settled in the bottle and was not drawn into the samples for analysis.

4. The geokinetics sample contained considerable water which bumped during the naphtha distillation. This contaminated naphtha was separated from water phase, the organic returned to the pot, and the distillation started over.

In distillations 1 and 3, a ten inch Vigreux column was used to try continuing the MGO cut distillation. The head temperature immediately rose above the allowed temperature limit so the run was stopped and all liquid returned to the pot.

In all distillations except 3, the complete naphtha distillation could be done at 700 mm Hg. In number 3, the first half was distilled at 700 then the pressure dropped to 100 mm Hg to reduce pot temperatures.

TABLE II

DOE Study Samples

<u>Distillation Cuts</u>				
Order of Distillation:	1	2	3	4
Sample of:	South LA Petroleum	H-Coal	Paraho Shale Oil	Geokinetics Shale Oil
Obtained from:	Texas A&M	HRI	Development Engg. Co.	Geokinetics
Feed to Still	Whole crude	ASOH	Whole crude	Whole crude
<u>Cuts obtained, weight percent of feed</u>				
Light Ends	0.78	0.56	0.00	0.00
Naphtha	14.87	45.18	4.32	5.63
LGO	30.01	50.13	30.96	52.59
MGO	8.48	0	12.48	17.76
Resid	44.54	3.32	51.65	22.09
Loss	1.32	0.82	0.59	1.94
<u>Feed received in:</u>	New 1 gal. paint can	New 1 & 2 gal. lacquer cans	55 gal Drum Bent Bung	Used 5 gal. motor oil can
Samples Forwarded for Analysis and Testing	Crude Naphtha LGO MGO Resid*	ASOH ASB VSOH* Naphtha LGO	Crude* Naphtha LGO MGO Resid*	Crude* Naphtha LGO MGO* Resid*

*Samples in screw-top vials. All others in sealed, evacuated glass ampoules

TABLE III

Observed Cut Points

	DOE Study Samples			
	(1) <u>South LA Petroleum</u>	(2) <u>H-Coal</u>	(3) <u>Paraho</u>	(4) <u>Geokinetics</u>
<u>Light Ends</u> - Collected in dry ice/acetone bath while naphtha distilled				
<u>Naphtha</u> (IBP to 350°F equivalence)				
Pressure, mm Hg	700.	700.	100.	700.
Temp., °C	172.	173.	116.	172.
<u>LGO</u> (350 to 650°F equivalence)				
Pressure, mm Hg	5.0	5.0	5.0	4.9
Temp., °C	180.	127.	179.	179.
<u>MGO</u> (650 to 850°F equivalence)				
Pressure, mm Hg	1.8	-	3.2	3.6
Temp., °C	194.	-	201.	220.
<u>Resid</u> (850°F plus equivalence)				
Reason to stop	Pot reached	Pot reached	Pot reached	Pot reached
Run	330°C	330°C	326°C	320°C

Prior to all runs, the still was cleaned with Isopropanol and methylene chloride and then flushed with acetone and blown dry. All tubing was changed and the pressure gauges checked against manometers.

As per the contract, the naphtha was cooled then the light ends recombined with the naphtha.

Analytical Testing of Crude Samples and Distillation Cuts

It is recognized that complete characterization (quantitative and qualitative analysis of the mixture constituents) of crude samples and their distillation cuts is impractical both technically and economically. Measurement of mutagenicity of specific compounds or specific groups of compounds is outside the scope of this study.

Some sample characterization is desirable, however, to insure that the samples studied are typical.

a) Tests Selected

Elemental analyses were selected as the most reasonable measure of the crude and fractions gross composition.

The ASTM Simulated Distillation Analysis (Boiling Range Distribution of Petroleum Fractions by Gas Chromatography) was chosen because it represents a means of monitoring the proper execution of the distillation operation and yields data on the boiling range distribution of the crude samples and the fractions.

Specific Gravity is a well recognized standard measurement in most petroleum laboratories and characterizes the sample in terms understood in the industry.

b) Facilities

All analytical testing was conducted in facilities of the E. I. du Pont de Nemours & Company, Inc., located at the Experimental Station, Wilmington, Delaware.

c) Tests Used

- Carbon-Hydrogen Analysis

Apparatus: Coleman Carbon-Hydrogen Analyzer
(or equivalent).

Technique: Combustion analysis followed by gravimetric determination of CO_2 and H_2O .

● Nitrogen Analysis

Apparatus: Nitrogen-Dumas

Technique: Combustion analysis followed by volumetric determination of N_2 .

Alternate equipment Perkin Elmer Auto Analyzer or Micro Kjeldahl apparatus.

● Oxygen Analysis

Apparatus: Laboratory Equipment Co. (LECO) Nitrox-6 Analyzer.

Technique: Combustion analysis - followed by gas chromatographic determination of CO .

● Sulfur Analysis

Apparatus: Philips Universal Vacuum Spectrometer (X-ray Fluorescence) equipped with:

1. An unfiltered chromium target tube operated at 50 KV and 35 ma.
2. A PET (pentaerythritol) analyzing crystal.
3. A gas flow proportional counter with a gas density compensator controlling the flow of P-10 gas to the detector.
4. A helium gas system to sweep the entire spectrometer chamber.

Technique: K-emissions from the sulfur in the sample are excited by radiation from a chromium target x-ray tube. K intensities in terms of concentration are measured, using a series of NBS standards of sulfur in residual fuel oil.

- Specific Gravity

Apparatus: Pycnometers, etc. as required.

Technique: Defined in ASTM method D-1217-54
D-1480-62

Water displacement in Hubbard-Carmick
pycnometer.

- Simulated Distillation Analysis

Apparatus: A Hewlett Packard 5730A gas chromatograph equipped with thermal conductivity detector. Data is collected and handled by the Du Pont PDP-10 GC Data Analysis System which includes some refinements not available in the ASTM method.

Technique: ASTM method D-2887-73 - Standard Method of Test for Boiling Range Distributions of Petroleum Fractions by Gas Chromatography.

Analytical Results

The analytical results from the tests listed above for four crudes and their distillation cuts are given in Tables IV-VII. The crudes studied are:

- Southern Louisiana Petroleum
- Paraho Shale Oil
- Geokinetics Shale Oil
- H-Coal

Biological Testing

Two types of accelerated biological tests are being used to screen these synthetic crude oils and their distillation fractions: The Ames Salmonella/microsome assay and Van Duren Initiation-promotion skin painting tests on mice. Testing using both of these methods is now underway on the original crude oils and their distillation fractions prepared as described above.

Ames Tests

Thus far, testing has been restricted to the standard plate incorporation assay using DMSO* as solvent. The major difficulty encountered up to this time has concerned the relative insolubility in DMSO of a number of the test fractions. It has been found that moderate heating of both test samples and DMSO-test sample mixtures decreases the severity of this problem and facilitates the preparation of more homogeneous, representative test solutions; although some separation of fractions is observed as the test solutions return to room temperature.

The test samples exhibit a wide spectrum of toxic and mutagenic effects in the assay. Addition of the microsome activation system tends to substantially decrease the toxic effect. Thus far, mutagenic activity has been observed only in the presence of the activation system.

Initiation-Promotion Mouse Skin Painting Tests

The initiation phase of these tests on the first four crude oils and their distillation fractions was conducted on December 20, 1979. The promotion phase began on January 3, 1979. No tumors have been detected after 33 days.

*Dimethylsulfoxide

REFERENCES

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3. ASTM D-2892-73: ASTM Book of Standards, Part 24, 1975.
4. F. C. Collins and V. Lantz, "Evaluation of Laboratory Distillation Apparatus," Industrial and Engineering Chemistry, 18:1, 673 (1946).
5. T. H. Gouw, "Removal of Water in the Distillation of Hydrocarbon Mixtures," Analytical Chemistry, 49:12, 1887 (1977).
6. ASTM D2887-73

TABLE IV
Analytical Results
Southern Louisiana Petroleum

Sample Description	Crude Oil	Naphtha Cut	Light Gas Oil Cut	Medium Gas Oil Cut	Resid
Notebook # 16928-	2-1 to 8	1-1 to 8	1-9 to 16	1-17 to 24	1-25 to 34

Elemental Analysis

C	86.39	86.33	85.93	86.80	86.51
H	12.25	14.13	12.86	12.46	11.09
N	0.54	< .01	< .10	0.42	0.67
O	0.26	0.07	0.08	0.10	0.35
S	0.90	0.02	0.42	0.83	0.94
<u>TOTAL</u>	<u>100.34</u>	<u>100.55</u>		<u>100.61</u>	<u>99.56</u>

Simulated Distillation Analysis
°C

% Light Ends (0-65)	4	10	0	0	0
% Naphtha (65-175)	20	72	0	0	0
% Lt. Gas Oil (175-340)	40	17	84	2	0
% Med. Gas Oil (340-430)	21	1	17	95	11
% Heavy Gas Oil (430-500)	12	0	0	3	68
% Unvolatilized Sample*	22.3	< 2.00	< 2.00	< 2.00	40.8
<u>Density (25°C)</u>	<u>.8953</u>	<u>.7564</u>	<u>.8563</u>	<u>.8995</u>	<u>.9513**</u>

*Quantitative measurement of wt. % of SDA sample remaining in GC vaporizer (unvolatilized) after the analysis.

**By water displacement in Hubbard-Carmick pycnometer.

TABLE V
ANALYTICAL RESULTS
Paraho Shale Oil

Sample Description	Crude Oil	Naphtha Cut	Light Gas Oil Cut	Medium Gas Oil Cut	Resid
Notebook # 16928-	8-1 to 8	7-1 to 8	7-9 to 16	7-17 to 24	7-25 to 34

Elemental Analysis

C	84.56	84.82	84.53	84.48	85.93
H	11.37	12.72	11.96	11.31	10.97
N	2.15	1.21	1.27	2.34	2.46
O	1.43	1.10	1.24	0.91	0.76
S	0.48	0.82	0.67	0.61	0.38
<u>TOTAL</u>	<u>99.99</u>	<u>100.67</u>	<u>99.67</u>	<u>99.65</u>	<u>100.50</u>

Simulated Distillation Analysis
°C

% Light Ends (0-65)	0	0	0	0	0
% Naphtha (65-175)	0	53	0	0	0
% Lt. Gas Oil (175-340)	32	46	81	5	2
% Med. Gas Oil (340-430)	33	2	19	91	7
% Heavy Gas Oil (430-500)	27	0	0	5	61
% Unvolatilized Sample*	< 2.00	< 2.00	< 2.00	< 2.00	13.7
 <u>Density (25°C)</u>	 .9246**	 .8024	 .8796	 .9872**	 1.0691**

*Quantitative measurement of wt. % of SDA sample remaining in GC vaporizer (unvolatilized) after the analysis.

**By water displacement in Hubbard-Carmick pycnometer.

TABLE VI
Analytical Results
Geokinetics Shale Oil

Sample Description	Crude Oil	Naphtha Cut	Light Gas Oil Cut	Medium Gas Oil Cut	Resid
Notebook # 16928-	10-1 to 8	10-9 to 16	10-17 to 24	10-25 to 32	11-1 to 10

Elemental Analysis

C	84.71	84.05	85.40	85.33	85.60
H	11.93	13.03	12.15	11.71	11.28
N	1.69	1.40	2.18	1.97	2.07
O	0.81	0.83	0.61	0.39	0.61
S	0.54	0.47	0.42	0.24	0.42
<u>TOTAL</u>	<u>99.68</u>	<u>99.78</u>	<u>100.76</u>	<u>99.64</u>	<u>99.98</u>

Simulated Distillation Analysis
°C

% Light Ends (0-65)	0	0	0	0	0
% Naphtha (65-175)	2	49	0	0	0
% Lt. Gas Oil (175-340)	55	50	87	0	1
% Med. Gas Oil (340-430)	32	1	13	94	7
% Heavy Gas Oil (430-500)	12	1	1	6	76
% Unvolatilized Sample*	< 2.00	< 2.00	< 2.00	< 2.00	< 2.00

<u>Density (25°C)</u>	.8898	.7926	.8647	.9159	.9636
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*Quantitative measurement of wt. % of SDA sample remaining in GC vaporizer (unvolatilized) after the analysis.

TABLE VII
Analytical Results
H-Coal - Syncrude Mode

Sample Description	Atm. Stl. Overheads	Naphtha Cut	Light Gas Oil Cut	Atm. Stl. Bottoms	Vac. Stl. Overheads
Notebook # 16928-	4-1 to 8	4-9 to 16	4-17 to 24	4-25 to 32	5-1 to 8

Elemental Analysis

C	86.82	85.83	88.54	89.58	90.27
H	11.07	12.66	10.04	8.79	7.89
N	0.17	0.16	0.17	0.17	1.10
O	1.65	1.40	1.91	1.12	0.99
S	0.23	0.21	.09	.09	0.12
<u>TOTAL</u>	<u>99.94</u>	<u>100.26</u>	<u>100.75</u>	<u>99.75</u>	<u>100.37</u>

Simulated Distillation
Analysis
°C

% Light Ends (0-65)	3	5	0	0	0
% Naphtha (65-175)	35	72	0	1	0
% Lt. Gas Oil (175-340)	61	24	100	70	41
% Med. Gas Oil (340-430)	2	0	0	27	49
% Heavy Gas Oil (430-500)	0	0	0	3	11
% Unvolatilized Sample*	< 2.00	< 2.00	< 2.00	< 2.00	2.65

<u>Density</u> (25°C)	.8797	.8107	.9362	1.0089	1.0640
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*Quantitative measurement of wt. % of SDA sample remaining in GC vaporizer (unvolatilized) after the analysis.