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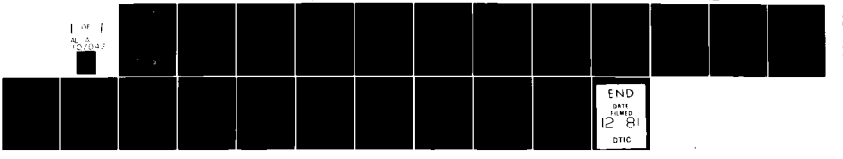

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FRACTIONATION OF DIESEL FUEL FROM PETROLEUM AND PARAHO SHALE OILS

DAVID W. TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Maryland 20084

FRACTIONATION OF DIESEL FUEL FROM
PETROLEUM AND PARAHO SHALE OILS

by

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Prepared for

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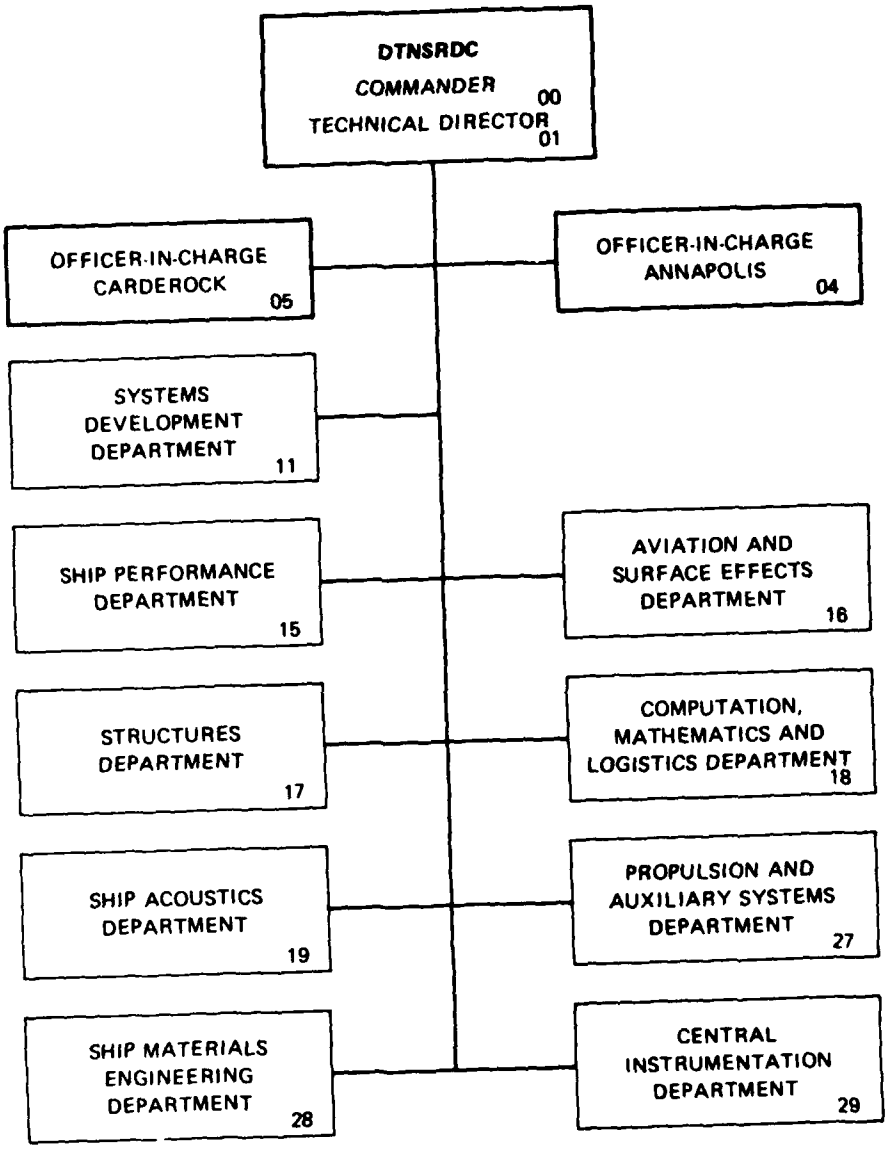

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A fractionation scheme has been developed to separate diesel fuels into neutral water solubles, acidic components, basic components, saturated hydrocarbons, substituted benzenes, polycyclic aromatic hydrocarbons, and polar neutrals. A sample of conventional petroleum diesel fuel and a sample of diesel fuel derived from Paraho crude shale oil by the Gary-Western process were fractionated by this procedure. Each fraction was further analyzed by

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gas chromatography and proton magnetic resonance spectroscopy. The petroleum sample was found to contain 17.5% total aromatics of which 9.5% were polycyclic aromatic hydrocarbons compounds. However, the Paraho-Gray Western shale oil fuel contained about twice as much total aromatics (38.2%) and polycyclic aromatic hydrocarbons compounds (19.3%). The total acyclic hydrocarbon straight chain compounds content was 66.7% for the petroleum sample and 59,3% for the Paraho-Gary Western shale sample. Suggestions for further work are also made.

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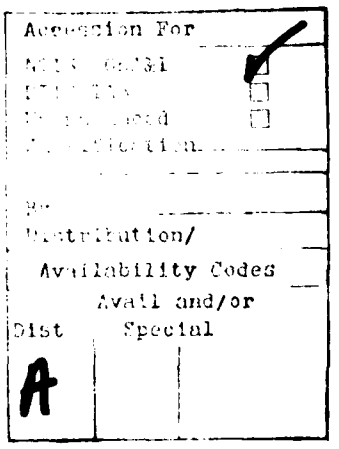

LIST OF ABBREVIATIONS

cm	Centimeter
DTNSRDC	David W. Taylor Naval Ship Research and Development Center
FT-NMR	Fourier Transform Nuclear Magnetic Resonance
g	Gram
ID	Inside diameter
ml	Milliliter
PAH	Polycyclic Aromatic Hydrocarbons
PMR	Proton Magnetic Resonance

ABSTRACT

A fractionation scheme has been developed to separate diesel fuels into neutral water solubles, acidic components, basic components, saturated hydrocarbons, substituted benzenes, polycyclic aromatic hydrocarbons, and polar neutrals. A sample of conventional petroleum diesel fuel and a sample of diesel fuel derived from Paraho crude shale oil by the Gary-Western process were fractionated by this procedure. Each fraction was further analyzed by gas chromatography and proton magnetic resonance spectroscopy. The petroleum sample was found to contain 17.8% total aromatics of which 9.5% were polycyclic aromatic hydrocarbons compounds. However, the Paraho-Gary Western shale oil fuel contained about twice as much total aromatics (38.2%) and polycyclic aromatic hydrocarbons compounds (19.3%). The total acyclic hydrocarbon straight chain compounds content was 66.7% for the petroleum sample and 59.3% for the Paraho-Gary Western shale sample. Suggestions for further work are also made.

ADMINISTRATIVE INFORMATION

This work was accomplished under Program Element 62545N, Task Area ZF4545100l, Work Unit 2831-162.

INTRODUCTION

It is the policy of the U.S. Navy to develop a source of energy independent of conventional petroleum fuels. Possible alternatives to these petroleum fuels are fuels derived from shale and coal. However, it is possible that the composition of these alternative fuels may differ from conventional fuels.

Of particular importance are fractions of fuels that contain polynuclear aromatic hydrocarbons (PAH).* Some of these organic compounds are carcinogenic and others are suspected of being carcinogenic.

Since fuels contain mixtures of hundreds of compounds[1,2]** some type of prior fractionation must be done before the PAH compounds can be analyzed.[3,4] Even then the PAH fractions are very complex mixtures that contain at least 200 compounds of which only about half have been identified to date.[3,4]

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*A list of abbreviations used in this text is given on page iv.

**A list of references is given on page 15.

A fractionation/extraction scheme was sought that would divide the mixtures into smaller classes of hydrocarbons and permit an insight into the compositional differences between conventional petroleum fuels and fuels from shale and coal.

The fractionation scheme developed is an adaptation of the methods used in the petroleum industry, and it is fully outlined below.

In this study a shale diesel fuel is compared with a petroleum diesel fuel. The shale sample analyzed was Paraho-Gary Western shale oil produced from Paraho crude shale oil by the Gary-Western process, using delayed coking to increase the yield of the distillate. It should be kept in mind that there are other processes which may give products of different properties and that the Gary-Western is not representative of expected commercial practice; hence the composition of the fuel produced by Gary-Western may not be typical of the shale diesel fuels expected in the future.

EXPERIMENTAL RESULTS AND DISCUSSION

One gallon samples of conventional diesel fuel (PA-O) and Paraho-Gary Western shale diesel fuel (SB-O) were obtained from DTNSRDC. These samples were stored in the anteroom of a cold room at about $8^{o}C$. Portions (200 g) were removed for analysis after careful mixing to ensure representative samples. Combustion analyses of these samples for percent carbon, hydrogen, nitrogen, sulfur, and oxygen are shown in Table 1.

TABLE 1 - ELEMENTAL COMBUSTION ANALYSIS OF DIESEL FUELS*

Sample	%C	%H	%N	%S	%O	Total (%)
SB-O	85.74	12.60	0.23	0.56	0.74	99.87
PA-O	86.14	13.03	0.01	0.60	0.15	99.93

*Analyses performed by Galbraith Laboratories, Knoxville, TN.

Two main differences are discernible. The shale sample (SB-O) has significantly larger percentages of nitrogen and oxygen while the carbon, hydrogen, and sulfur contents are similar.

The fractionation procedure used here is a scaled-down adaptation of the methods of Thompson[1] for coal liquids and high-boiling petroleum distillates.[2] The scheme is shown in Figure 1.

The original diesel fuel sample (200 g) was extracted with 1.5N NaOH in 1:1 methanol/water (5 x 50 ml), yielding an oil layer and an aqueous layer, which was extracted overnight in a continuous liquid-liquid extractor with ether (250 ml). Evaporation of the ether gave a moist residue, which was redissolved in ether (100 ml), and the water separated. Removal of these ether gave Fraction 1, which should be the neutral and basic components soluble in 1:1 methanol/water. The basic water layer left from the above ether extraction was neutralized with HCl to Litmus end point and again continuously extracted overnight with ether (250 ml). Evaporation of the ether gave Fraction 3, which should be the acidic components. The remaining water layer was freeze-dried to give salts (Fraction 2). A flame test on Fraction 2 did not burn or exhibit any charring, revealing that no organic components were present. The salts of Fraction 2 were then discarded.

The oil layer was then further extracted with 1.5N HCl in 1:1 methanol/water (5 x 50 ml), yielding an aqueous layer and an oil layer (Fraction 6), which was dried over anhydrous $MgSO_4$ and divided into two equal parts (Fractions 6A and 6B). The aqueous layer was neutralized with NaOH to ph8 and continuously extracted overnight with ether (250 ml). Evaporation of the ether gave a sticky moist residue which was redissolved in ether (100 ml). Separation and evaporation of the ether gave Fraction 4, which should be the basic components not soluble in 1:1 methanol/water. The aqueous layer was freeze-dried yielding salts (Fraction 5) which did contain organic components as shown by a flame test.

Nitrogen gas was passed for 20 hr over Fraction 6A, placed in a round-bottomed flask which was heated in an oil bath at 59±1°C. The volatiles (Fraction 7A) were collected in a liquid nitrogen-cooled glass cold-finger trap. A Drierite tube was attached to the exit of the trap to prevent water vapor from condensing back into the trap. The oil remaining in the flask (Fraction 8A) was divided into five equal portions so that each portion now represents one-tenth of the original diesel fuel sample.

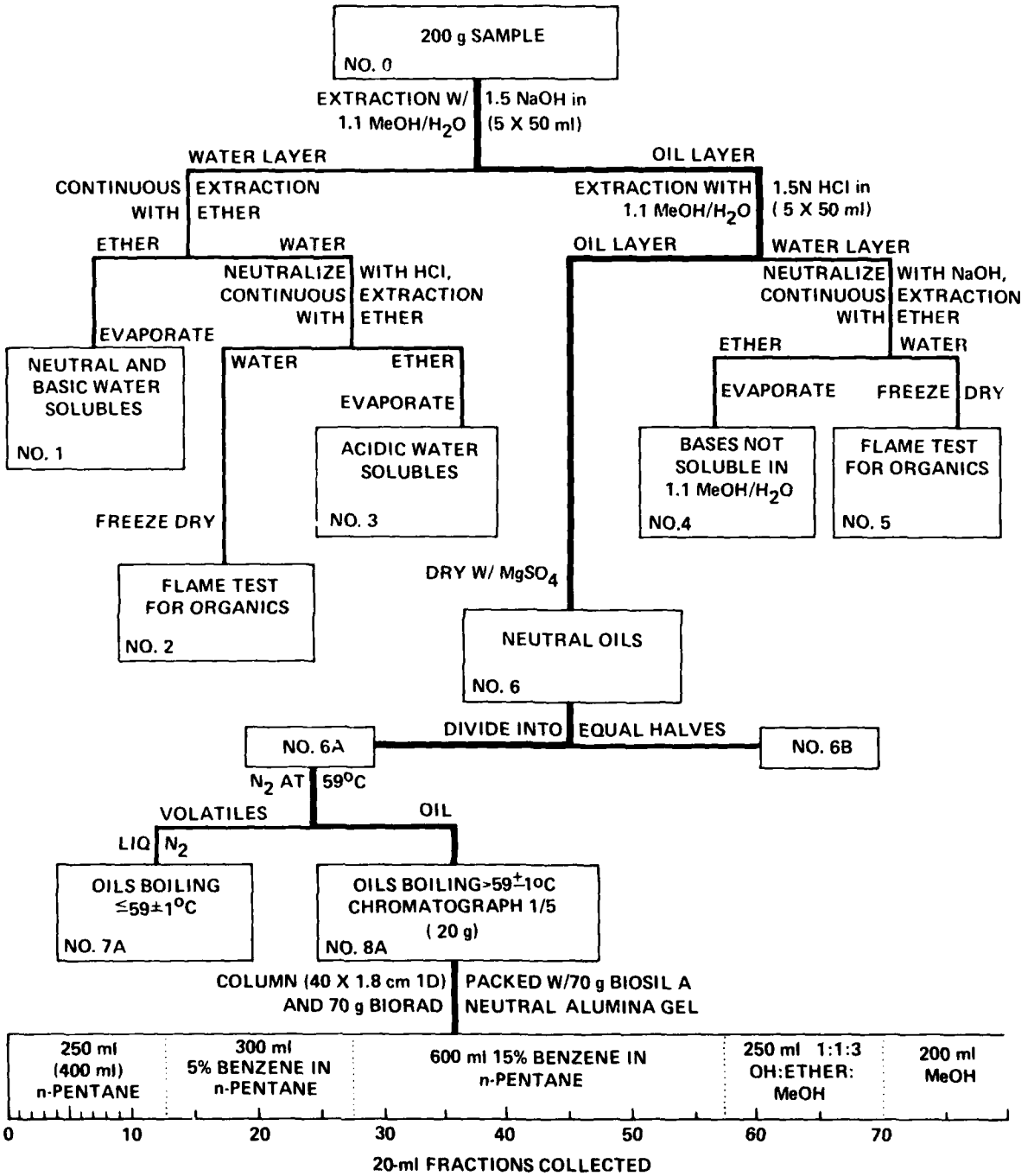

Figure 1 - Analysis of Fuel Oils

A portion of Fraction 8A dissolved in an equal volume of n-pentane was placed on a glass chromatographic column (40- x 1.8-cm ID) containing BioSil A (70 g) on top of BioRad neutral alumina gel (70 g) in n-pentane. The column was then gradient eluted successively with n-pentane (250 ml), 5% benzene in n-pentane (300 ml), 15% benzene in n-pentane (600 ml), 1:1:3 benzene/ether/methanol (250 ml), and methanol (200 m) while 20 ml fractions were collected. The n-pentane was removed at 59±1°C, while the fractions containing benzene were finally heated at ~80°C to remove the benzene.

Gas chromatograms using a 6-ft 10% silicon-rubber-UCS 982 on 80/100 WHP column in a gas chromatograph, equipped with a flame ionization detector at 250°C, was obtained on each of the fractions collected. Fractions having similar gas chromatograms were combined.

The combined fractions were then analyzed by proton FT-MNR (PMR) to obtain integrated data on the regions containing aromatic hydrogens, alkene hydrogens, $-\overset{|}{C}H$ and $C=C-CH_x$ hydrogens, $-CH_2-$ hydrogens and CH_3- hydrogens. The data, including the weights of each extraction fraction and combined column chromatographic fractions, are given in Tables 2 and 3 for the Paraho diesel fuel sample (SB-O) and conventional petroleum diesel fuel sample (PA-O), respectively. The PMR data were analyzed three ways. The first method uses the proton integration data directly to calculate the percentages of the different types of hydrogens present in the samples. For example, SB-O has 3.83% aromatic hydrogens, 1.44% alkenic hydrogens, and 94.74% saturated hydrogens, whereas PA-O has only aromatic and saturated hydrogens of 5.68% and 94.32%, respectively. Thus, the petroleum sample does not contain any alkene components.

TABLE 2 - NMR DATA ON PARAHO-GARY WESTERN SHALE DIESEL FUEL FRACTIONS

Sample Fraction	Weight (g)	% Total	Aromatics				Alkenes				Alkanes			
			I_H Int.	%	No. C*	%	I_H Int.	%	No. C*	%	I_H Int.	%	No. C*	%
SB-0	200.08	-	8.0	3.83	12.70	11.9	3.0	1.44	2.00	1.9	198.0	94.74	92.09	86.2
SB-1	0.9957	0.48	14.6	6.19	23.18	18.4	0	-	-	-	221.2	93.81	102.88	81.6
SB-3	0.0264	0.01	13.2	9.45	20.95	26.3	0	-	-	-	126.5	90.55	58.84	73.7
SB-4	1.0753	0.53	14.5	8.98	23.02	25.1	1.5	0.93	1.00	1.1	145.5	90.09	67.67	73.8
SB-7	0.3940	0.19	15.0	7.25	23.81	20.2	24.8	11.98	16.53	14.0	167.2	80.77	77.77	65.8
SB-8A(0)	19.187	95.93	8.5	4.53	13.49	13.8	3.5	1.86	2.33	2.4	175.8	93.61	81.77	83.8
(1-8)	0.0876	0.44	14.2	6.60	22.54	19.4	0	-	-	-	201.0	93.40	93.49	80.6
(9)	0.1108	0.55	0	-	-	-	0	-	-	-	230.2	100.0	107.07	100.0
(10-12)	5.4164	27.08	0	-	-	-	3.5	1.82	2.33	2.6	98.18	87.91	87.91	97.4
(13-18)	5.4406	27.20	1.4	1.04	2.22	3.4	2.3	1.71	1.53	2.4	131.0	97.25	60.93	94.2
(19-22)	2.3930	12.00	9.0	6.02	14.29	17.8	2.3	1.54	1.53	1.9	138.2	92.44	64.28	80.3
(23-28)	0.2368	1.53	12.1	7.74	19.21	22.2	1.8	1.15	1.20	1.4	142.5	91.11	66.28	76.5
(29-36)	0.1903	0.95	19.2	11.61	30.48	30.9	0	-	-	-	146.2	88.39	68.00	69.1
(37-44)	0.8584	4.29	38.4	18.38	60.95	43.5	0	-	-	-	170.5	81.62	79.30	56.5
(45)	Lost													
(46-50)	0.4871	2.99	47.2	22.95	74.92	50.4	0	-	-	-	158.5	117.05	73.72	49.6
(51-59)	0.3755	1.87	65.8	25.15	104.44	53.4	0	-	-	-	195.8	74.85	91.07	46.6
(60-68)	0.2581	1.29	79.4	32.09	126.03	61.7	0	-	-	-	168.0	67.91	78.14	38.3
(69)	0.1535	0.77												
(70-76)	0.5973	2.99	80.0	37.97	126.98	67.6	0	-	-	-	130.7	62.03	60.79	32.4
(77-82)	0.2462	1.23	106.5	40.49	169.05	69.9	0	-	-	-	156.5	59.21	72.79	30.1
(83-87)	0.3049	1.52	99.5	39.44	157.94	69.0	0	-	-	-	152.8	60.56	71.07	31.0
(88-92)	0.2650	1.33	54.8	23.02	86.98	50.5	0	-	-	-	183.3	76.98	85.26	49.5
(93-100)	1.4759	7.38	15.0	9.20	23.81	25.7	0	-	-	-	148.0	90.80	68.84	74.3
(101-110)	0.2430	1.22	10.0	5.56	15.87	16.5	0	-	-	-	173.0	94.54	80.47	83.5
(111-117)	0.1853	0.92	0	-	-	-	0	-	-	-	97.2	100.0		100.0
Total	199.63	99.62												

*To obtain an estimate of the No. C equivalent, the aromatic proton integration was divided by 0.63, which is the average number of hydrogens per carbon in the mono-substituted mono- to penta-cyclic aromatics, while the alkane proton integration data were divided by 2.15, which was the experimentally determined value found for the original sample (SB-0) for the $R-CH_3$, $R-CH_2-R'$ and R_3CH + = $C-CH_x$ proton data, and the alkene proton data were divided by 1.5, an average of the number of protons present in mono-, di-, tri- and tetra-substituted alkenes.

TABLE 2 (Continued)

$R-CH_3$		$R-CH_2-R'$		$R_3CH,=C-CH_x-$		Ratio of	Comments
Int.	13.0	Int.	12.0	Int.	11.75	$CH_3-:CH_2-:CH,=C=CH_x-$	
42.0	14.00	105.5	52.75	50.5	28.86	1:3.77:2.07	Original oil sample
43.8	14.60	81.4	40.70	95.0	54.29	1:2.79:3.72	No alkenes
20.2	6.73	47.8	23.90	58.5	33.49	1:3.55:4.97	No alkenes, highly aromatic
30.2	10.07	59.8	29.90	55.5	31.74	1:2.94:3.12	High aromatic content
62.0	20.67	81.0	40.50	24.2	13.83	1:1.96:0.67	High methyl, aromatic, alkenic content
45.0	15.00	98.6	49.30	32.2	18.97	1:3.29:1.26	Sample placed on chromatography column
52.5	17.50	120.0	60.00	28.5	16.29	1:3.43:0.91	
38.2	12.73	192.0	96.0	0	-	1:7.56:0	Long chain saturated hydrocarbons
49.5	16.50	126.5	63.25	10.0	5.71	1:3.83:0.35	Saturated hydrocarbons with some alkenes
35.5	11.83	84.5	42.25	11.0	6.29	1:3.57:0.53	Saturated hydrocarbons with traces of aromatic and alkenes
34.2	11.40	68.5	34.25	35.5	20.29	1:3.00:1.78	Probably about one-third hydrocarbons
33.0	11.00	64.5	32.25	45.0	25.71	1:2.93:2.34	Substituted benzenes
34.5	11.50	57.5	28.75	54.2	30.97	1:2.50:2.69	Substituted benzenes
31.5	10.50	53.5	26.75	85.5	48.85	1:2.65:4.65	Polycyclic aromatics
							Sample lost (= small amount)
15.5	5.67	36.5	18.25	106.5	60.86	1:3.22:10.73	More than 50% aromatic carbons
20.0	6.67	47.0	23.50	128.8	73.6	1:3.52:11.03	More than 50% aromatic carbons
17.6	5.87	37.6	18.80	112.8	64.46	1:3.20:10.98	More than 60% aromatic carbons
12.0	4.00	27.5	13.75	91.2	52.11	1:3.44:13.03	
13.5	4.50	34.5	17.25	108.5	62.00	1:3.83:13.78	Two-thirds aromatic carbons
12.0	4.00	35.6	17.80	105.2	60.11	1:4.45:15.03	Two-thirds aromatic carbons
25.0	8.33	56.5	28.25	101.8	58.17	1:3.39:6.98	One-half aromatic carbons
36.5	12.17	53.0	26.50	58.5	33.43	1:2.18:2.75	One-fourth aromatic carbons, polar aromatics
32.2	10.73	65.0	32.50	75.8	43.31	1:3.03:4.04	One-sixth aromatic carbons, polar aromatics
14.2	4.73	33.5	16.75	49.5	28.29	1:3.54:5.98	No aromatics, polar components
							Total recovery of 8A = 103%

TABLE 3 - NMR DATA ON CONVENTIONAL
PETROLEUM DIESEL FUEL FRACTIONS

Sample Fraction	Weight g	% Total	Aromatics				Alkenes				Alkanes				$R-CH_3$	
			^1H Int.	%	No. C*	%	^1H Int.	%	No. C*	%	^1H Int.	%	No. C*	%	Int.	3.0
PA-0	200.00		12.0	5.68	19.05	16.5	0	-	-	-	199.2	94.32	96.23	83.5	27.2	9.07
PA-1	0.8679	0.43	7.0	5.88	11.11	17.0	0	-	-	-	112.0	94.12	54.11	83.0	19.0	6.33
PA-3	0.5555	0.28	0	-	-	-	0	-	-	-	199.2	100.0	96.23	100.0	29.0	9.67
PA-4	0.5240	0.26	9.0	5.09	14.29	15.0	0	-	-	-	167.8	94.91	81.06	85.0	31.3	10.43
PA-7A	0.06	0.06	0	-	-	-	0	-	-	-	178.5	100.0	86.23	100.0	61.5	20.50
PA-8A(8)	19.4526	97.26	6.7	3.97	10.63	12.0	0	-	-	-	162.0	96.03	78.2	88.0	50.4	16.80
(1-9)	0.0352	0.18	6.8	3.96	10.79	11.9	0	-	-	-	186.8	100.0	79.71	88.1	25.0	8.33
(10)	0.0165	0.08	0	-	-	-	0	-	-	-	186.8	100.0	90.24	100.0	57.8	19.27
(11-16)	13.3252	66.63	0	-	-	-	0	-	-	-	187.5	100.0	90.58	100.0	61.4	20.47
(17-19)	0.9967	4.98	18.2	10.50	28.89	27.8	0	-	-	-	155.2	89.50	74.98	72.2	37.4	12.47
(20-24)	0.4339	2.17	21.8	10.36	34.60	27.5	0	-	-	-	188.6	89.64	91.11	72.5	86.5	28.53
(25-26)	0.1032	0.52	25.5	11.64	40.48	30.2	0	-	-	-	193.3	88.34	93.38	69.8	38.5	12.83
(27-35)	1.0062	5.03	68.2	27.29	108.25	55.2	0	-	-	-	181.7	72.71	87.78	44.8	31.2	10.40
(36-38)	0.0854	0.43	42.0	24.91	66.67	55.2	0	-	-	-	126.6	75.09	61.16	47.8	11.2	3.73
(39-40)	0.1260	0.63	54.8	24.49	86.98	51.6	0	-	-	-	169.0	75.51	81.64	48.4	12.2	4.07
(41-43)	0.1041	0.52	76.5	27.62	121.43	55.6	0	-	-	-	200.5	72.38	96.86	44.4	24.5	8.17
(44)	0.0535	0.27	57.8	30.70	91.75	59.3	0	-	-	-	130.5	69.30	63.04	40.7	16.2	5.40
(45)	0.0473	0.24	90.8	33.09	144.13	61.9	0	-	-	-	183.6	66.91	88.70	38.1	19.6	6.53
(45-46)	0.0849	0.42	105.2	39.97	166.98	68.6	0	-	-	-	158.0	60.03	76.33	31.4	26.2	8.73
(47-49)	0.0842	0.42	55.5	35.81	88.10	64.7	0	-	-	-	99.5	64.19	48.07	35.3	14.6	4.87
(50-53)	0.0741	0.37	55.8	26.22	88.57	53.9	0	-	-	-	157.0	73.78	75.85	46.1	23.5	7.83
(54-63)	0.1367	0.68	38.0	24.20	60.32	51.2	0	-	-	-	119.0	75.80	57.49	48.8	18.0	6.00
(64)	0.0715	0.36	38.5	15.34	61.11	37.3	0	-	-	-	212.4	84.66	102.61	62.7	44.8	14.93
(65-66)	0.1783	0.89	21.0	9.99	33.33	26.7	0	-	-	-	189.2	90.01	91.40	73.3	46.6	15.53
(66-77)	0.1331	0.67	0	-	-	-	0	-	-	-	103.6	100.0	50.05	100.0	21.8	7.27
Total	173.0280	86.52														

*To obtain an estimate of the No. 3 equivalent, the aromatic proton integration data were divided by 0.63, which is the average number of hydrogens per carbon in mono- to penta-cyclic aromatics, while the alkane integration data were divided by 2.07, which was the experimentally determined value found for the original sample (PA-0) for the RCH_3, $R-CH_2-R'$ and R_3CH + = $C-CH_x$ data.

Table 3 (Continued)

RCH_2-R'		R_3CH, $=C-CH_x-$		Ratio of	Comments
Int.	±2.0	Int.	±1.75	$CH_3-:-CH_2-:-CH,+C-CH_x-$	
118.5	59.35	53.5	30.57	1:6.53:3.37	Original oil sample (no alkenes)
40.0	20.0	53.0	30.29	1:3.16:4.97	Neutral and basic 1:1 $MeOH/H_2O$ solubles
64.2	32.10	80.2	45.83	1:3.32:4.74	Acidic components soluble in $MeOH/H_2O$
44.5	22.25	92.0	52.57	1:2.14:5.05	Basic components soluble in $MeOH/H_2O$
60.0	30.00	57.0	32.57	1:1.46:1.59	Volatiles boiling $\leq 59\pm1^{\circ}C$
80.8	40.20	30.8	17.60	1:2.39:1.05	Cleaned-up fuel oil sample
102.0	51.00	38.0	21.71	1:6.12:2.61	
115.0	57.50	14.0	8.00	1:2.98:0.42	Saturated hydrocarbons
112.6	56.30	13.5	7.01	1:2.75:0.37	Saturated hydrocarbons
57.8	28.90	60.0	34.29	1:2.32:2.75	Substituted benzene
60.8	30.40	42.2	24.11	1:1.07:0.85	Substituted benzenes
48.0	24.00	106.8	61.03	1:1.87:4.76	Polycyclic aromatics
36.5	19.25	114.0	65.14	1:1.75:6.26	Polycyclic aromatics >55% aromatic carbons
27.6	13.80	87.8	50.17	1:3.70:13.45	Polycyclic aromatics
44.8	22.40	99.8	57.03	1:5.50:14.0	Polycyclic aromatics
54.5	27.25	121.5	69.43	1:3.34:8.50	Polycyclic aromatics
35.3	17.65	79.0	45.14	1:3.27:8.36	Polycyclic aromatics
46.2	23.10	117.8	67.31	1:3.54:10.31	Polycyclic aromatics >60% aromatic carbons
43.2	21.60	111.8	63.89	1:2.47:7.32	Polycyclic aromatics >68% aromatic carbons
25.7	12.85	59.2	33.83	1:2.64:6.95	Polycyclic aromatics >65% aromatic carbons
50.0	25.00	83.5	47.71	1:3.19:6.09	Polycyclic aromatics >50% aromatic carbons
46.5	23.25	54.5	31.14	1:3.88:5.19	Polycyclic aromatics >50% aromatic carbons
68.2	34.10	99.4	56.80	1:2.28:3.80	Polar aromatics
67.4	33.70	75.2	42.97	1:2.17:2.77	Polar aromatics
48.8	24.40	33.0	18.86	1:3.36:2.59	Polar non-aromatic components
					Total recovery of 8A = 95%

However, the hydrogen percentages can be very misleading because the average number of hydrogens per aromatic carbon is only 0.63,* while the average number of hydrogens per saturated carbon is 2.15 and 2.07 for SB-0 and PA-0, respectively. From the elemental analyses given in Table 1, it is clear that the major element present is carbon, not hydrogen. To obtain an estimate of the types of carbons present, the hydrogen integration data was divided by 0.63 for aromatics, 1.5 for alkenes, and either 2.15 or 2.07 for SB-0 and PA-0, respectively. Now SB-0 has 11.9% aromatic carbons, 1.9% alkenic carbons, and 86.2% saturated carbon while PA-0 has 16.5% aromatic carbons and 83.5% saturated carbons. These are estimates that include several assumptions, but it shall be shown below that the carbon percentages are a better gauge of PAH content than the hydrogen percentages.

The third calculation presented in Tables 2 and 3 used the saturated hydrogen data to compute a ratio of methyl (CH_3-) carbons: methylene (-CH_2-) carbons: methine ($-\overset{|}{\underset{|}{C}}H$) carbon plus any saturated group attached to aromatic or alkenic carbon (=C-CH_x) . These ratios provide useful information on the degree of branching in the hydrocarbon chains as well as the amount of substitution on the PAH components. For example, fractions PA-8A (10) and PA-8A (11-16) are moderately branched saturated hydrocarbons with CH_3:CH_2:CH ratios of 1:2.98:0.42 and 1:2.75:0.37, respectively, whereas SB-8A (9) is a mixture of long saturated hydrocarbons (averaging C_{14}-C_{16}) with no branching as shown by the ratio of 1:7.56:00. Except for some alkenic carbons, sample SB-8A (10-12) is similar to the corresponding PA-8A (10) and PA-8A (11-16) because the ratio is 1:3.83:0.35. This ratio also shows that the polynuclear aromatic hydrocarbon fractions of both the petroleum (PA-8A (25-63)) and the shale (SB-8A (39-97)) samples are highly substituted with moderately branched side chains as shown by the average ratios of 1:2.55:7.29 and 1:3.30:9.29, respectively, and the high average percent aromatic carbon content of 54.4% and 55.3%, respectively. In fact, these data suggest that in the petroleum sample, aromatics are somewhat more branched than in the shale sample.

*This number was obtained by taking the average H/C ratio for all possible unsubstituted and mono-substituted mono- to penta-cyclic aromatic compounds. Multiple substitution will lower the ratio still more.

Thus, it is clear that the treatment of the data given in Tables 2 and 3 allows many interesting conclusions without attempting the almost impossible task of identifying the specific structures. A summary of the composition of these diesel fuels, based on Tables 2 and 3, is given in Table 4.

TABLE 4 - COMPOSITION OF THE DIESEL FUEL SAMPLES

Fraction, Composition	Percent of Sample*		Comments
	SB-0	PA-0	
1 Neutral and Basic Solubles	0.48	0.43	
3 Acidic Components	0.01	0.28	Possible phenolics
4 Basic Components	0.53	0.26	Possible anilines
7A Volatiles, bp $\leq 59 \pm 1^{\circ}C$	0.39	0.06	C_4-C_5 hydrocarbons
8A Extracted Oil Sample	95.9	97.3	
% Extraction Recovery	97.3%	98.3%	
Chromatography of 8A			
Forerun	0.4	0.2	
Saturated Hydrocarbons	0.6	66.7	
Saturated and Alkene and Hydrocarbons	59.3	0	Trace of benzenes
Subtotal Hydrocarbons	59.9	66.7	
Substituted Benzenes	10.4	7.1	
PAH*	19.3	9.5	
Polar Components with Aromatics	8.5	1.2	
Polar Components without Aromatics	0.9	0.7	
8A Rocovery	103%	95%	
Total Aromatics	38.2	17.8	

*Recovered weight percent.

The most important difference between the shale and the conventional petroleum diesel fuel samples studied is the total aromatics content and PAH content. The shale sample has 38% total aromatics of which 19.3% are potentially dangerous PAH. The conventional petroleum sample contains only about half as much (17.8%) total aromatics, of which 9.5% are PAH.

CONCLUSIONS

The extraction/chromatographic procedure developed has worked well with the two diesel fuel samples studied. The acid-base cleanup procedure removes only about 1.0% of the samples; however, about 2% of the samples were lost in the process, mostly from drying Fraction 6 over $MgSO_4$. The chromatography/subsequent analyses are particularly interesting. The petroleum sample does not have alkenes while the shale sample contains about 2% alkenes. The acyclic hydrocarbon (straight chain compounds) content was 67% and 60%, respectively, for the petroleum and shale fuels. Of greatest interest is the aromatic content of the samples. The shale sample contains about 38% aromatic rings with alkyl and some alkenic side chains, while the petroleum sample contains only 18%. About half of these, i.e., 18.3% of the shale sample and 9.5% of the petroleum sample, are PAH and thus may contain some of the carcinogenic or suspected carcinogenic compounds.

It is important not to use this data to draw inferences about the composition of shale diesel fuels made by other processes; composition is expected to vary significantly with processing differences.

Based on the work completed here, we recommend the following:

1. Ames tests should be made on the PAH fractions to determine which fractions are carcinogenic.

2. Attempts should be made to determine the quantities of unknown carcinogenic PAH compounds. The harmful fractions should be further fractionated by gas chromatography-mass-infrared spectometry to determine the structures of the dangerous compounds.

3. Studies should be made to determine the concentration levels of the dangerous PAH compounds that may be present in head vapors at the various temperatures that might be encountered aboard ship.

4. Only one sample of each fuel type has been analyzed. Diesel fuels from other petroleum sources and fuels from other shale and coal sources more representative of expected commercial practice should be analyzed since compositions would differ significantly among potential fuel sources and refining methods.

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