

Analysis of Commercial Diesel Fuels by  
Preparative High Performance Liquid Chromatography and  
Gas Chromatography - Mass Spectrometry

S. G. Thomas, J. P. Kleiman and V. O. Brandt

Ethyl Corporation  
Ethyl Technical Center  
P. O. Box 14799  
Baton Rouge, LA 70898

INTRODUCTION

Diesel fuel is a complex mixture of hydrocarbons with a boiling range from about 400 to 670°F. Recently, the emphasis on the diesel engine in passenger cars increased (1). It is expected that the demand for middle distillates will increase while the quality of feedstocks will decrease (2-5). Cetane number and stability are two measures of diesel fuel quality. Nozzle coking in diesel engines for passenger cars is another problem (6). This expected lower quality is related to the increased use of blending components from heavy oil cracking processes. The ability to define diesel fuel composition will become increasingly important to understand the relationship between fuel composition and cetane number, stability, coking tendency and other performance parameters.

A major problem is the separation and identification of pure compounds or classes of compounds from the complex hydrocarbon mixtures in diesel fuel. Many refinery test laboratories use the fluorescent indicator analysis method (FIA; ASTM D-1319) to separate and quantify saturates, olefins and aromatic hydrocarbons in diesel fuels. Another approach is to determine aromatic content by nuclear magnetic resonance spectroscopy (7). As pointed out by M. E. Myers (7) these methods do not give the same result because they do not measure the same properties.

Types of hydrocarbons in middle distillates may be determined by a combination of silica gel chromatography and mass spectrometry (ASTM D-2425 and -2549). A major disadvantage to this approach is the slowness of open column chromatography. We have developed an alternate to this ASTM procedure by using a preparative High Performance Liquid Chromatograph and a Gas Chromatograph-Mass Spectrometer to analyze two commercial diesel fuels. This modified ASTM method is faster and provides more efficient separations than ASTM D-2549. In this paper, this modified ASTM procedure will be described and the results compared to those obtained from the FIA (ASTM D-1319) and NMR procedures (7). Application of solvent extraction and clay chromatography also is demonstrated. These techniques separate polar components and polynuclear aromatics from other diesel fuel components.

EXPERIMENTAL

Instrumentation

The prep HPLC used to separate the diesel fuels into hydrocarbon group types was a Prep LC/System 500 with a refractive index detector from Waters Associates. An ultraviolet detector from Gow Mac was also used to monitor aromatic components. Qualitative hydrocarbon group types in chromatographic fractions were obtained with a Hewlett-Packard

5993 GC-MS while quantitative estimates were obtained with a Finnigan MAT-4000 GC-MS. ASTM D-2425 was employed for these quantitative estimates. A Varian FT-80A NMR was used for proton NMR analysis.

#### Chromatographic Separations

About 10 grams of diesel fuel was added to a silica gel column on the Prep HPLC. HPLC grade hexane was used to separate the sample into seven 250 mL fractions. Hexane was removed from each fraction with a rotary evaporator. Each fraction was weighed and analyzed by GC-MS for hydrocarbon type. Recovery from the chromatographic column with hexane was about 90 wt%.

#### Gas Chromatographic Analysis of Paraffin Fraction

The column was stainless steel (6 ft by 1/8 inch) with 10% OV-101 on 80/100 W HP. Initial column temperature was 75°C and programmed at a rate of 5°C/min to a final temperature of 330°C. A thermal conductivity detector was used with helium as a carrier gas (30 cc/min) and a 1.5 µl injection volume.

#### Dimethylsulfoxide Extraction

200 mL of diesel fuel was extracted with 50 mL of reagent grade dimethylsulfoxide (DMSO). The bottom DMSO layer was separated from the top hydrocarbon layer. About 120 mL of distilled water was added to the DMSO layer. A ring of dark colored liquid separated on top, which was the polar components. 10 mL of heptane was then added and the contents mixed. This top organic layer was isolated, dried with sodium sulfate and filtered. The heptane was evaporated under a stream of nitrogen and this organic layer analyzed by GC-MS.

#### Clay Chromatography

The procedure, which was developed by Pei, Britton and Hsu and described in reference (8) was used.

### RESULTS AND DISCUSSION

#### Hydrocarbon Composition of Diesel Fuels

Two 38 cetane number (ASTM D613) commercial diesel fuels were separated on silica gel into fractions. Hydrocarbon composition of each fraction was determined by qualitative and quantitative (ASTM D-2425) GC-MS.

Qualitative GC-MS analyses confirmed that silica gel chromatographic separation yields fractions rich in paraffins and cycloparaffins, alkylbenzenes, indanes or tetralins, naphthalene, alkyl naphthalenes, acenaphthenes and biphenyls and tricyclic aromatics. The separation of each group type of hydrocarbons in "Fuel B" as a function of elution volume (polarity) is summarized in Figure 1. Because this separation is done on a preparative scale, each class of hydrocarbons is not completely separated. Each fraction contains two or more classes of hydrocarbons. In the conventional ASTM method, individual hydrocarbon types or classes are not separated. Aromatics are separated from non-aromatics and characterized by mass spectrometry.

Although individual hydrocarbon classes are not separated

completely, this modified quantitative GC-MS approach allows a comparison of the concentration of group types of hydrocarbons of different fuels. A comparison between "Fuel A" and "Fuel B" is summarized in Table 1.

The major difference in hydrocarbon composition between the two fuels is in alkyl naphthalene concentration. Naphthalenes are present at 31 wt% concentration in "Fuel B" and 9.1 wt% in "Fuel A." Other differences are in alkylbenzenes and indanes or tetralins present. We are not certain that differences in alkylbenzene concentration are analytically significant (7.7 wt% in "Fuel B" and 11.7 wt% in "Fuel A"), whereas we believe that differences in indane or tetralin are significant. "Fuel A" has a higher concentration of indanes or tetralins (10.3 wt%) than "Fuel B" (1.2 wt%). Other differences found are of the order of the reproducibility of ASTM D-2425.

Although aromatic content is about the same in both fuels by FIA analysis (40.5 vol% in "Fuel A" and 42 vol% in "Fuel B"), they differ by proton NMR (7) analysis (28.9 mole% in "Fuel A" and 36.7% in "Fuel B"). This difference is due to the fact that only aromatic moieties (carbons) are counted by NMR whereas alkyl aromatics and indane types are counted in the FIA method. Total weight percent of alkylbenzenes, indanes or tetralins and alkylnaphthalenes in "Fuel A" (31 wt%) are equal to the total amount of alkylnaphthalenes found in "Fuel B" (31 wt%). The higher number of aromatic carbons in naphthalenes versus benzenes or indanes or tetralins is the reason that "Fuel B" shows a higher amount of aromatics by NMR than "Fuel A."

The total concentration of aromatics found by GC-MS is about the same as that found by FIA analysis (about 40.4 wt% in "Fuel A" and 42.8 wt% in "Fuel B.") One difference between the methods is that GC-MS measures weight percent and FIA volume percent. Both methods use a silica gel column for the separation and count as aromatic the total weight or volume of any components that contain aromatic rings. For these reasons, it is not surprising that both methods give similar results. However, neither FIA nor NMR should be used alone to obtain aromatic content. The combination provides some insight into the type of aromatics that may be present and a more accurate picture of total aromatic composition.

#### Composition of Paraffinic Fraction

The paraffinic fraction composition of two fuels was studied by gas chromatography and revealed more than 45 peaks. About 52-54 normalized weight percent of the paraffinic fractions were normal paraffins with the remainder being branched paraffins, olefins and/or cycloparaffins. "Fuel A" has a higher relative concentration of C<sub>10</sub> to C<sub>13</sub> n-paraffins, while "Fuel B" is higher in C<sub>14</sub> to C<sub>21</sub> n-paraffins. These results are summarized in Table 2.

#### Polar Components in Fuels

"Fuel A" and "Fuel B" were extracted with dimethylsulfoxide to isolate polar components for identification. GC/MS analysis of this polar fraction showed alkylated condensed aromatic derivatives of naphthalene, anthracene, phenanthrene, dibenzothiophene, carbazole and dibenzofuran.

About 1 gallon of "Fuel B" was chromatographed on a clay

column (prep HPLC) to remove polar components for identification. GC-MS of the polar fraction identified it to be alkylated carbazoles.

Table 3 lists example structures of components found in polar fractions.

#### SUMMARY

Compositions of hydrocarbons in two commercial diesel fuels have been obtained by a combination of preparative High Performance Liquid Chromatography (prep HPLC) and Gas Chromatography-Mass Spectroscopy (GC-MS). Two different GC-MS approaches are used; the first is qualitative and the second quantitative (modified ASTM-D-2425). Fuels are separated on a preparative silica gel column with a hexane solvent into group hydrocarbon types: paraffins, alkylbenzenes, indanes or tetralins and alkyl naphthalenes. Concentrations of each class of identified hydrocarbons are measured and compared for the two fuels.

Each commercial fuel also was analyzed by Nuclear Magnetic Resonance (NMR) and the Fluorescent Indicator Analysis (FIA ASTM-D-1319) specifically for aromatic content. Differences in aromatic content obtained for each fuel by these two techniques are explained by results from the prep HPLC/GC-MS approach. This paper demonstrates how aromatic content obtained by either the NMR or FIA methods alone is not adequate and may be misleading.

It is important to understand the relationships between fuel composition and cetane number, stability and coking tendency. By studying and understanding these relationships, the refiner will be able to more accurately prescribe treat levels of diesel ignition improvers (such as Ethyl's DII-3) or broader treatment products (such as Ethyl's DPI's) which reduce coking, enhance stability and provide other benefits.

In an effort to isolate and identify polar components in fuels, two approaches have been explored: (1) dimethylsulfoxide (DMSO) extraction; and (2) clay chromatography in combination with GC-MS. The following types of polar compounds and polynuclear hydrocarbons were identified in DMSO fuel extracts: anthracenes, naphthalenes, phenanthrenes, carbazoles, dibenzothiophenes, dibenzofurans, etc. Preparative clay chromatography of one of these 38 cetane number diesel fuels selectively allows separation of only carbazoles.

Besides providing detailed fuel composition, multigram quantities of selected hydrocarbons, can be isolated by the preparative chromatography approach outlined in this paper. These hydrocarbons could be used as analytical standards, further separated and analyzed or tested with or without additives in a bench test or engine. Results from this test work could provide a more fundamental understanding of the relationship between fuel structure and additive response.

#### ACKNOWLEDGEMENT

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FIGURE 1

Separation of "Fuel B" into Hydrocarbon

Group Types on Silica Gel

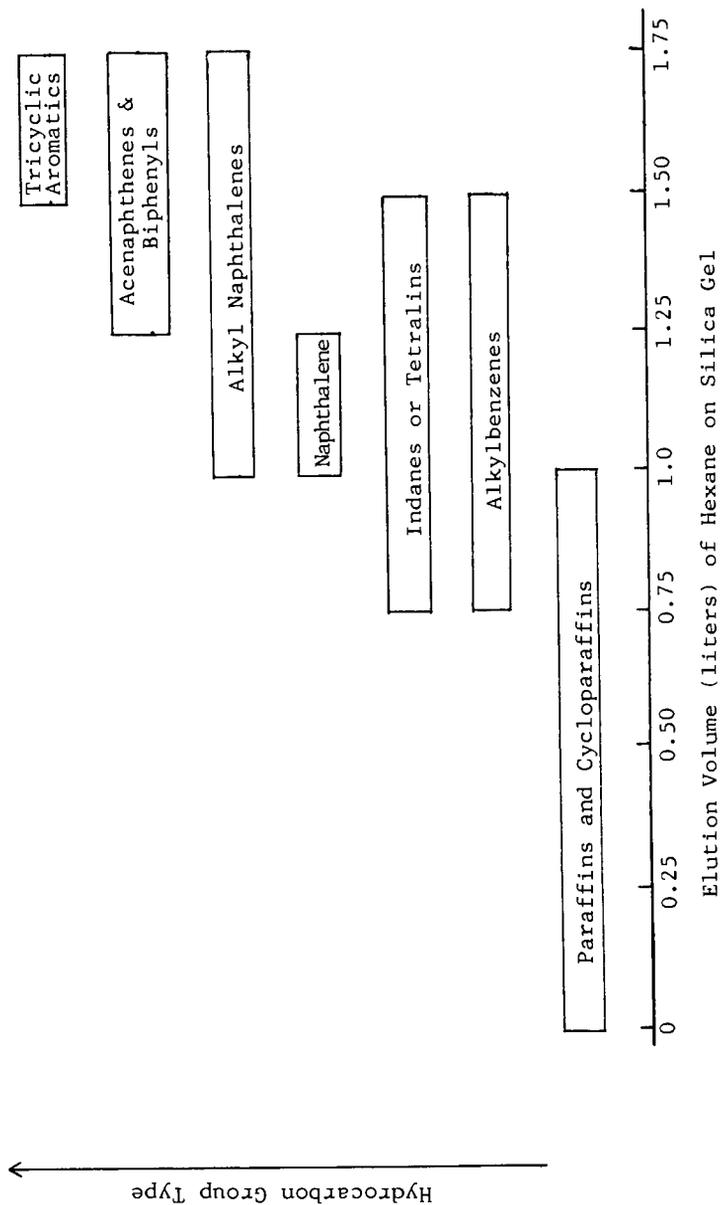
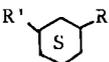
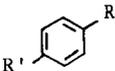
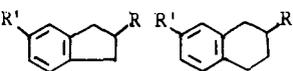
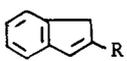
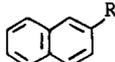
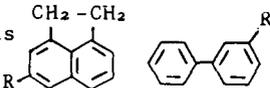
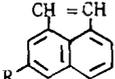
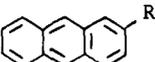


TABLE 1

Hydrocarbon Composition of "Fuel A" and "Fuel B"  
by Gas Chromatography - Mass Spectrometry (ASTM D2425)

<u>Hydrocarbon Group Type</u>	<u>Example</u>	<u>"Fuel B"</u> <u>(wt%)</u>	<u>"Fuel A"</u> <u>(wt%)</u>
Paraffins	$\text{CH}_3-(\text{CH}_2)_{1-4}-\text{CH}_3$	46.2	50
Monocycloparaffins		2.2	1
Alkylbenzenes		7.7	11.7
Indanes or Tetralins		1.2	10.3
Indenes		0	1.1
Naphthalene		0.1	0.6
Alkyl Naphthalenes		31.0	9.1
Acenaphthenes and biphenyls		2.9	3.9
Acenaphthylenes		0.5	1
Tricyclic aromatics		<u>0.1</u>	<u>2.2</u>
Material Balance			
Total Diesel Fuel Components Accounted For		91.9	91.5

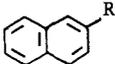
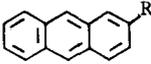
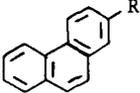
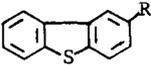
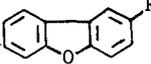
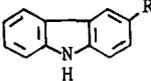
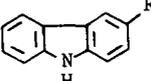
R' and R - alkyl groups or hydrogen

TABLE 2  
Relative Amounts of Normal Paraffins  
in Paraffinic Fractions of Diesel Fuels by Gas Chromatography

<u>Normal Paraffin</u>	<u>Normalized Wt%</u>	
	<u>"Fuel A"</u>	<u>"Fuel B"</u>
C <sub>10</sub>	0.9	0.4
C <sub>11</sub>	2.9	1.1
C <sub>12</sub>	4.9	2.0
C <sub>13</sub>	6.7	3.8
C <sub>14</sub>	8.5	8.9
C <sub>15</sub>	8.0	9.9
C <sub>16</sub>	7.4	9.0
C <sub>17</sub>	6.0	8.6
C <sub>18</sub>	2.8	3.8
C <sub>19</sub>	1.3	3.0
C <sub>20</sub>	0.8	1.6
C <sub>21</sub>	0.7	0.9
C <sub>22</sub>	0.5	0.5
C <sub>23</sub>	0.3	-
Total Weight Percent	51.7	53.5

TABLE 3

Example Structures of Components in Polar Diesel Fuel Fractions  
Identified by Gas Chromatography - Mass Spectrometry

<u>Fuel</u>	<u>Method</u>	<u>Components</u>	<u>Name</u>
"Fuel A" and "Fuel B"	Dimethylsulfoxide Extraction		alkyl naphthalene
			alkyl anthracene
			alkyl phenanthrene
			alkyl dibenzothiophene
			alkyl dibenzofuran
			alkyl carbazole
"Fuel B"	Clay Chromatography		alkyl carbazole

R - alkyl groups