Validation of the aromatic ring distribution in diesel fuel refinery streams by supercritical fluid chromatography and mass spectrometry

Evan N. Chen, Jr.*, Patrice D. Cusatis and Edward J. Popiel

Texaco Research & Development, P.O. Box 509, Beacon, NY 12508 (USA)

ABSTRACT

In anticipation of stricter environmental mandates, a new supercritical fluid chromatographic (SFC) method has been developed to determine the aromatic ring distribution in various diesel fuel refinery streams. Although preparative open column liquid chromatography (OCLC) followed by mass spectral (MS) quantitation is often used to determine the individual aromatic ring types, this procedure is quite time consuming and labor intensive. The SFC technique described here provides rapid, quantitative hydrocarbon analysis of the aromatic ring species without prior OCLC separation. Nearly fifty test diesel fuels, ranging from 6.0 to 48.0% (w/w) total aromatics, originating from separate refineries, have been analyzed. Excellent correlation has been established between the OCLC–MS data and the SFC results confirming the validity of this new SFC method.

INTRODUCTION

Various state and local environmental laws have stipulated that drastic reductions in the level of aromatic hydrocarbons in diesel fuels must be made in order to decrease harmful exhaust emissions which can lead to smog. Anticipating this to be federal regulation, appropriate analytical methods are needed to insure that diesel fuels meet these restrictions.

In the petroleum industry, classical liquid chromatography (LC) is widely used for determination of aromatics in light and middle distillate fuels. Unfortunately, the fluorescence indicator adsorption method (ASTM D1319) [1] and preparative open column liquid chromatography (OCLC) (modified ASTM D2549) [2] are labor intensive, time consuming, and cannot be automated. In addition, the precision of the fluorescence indicator adsorption method is poor since diesel fuels are beyond the scope of this method.

Hydrocarbon analysis by high-performance liquid chromatography (HPLC) has been successful [3–6], but this technique lacks a universal detector which can respond uniformly to the hydrocarbons typically found in petroleum fractions. Nuclear magnetic resonance (NMR) and mass spectrometry (MS) are effective in providing detailed structural information compositional analysis. Unfortunately, NMR results are usually reported in terms of aromatic carbon [7,8] and prior sample preparation is often required for MS [9] rendering these techniques less desirable for routine analysis.

Supercritical fluid chromatography (SFC) with flame ionization detection (FID) has proven to be quite effective for the analysis of total aromatics in diesel fuels [10–14]. In addition, the American Society for Testing and Materials (ASTM) has recently approved a new standard test method to determine the aromatic content in diesel fuels (ASTM D5186) [15]. Unfortunately,

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* Corresponding author.

these techniques do not describe the separation and quantitation of the aromatic ring distribution. Although the total aromatic content is generally considered the parameter responsible for hazardous emissions, recent studies suggest that diaromatics and triaromatics have a stronger influence on diesel particulates than mono-aromatics [16].

Aromatic types in middle distillates are typically determined by separating the saturate components from the aromatics by OCLC with subsequent MS quantitation [17] of the individual ring species. The precision and accuracy of the data are good, however, this procedure is quite time consuming. In addition, running the OCLC–MS requires a large amount of solvent, tedious evaporation step, and the high cost of specialty glassware and mass spectral instrumentation.

This paper reports the development of an improved, automated SFC method which is time and cost efficient, not as labor intensive, and applicable to different diesel refinery streams. More importantly, this technique covers the hydrocarbon analysis and quantitation of the aromatic ring distribution without the need for prior OCLC separation.

EXPERIMENTAL

Apparatus

A Computer Chemical Systems 7000 controller/fluid delivery system (CCS, Avondale, PA, USA) was used to convert a 5890 gas chromatograph (Hewlett-Packard, Paramus, NJ, USA) into a fully functional SFC system. The system was equipped with a 50-ml syringe pump, a $0.1-\mu l$ injection valve, and a FID system. The chromatographic data were processed using the Hewlett-Packard HP-3350 laboratory automation system with C-PLOT software.

Materials

Hexane and carbon disulfide (CS_2) (Aldrich, Milwaukee, WI, USA) were of HPLC grade. The carbon dioxide mobile phase (Scott Specialty Gases, South Plainfield, NJ, USA) was of SFC grade and contained a 1500 p.s.i. (1 p.s.i. = 6894.76 Pa) cylinder head pressure. The per-

formance mixture consisted of hexane, hexadecane (Aldrich) benzene, toluene, indane, phenyldecane, naphthalene, 2,3,6-trimethylnaphthalene, fluorene, dibenzothiophene, anthracene, fluoranthene and pyrene (ChemService, West Chester, PA, USA).

Validation of SFC system

Total aromatic content. To verify the accuracy of the SFC system, each test diesel fuel was first separated into their actual saturate and aromatic fractions by OCLC. The actual aromatic fraction was then compared to the total aromatic FID response of the original diesel fuel as shown in Fig. 1. Excellent correlation was obtained for diesel fuels ranging from 6.0 to 48.0% (w/w) total aromatics and was consistent with different refinery streams.

Aromatic ring distribution. Initially, the aromatic fraction obtained by OCLC of each standard sample was further quantitated for the individual ring species by MS and SFC. The separation scheme used to validate the SFC system for aromatic types is given in Fig. 2. It should be noted that the OCLC procedure [2] was modified for middle distillates in order to achieve the highest possible recovery of the individual hydrocarbon fractions. Upon validation, the original diesel fuels were then injected directly into the SFC system for aromatic type analysis, bypassing the OCLC separation and the need for solvent evaporation.
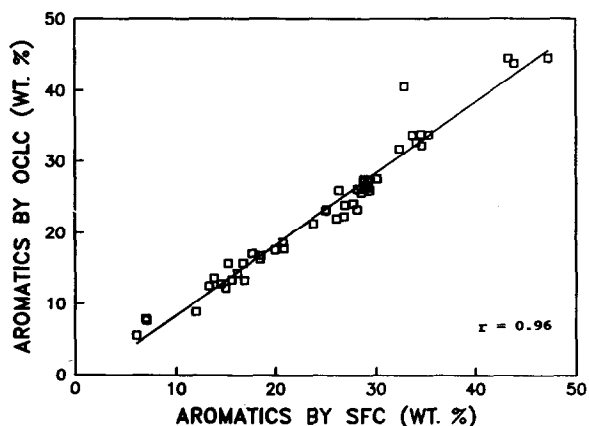

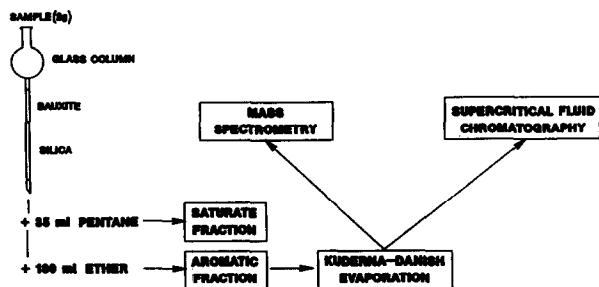Fig. 1. Analysis of total aromatics in diesel fuels by OCLC *versus* SFC.

Fig. 2. Separation scheme for the validation of the aromatic ring distribution in diesel fuels.

Fig. 3. SFC chromatogram of (a) performance mixture and (b) original diesel fuel employing the same chromatographic conditions.

Chromatographic procedure

The hydrocarbon group separation was accomplished with a Chromegabond cyano column (25 cm × 2.0 mm I.D., 5 μm spherical particle size) connected in series with a Chromegasphere SI-60 silica column (25 cm × 2.0 mm I.D., 5 μm spherical particle size) (ES Industries, Marlton, NJ, USA). The columns were maintained at a constant temperature (40°C) and pressure (4500 p.s.i.) throughout the entire analysis.

The CO_2 flow-rate exiting the tapered stainless-steel post-column restrictor was 45 ml/min. The FID system was operated at 350°C and the air and hydrogen flows were 300 and 47 ml/min, respectively. These parameters represent the most optimal conditions for separating the saturate and aromatic ring fractions on this SFC system.

The performance mixture was prepared by making a 0.2% (w/w) solution of each component in hexane. Upon equilibration, 0.1 μl of original diesel fuel was injected into the SFC system and the entire analysis was accomplished in less than 45 min.

RESULTS AND DISCUSSION

For aromatic type analysis, the performance mixture was injected and the retention time regions according to aromatic ring number were recorded as shown in Fig. 3a. A corresponding SFC chromatogram of a diesel fuel is shown in Fig. 3b. The first peak of the model compounds consisted entirely of hexane and hexadecane, while all the monoaromatics eluted in the region between benzene and just before naphthalene;
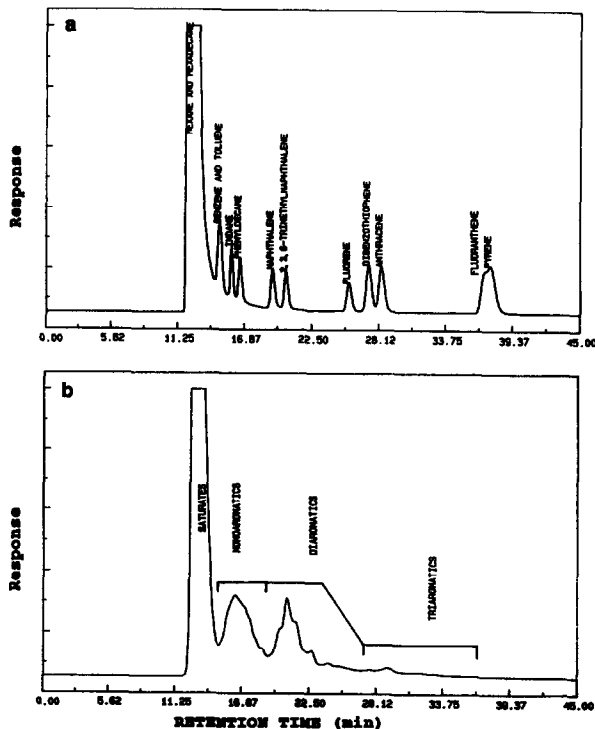
all the diaromatics between naphthalene and just before dibenzothiophene; and all the triaromatics and higher between dibenzothiophene and the final return to the baseline at the end of the chromatogram. For the fuels analyzed, we did not find any aromatic components containing more than three rings. The aromatic retention time ranges of the performance mixture were recorded before every set of five diesel fuels. This accounted for any fluctuations in the retention time of the sample caused by the plugging of the restrictor or column degradation.

Using the validation procedure shown in Fig. 2, the OCLC aromatic fraction of each fuel was analyzed by both MS and SFC techniques. Fig. 4 shows the comparison between the OCLC–MS and OCLC–SFC data for the aromatic ring distribution of nearly fifty test diesel fuels. There was a slight bias towards higher SFC results for the monoaromatics as shown in Fig. 4a. On the other hand, Fig. 4b shows that the diaromatics resulted in higher values by MS. Both the
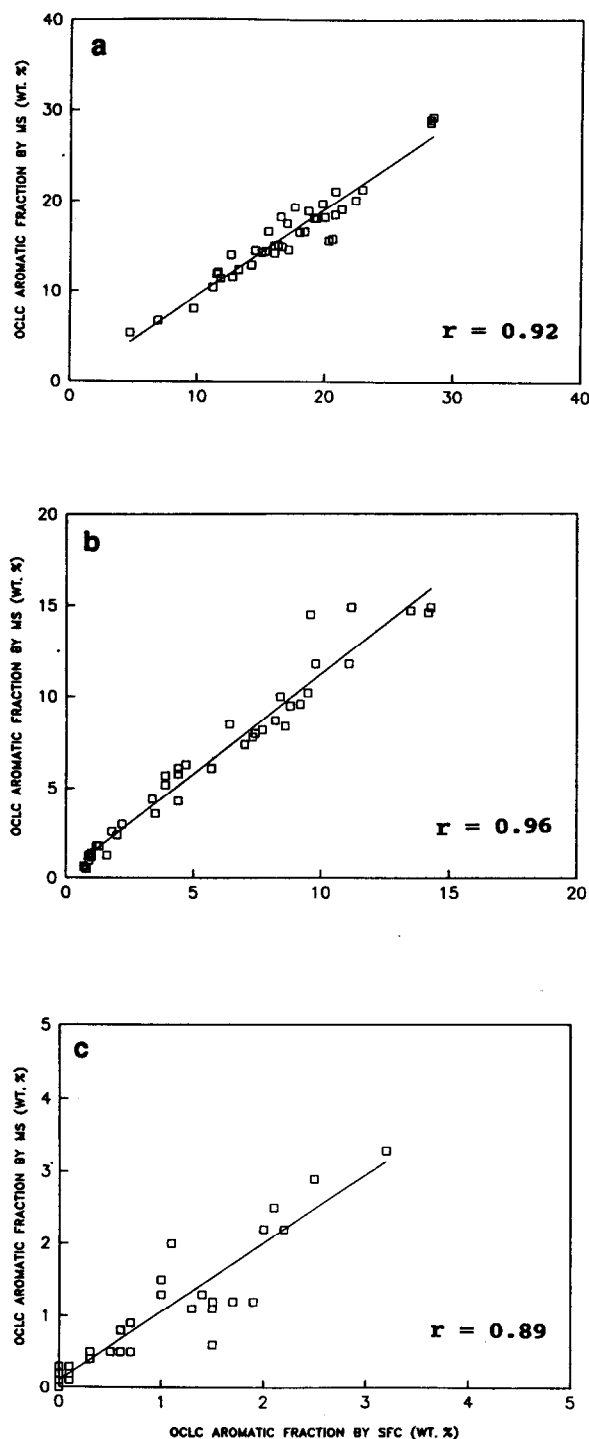
Fig. 4. Analysis of the OCLC aromatic fraction by MS *versus* SFC for (a) monoaromatics, (b) diaromatics and (c) tri-aromatics in diesel fuels. Note the different scales for each ring type.

monoaromatic and diaromatic type analyses gave correlation coefficients greater than 0.90. In spite of the incomplete resolution among the hydrocarbon fractions in Fig. 3b, a good correlation was established between the results obtained by this SFC method and the mass spectrometry data.

Although the correlation coefficient for the triaromatics was 0.89, a good comparison of the MS and SFC was achieved as shown in Fig. 4c. A typical summary of the mass spectral quantitation of the individual ring types is shown in Table I. In general, the diesel fuels analyzed contained low concentrations of three ring aromatics, thus, peak areas were more difficult to integrate due to lower resolution. Also, nitrogen and sulphur containing materials may have contributed to some SFC–FID response differences.

One of the goals of this SFC method was to analyze diesel fuels routinely and efficiently. Since the OCLC–SFC data in Fig. 4 were favorable and have been validate by MS, our intent was to determine the individual ring species without prior OCLC separation and solvent evaporation. An excellent comparison of the

TABLE I

MASS SPECTRAL QUANTITATION OF THE AROMATIC RING TYPES IN A DIESEL FUEL

ASTM test D2425: Hydrocarbon type analysis of middle distillates by mass spectrometry.

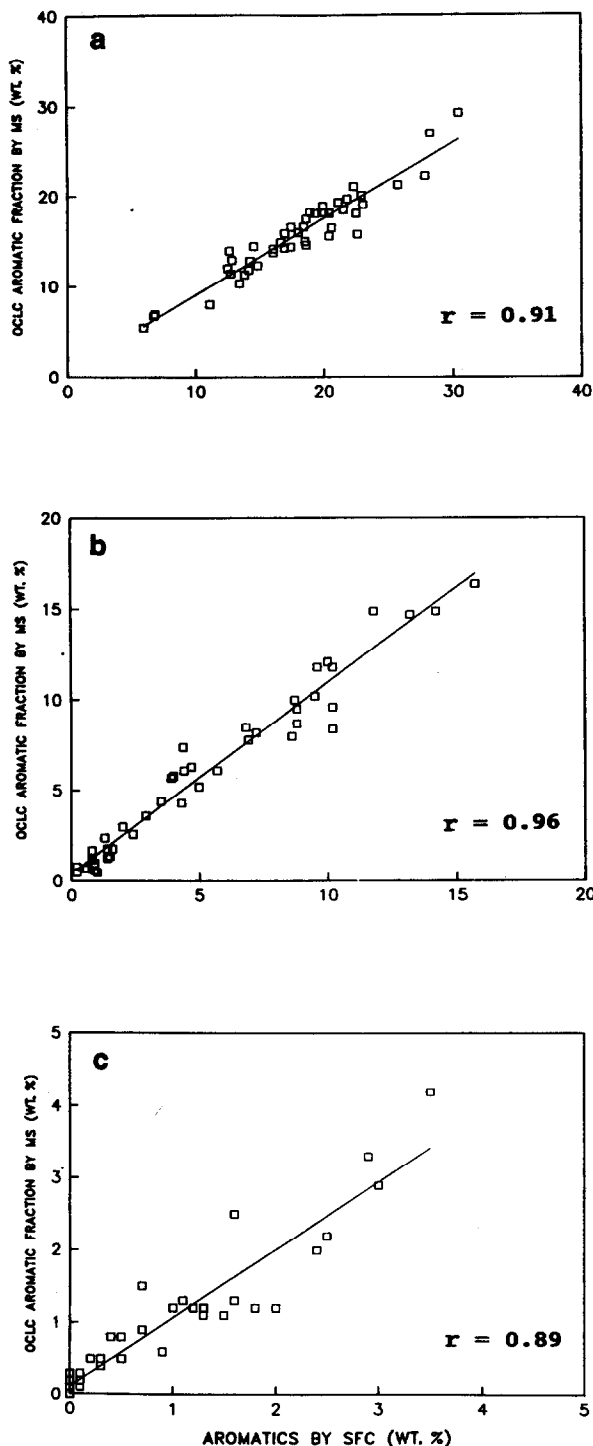| Hydrocarbon type	% (w/w)
Paraffins	42.3
Monocycloalkanes	10.1
Dicycloalkanes	11.3
Tricycloalkanes	3.9
Total saturates	67.6
Alkylbenzenes	8.8
Indanes/tetralins	9.1
Dinaphthenebenzenes	2.7
Naphthalenes	4.2
Biphenyls	4.5
Fluorenes	2.1
Phenanthrenes	1.0
Total aromatics	32.4
Total	100.0

Fig. 5. Analysis of the OCLC aromatic fraction by MS *versus* the original diesel fuel (without prior OCLC separation) for (a) monoaromatics, (b) diaromatics and (c) triaromatics. Note the different scales for each ring type.

TABLE II

REPEATABILITY OF SFC–FID FOR AROMATIC TYPE ANALYSIS OF A DIESEL FUEL

Injection	Aromatic types (%, w/w)		
	Monoaromatic	Diaromatic	Triaromatic
1	15.7	13.3	2.2
2	15.5	12.8	2.1
3	15.0	13.0	2.1
4	15.0	13.0	1.5
5	15.4	14.1	2.0
6	15.8	13.8	2.2
7	15.7	13.1	1.4
8	15.1	13.6	1.9
9	15.4	13.3	1.4
10	15.6	13.2	1.9
11	15.5	13.6	1.9
Mean	15.4	13.3	1.9
Standard deviation	±0.3	±0.4	±0.3

OCLC–MS results and the original diesel fuel (without prior OCLC separation) quantitated by SFC is shown in Fig. 5. Similar correlation coefficients were obtained for each ring type as previously discussed in Fig. 4. The repeatability of this SFC method is shown in Table II. Excellent precision was obtained for eleven injections of the original diesel fuel in Fig. 3b over a 36-day period.

CONCLUSIONS

An improved SFC technique was developed to provide rapid hydrocarbon analysis of the aromatic ring distribution in diesel fuels ranging from 6.0 to 48.0% (w/w) total aromatics. The method is routine, not operator intensive, and applicable to different refinery streams without prior OCLC separation and solvent evaporation. The precision of the SFC data was excellent. Work is currently underway to improve the resolution between each hydrocarbon fraction and to analyze other petroleum fuels.

ACKNOWLEDGEMENTS

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