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DETAILED CHARACTERIZATION OF THE PHYSICAL AND CHEMICAL PROPERTIES OF THE REFORMULATED FACE DIESEL FUELS: FD2B, FD4B, AND FD7B

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Detailed Characterization of the Physical and Chemical Properties of the Reformulated FACE Diesel Fuels: FD2B, FD4B, and FD7B

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TABLE OF CONTENTS

FIGURES

TABLES

ACRONYMS

1-D	one-dimensional
2-D	two-dimensional
ASTM International	Formerly the American Society for Testing and Materials
COA	certificate of analysis
CI	cetane index
CN	cetane number
CPChem	Chevron Phillips Chemical Company
CRC	Coordinating Research Council
DCN	derived cetane number
DHA	detailed hydrocarbon analysis
DOE	U.S. Department of Energy
FACE	Fuels for Advanced Combustion Engines (CRC)
FBP	final boiling point
FD	FACE diesel (used to refer to the blend reported on here, as in FD2A)
FIA	fluorescent indicator adsorption
FID	flame ionization detector
FIMS	field ionization mass spectrometry
GC	gas chromatography/chromatographic
GCxGC	2-dimensional gas chromatography
IBP	initial boiling point
IQT	ignition quality tester
LC	liquid chromatography
MS	mass spectrometry/spectrometric
n-	normal (as in normal paraffins)
NMR	nuclear magnetic resonance
NREL	National Renewable Energy Laboratory
ORNL	Oak Ridge National Laboratory
PAH	polycyclic aromatic hydrocarbon
PIONA	paraffins, isoparaffins, olefins, naphthenes, and aromatics
PNNL	Pacific Northwest National Laboratory
RT	retention time
SFC	supercritical fluid chromatography
SOAP	saturates, olefins, aromatics, and polars
SPE	solid phase extraction
TOF	time-of-flight
WSD	wear scar diameter

ACKNOWLEDGMENTS

EXECUTIVE SUMMARY

This report documents the results of detailed analyses of the physical and chemical properties of three FACE Diesel Fuels that were reformulated: FD2B, FD4B, and FD7B. The original matrix of FACE Diesel Fuels was designed by the Fuels for Advanced Combustion Engines (FACE) Working Group of the Advanced Vehicle/Fuel/ Lubricants (AVFL) Committee of the Coordinating Research Council (CRC) and blended and made commercially available for sale by ChevronPhillips Chemical Company (CPChem). The FACE Diesel Fuels matrix is built around three fuel properties of primary importance to the performance of combustion engines: ignition quality (represented by cetane number, CN); fuel chemistry (represented by aromatics content); and a measure of back-end volatility (T90). This standardized matrix of research fuels was developed to enable combustion researchers to determine the effects of diesel fuel properties on engine performance and to cross-compare results across different engine platforms and different laboratories. To aid the efforts to relate engine performance to fuel composition, previously the FACE Working Group conducted detailed chemical and physical analyses of the original set of FACE Diesel Fuels. That CRC report was published in July, 2010.

To enable international sales, three of the fuels (#2, #4, & #7) were subsequently reformulated to replace components having only US registration with components having both international and US registrations. (The original and reformulated fuels are designated by the suffixes "A" and "B", respectively). The design targets were the same for the reformulated and original fuels.

The purpose of the current project was to characterize as fully as possible the chemical and physical properties of the reformulated fuels and to compare them with the properties of the original fuels. AVFL-19 working group members composed of representatives from the energy companies, US national labs, and a Canadian national lab performed the analyses that are included in this report. A suite of ASTM tests were run to measure: cetane number [measured by engine and ignition quality tester (IQT) methods]; cetane index; distillation properties; aromatics, saturates, and olefins content; elemental C and H contents; S and N contents; bromine number; specific gravity; net heat of combustion; kinematic viscosity; cloud point; pour point; flash point; and lubricity.

In addition to the ASTM tests, several emerging advanced characterization techniques were conducted by the national labs to obtain more detailed chemical and structural information for the fuels. These techniques included: gas chromatography-field ionization mass spectrometry (GC-FIMS) coupled with paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) analysis and detailed hydrocarbon analysis (DHA); one- and two-dimensional (2-D) gas chromatography-mass spectrometry (GCMS); 2-D gas chromatography using a flame ionization detector (FID); and nuclear magnetic resonance (NMR). Each analysis offers a different perspective on the makeup of the fuels.

All of the reformulated fuels were found to meet the cetane, aromatics level, and T90 design targets at least as well as the original fuels. Compared to the original FACE#2 fuel (FD2A), the reformulated fuel (FD2B) appears to have: significantly less isoparaffins; significantly more cycloparaffins; less monoaromatics; and more diaromatics. Compared to the original FACE#4 fuel (FD4A), the reformulated fuel (FD4B) appears to have: slightly less monoaromatics and slightly more diaromatics. Compared to

the original FACE#7 fuel (FD7A), the reformulated fuel (FD7B) appears to have: more monoaromatics and less diaromatics. All of the reformulated fuels appear to have more methyl-substituted naphthalenes and the diphenyl alkanes in the original FD7A fuel appear to have been eliminated. This is good as naphthalenes are more representative of the diaromatics in commercial ULSDs than diphenyl alkanes.

NMR results, which characterize individual carbon atoms rather than whole molecules, indicate that the reformulated fuels have greater quantities of poly-aromatic carbons and greater amounts of alkyl substituents on aromatic rings. The reformulated versions of FD2 and FD4 have lower paraffinic carbon content than the original versions, while cycloparaffinic-type carbons increased for the reformulated FD2 and decreased for the reformulated FD7.

It is hoped that engine and combustion researchers will include the use of the FACE Diesel Fuels in their tests and use the detailed information in this and the previous report to better relate performance and emissions in engines to the physical and chemical properties of fuels.

1. BACKGROUND

This report presents the results of detailed physical and chemical analyses of reformulations of three FACE Diesel Fuels: #2 (FD2B), #4 (FD4B), and #7 (FD7B). The original matrix of FACE Diesel Fuels was designed by the Fuels for Advanced Combustion Engines (FACE) Working Group of the Advanced Vehicle/ Fuel/Lubricant (AVFL) Committee of Coordinating Research Council (CRC) and blended and made commercially available for sale by ChevronPhillips Chemical Company (CPChem). The original fuels are designated by the suffix "A".

As shown in Figure 1 below, the matrix is built around three fuel properties of primary importance to the performance of combustion engines: ignition quality (represented by cetane number, CN); fuel chemistry (represented by aromatics content); and a measure of back-end volatility (T90). For the most part, these fuels were prepared from refinery based blendstocks.
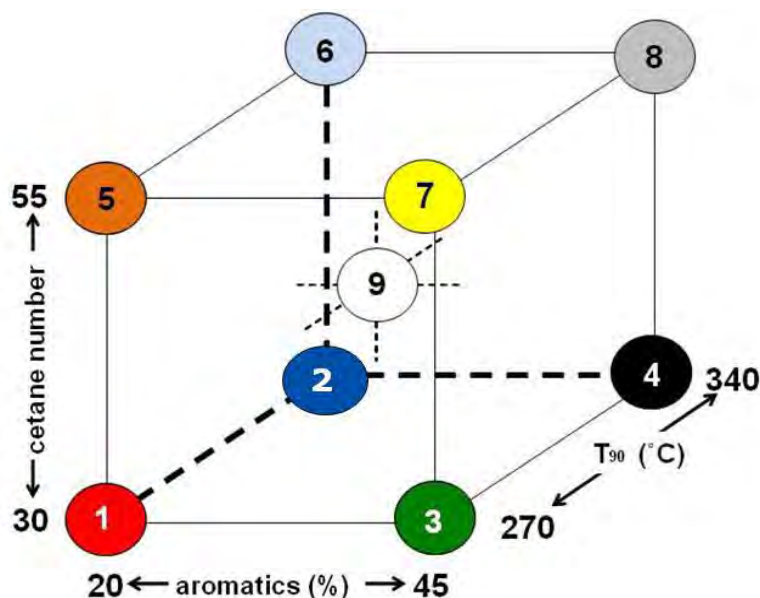
Figure 1: FACE Diesel Fuels Design Matrix

This standardized matrix of research fuels was developed to enable combustion researchers to determine the effects of diesel fuel properties on engine performance and to cross-compare results across different engine platforms and different laboratories. To aid the efforts to relate engine performance to fuel composition, previously the FACE Working Group conducted detailed chemical and physical analyses of the original set of FACE Diesel Fuels (1, 2).

To enable international sales, three of the fuels (#2, #4, & #7) were subsequently reformulated to replace components having only US registration with components having both international and US registrations.   The target properties were the same as those of the original fuels.

The purpose of the current project was to characterize as fully as possible the chemical and physical properties of the reformulated fuels and to compare with the properties of the original fuels. Several organizations contributed analyses that are included in this report. A suite of ASTM tests were run to measure: cetane number [measured by engine and ignition quality tester (IQT) methods]; cetane index; distillation properties; aromatics, saturates, and olefins content; elemental C and H contents; S and N contents; bromine number; specific gravity; net heat of combustion; kinematic viscosity; cloud point; pour point; flash point; and lubricity.

In addition to the ASTM tests, several emerging advanced characterization techniques were used to obtain more detailed chemical and structural information for the fuels. These techniques included: gas chromatography-field ionization mass spectrometry (GC-FIMS) coupled with paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) analysis and detailed hydrocarbon analysis (DHA); one- and two-dimensional (2-D) gas chromatography-mass spectrometry (GCMS); 2-D gas chromatography using a flame ionization detector (FID); and nuclear magnetic resonance (NMR). Each analysis offers a different perspective on the makeup of the fuels.

The report is organized into sections based on the different analytical techniques:

- Section 2 includes the traditional ASTM-type diesel fuel analyses
- Section 3 presents results from 1D GC-MS
- Section 4 discusses results from PIONA and DHA analyses to characterize the hydrocarbon fractions having boiling points up to 392˚F (200˚C)
- Section 5 contains the results of saturate-olefin-aromatic-polar (SOAP) solid phase extraction analysis for hydrocarbons that boil above 392˚F
- Section 6 includes the results that characterize the hydrocarbons over the full boiling range using several techniques including: 2D-GC FID, PIONA + GC-FIMS, and PIONA + solid phase extraction GC-MS
- Section 7 compares the results from various methods
- Section 8 covers characterization by ^{1}H and ^{13}C NMR

References:
1. Alnajjar, M.; Cannella, B.; Dettman, H.; Fairbridge, C.; Franz, J.; Gallant, T.; Gieleciak, R.; Hager, D.; Lay, C.; Lewis, S.; Ratcliff, M.; Sluder, S.; Storey, J.; Yin, H.; Zigler, B., "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1 (2010).
2. Gallant, T.; Franz, J.; Alnajjar, M; Storey, J.; Lewis, S.; Sluder, S.; Cannella, W.; Fairbridge, C.; Hager, D.; Dettman, H.; Luecke, J.; Ratcliff, M.; Zigler, , "Fuels for Advanced Combustion Engines Research Diesel Fuels: Analysis of Physical and Chemical Properties", SAE Paper 2009-01-2769 (2009).

2. RESULTS FROM ASTM STANDARD TESTS

In this section, results of the standardized ASTM tests are discussed. CanmetENERGY, BP, Phillips 66, and a contract laboratory conducted the analyses. Also included are results from CPChem's analyses reported on their fuel certificates of analysis (COAs). As noted in the report of the original FACE Diesel Fuels (1), since the matrix was designed to be a research set of fuels, the properties of some of the fuels fall outside the ranges for which the ASTM tests were designed. This can lead to larger levels of variation in the results from laboratory-to-laboratory and test-to-test than is typically obtained for marketplace fuels.

Tabular data for the fuels are located in Table 2.9 at the end of this chapter.

2.1 ASTM TEST RESULTS FOR THE DESIGN VARIABLES (CETANE, AROMATICS, T90 DISTILLATION)

Cetane numbers (CN) for each fuel were measured using the engine-based ASTM D613 method (2) and are plotted in Figure 2.1. Design target values are indicated by the dashed lines across each group of columns. For a given fuel, a blank spot indicates that a particular lab did not analyze that fuel. For the two low cetane reformulated fuels (FD2B and FD4B), the average values are close to the target values and slightly higher than the average values for the original fuels (FD2A and FD4A). For the high cetane reformulated fuel (FD7B) the average value is quite a bit lower than the target value of 55, but slightly higher than the average value of the original fuel (FD7A). For the FD7 fuels, it was difficult to simultaneously meet the constraints of high cetane number and high aromatics content. The lab-to-lab reproducibility for fuels FD4B and FD7B are within the ASTM limits, but not for fuel FD2B where there is greater lab-to-lab variability in the measured values.
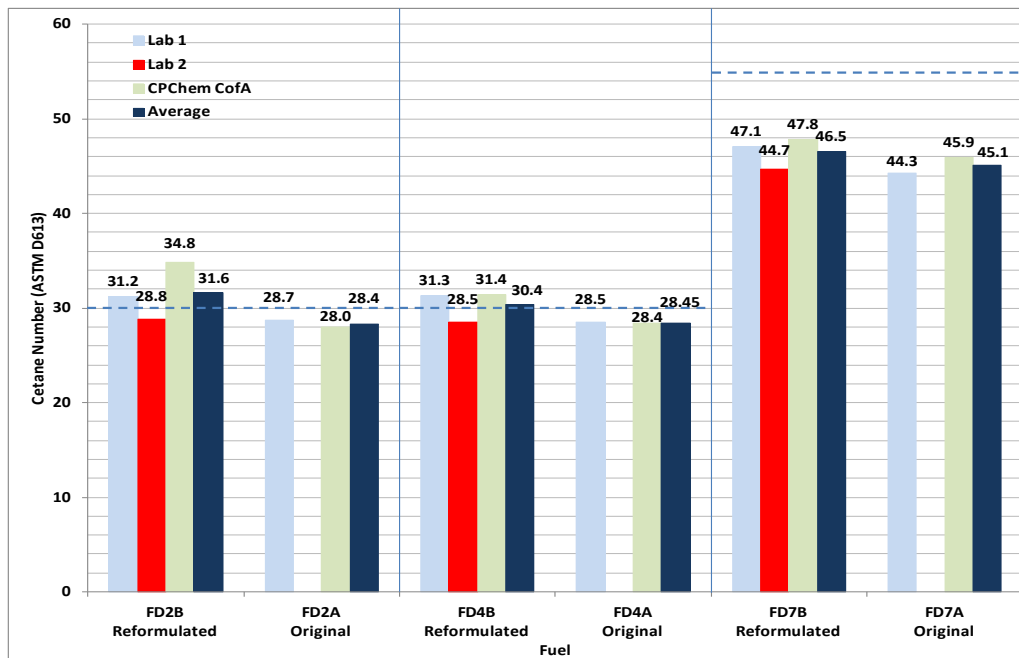
Figure 2.1   Cetane number results from ASTM D613 tests

The aromatics content for each fuel was determined by the Fluorescence Indicator Adsorption (FIA) method of ASTM D1319 (3). Results are presented in Figure 2.2. The dashed lines represent the original design target values. For all three reformulated fuels, the average values are close to the target values. However, there is quite a bit of lab-to-lab variability, especially for fuel FD4B. For fuel FD2B, most of the variability is from the results of one lab. Variability was also seen previously for the original fuels, although the magnitude appears to be larger for the reformulated fuels. At the 20 vol% level, the reproducibility of the ASTM D1319 test is reported to be 2.5-3 vol% and 3.5 vol% at the 45 vol% level (3). The larger reproducibility range of the FACE Diesel Fuels may be attributed to the fact that these formulations fall somewhat outside the envelope of conventional fuel formulations for which the ASTM tests were designed. Comparing the average results of the reformulated and original fuels obtained by labs that ran both fuels, it appears that the aromatics values are slightly higher for the reformulated vs. the original version of FD2, lower for the reformulated vs. the original version of FD4, and slightly higher for the reformulated vs. the original version of FD7.
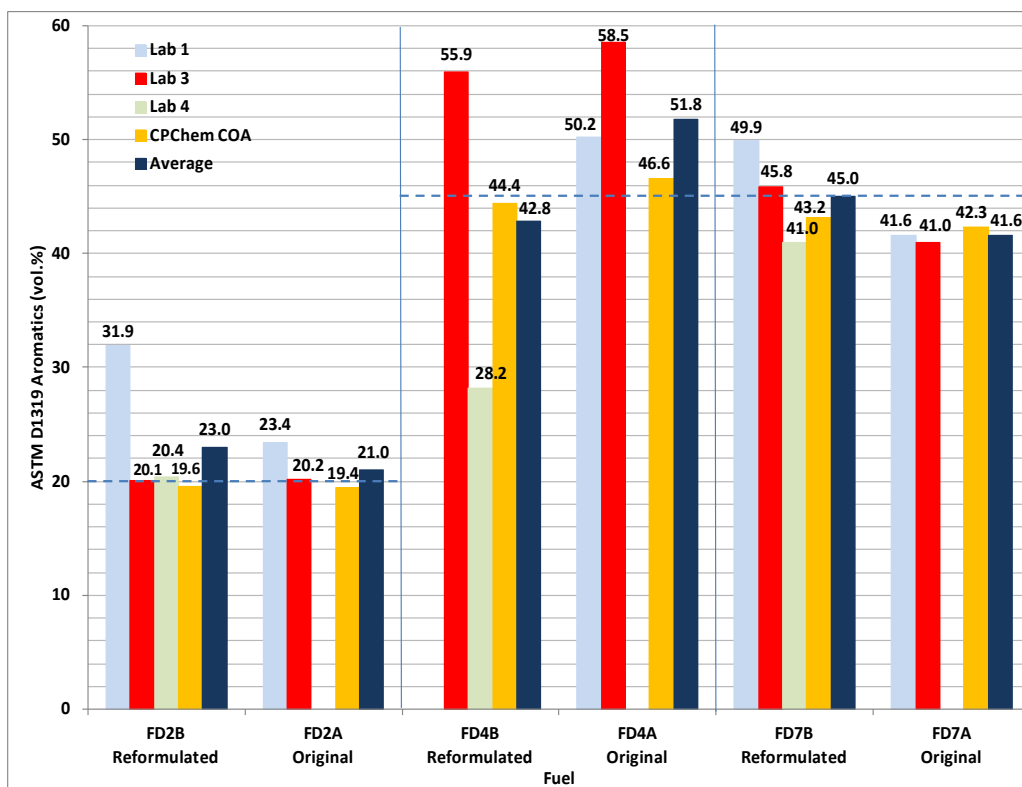
Figure 2.2   Fuel aromatics content results from ASTM D1319 tests

T90 values were measured using method ASTM D86 (4) and are reported in Figure 2.3. There is excellent agreement between the labs for all fuels. The values for the reformulated fuels and the original fuels are very close to each other and to the target values.
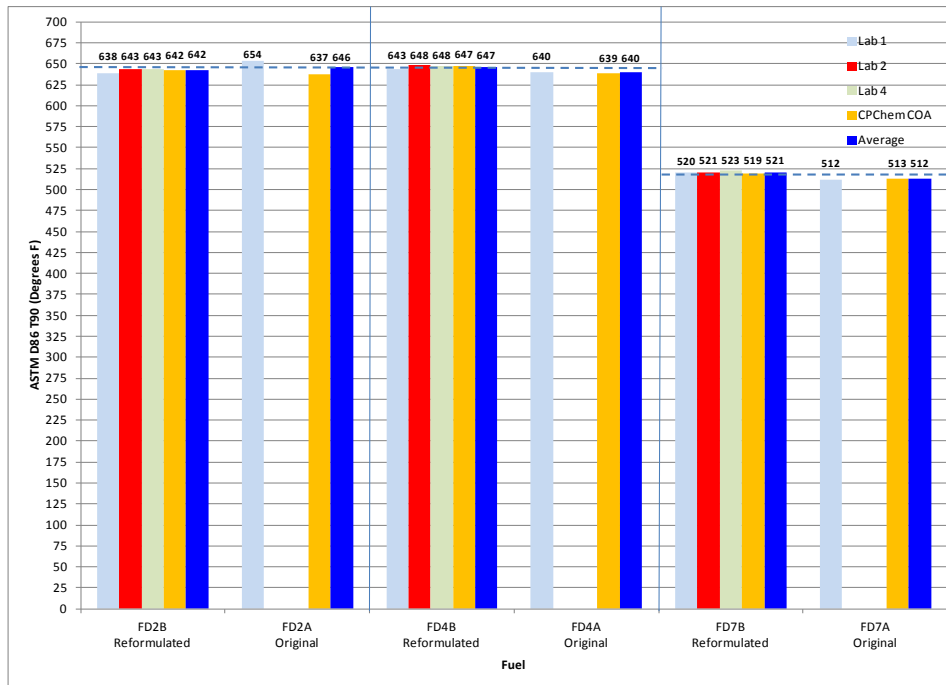
Figure 2.3 Fuel 90% recovery temperature (T90) results from ASTM D86 distillation tests

2.2 MEASUREMENTS OF OTHER PHYSICAL PROPERTIES BY ASTM METHODS

ASTM methods were used to measure the specific gravities, kinematic viscosities, cloud points, flash points, net heats of combustion, cetane index, complete distillation curves, and lubricities of all of the fuels. These are summarized below and in Table 2.9 located at the end of this chapter.

2.2.1   Derived Cetane Number and Cetane Index

In addition to characterizing the fuels' reactivity by cetane number (discussed in Section 2.1), derived cetane numbers (DCN's) and cetane indices were also calculated using measurements from ASTM methods D6890 (5) and D976 (6), respectively. Although the measurements were conducted in several labs for the reformulated fuels (but only one previously for the original fuels), the reproducibility was excellent and so only the average values are reported here (but individual values are reported in Table 2.9). DCN's and cetane index results are presented in Figure 2.4, along with the cetane number values. The DCN values of the reformulated versions of each fuel are virtually identical to the values for the original versions. For the lower cetane fuels, FD2 and FD4, the DCN's are slightly higher than the cetane numbers for both the original and reformulated versions, but essentially identical for the higher cetane FD7 fuels. The cetane indices for the reformulated versions of all three fuels are significantly higher than those of the original fuels. It is interesting that the differences are much larger than the differences obtained from the cetane number measurements.   Also, the cetane indices for both the reformulated and original versions of the two high T90 fuels (FD2 and FD4) are significantly higher than the cetane number values, while the values are close for the low T90 fuel (FD7). It should be noted that the D976 method was originally developed for straight run fuels, catalytically cracked stocks, and their blends and may not be entirely applicable to the FACE Diesel Fuel blends.
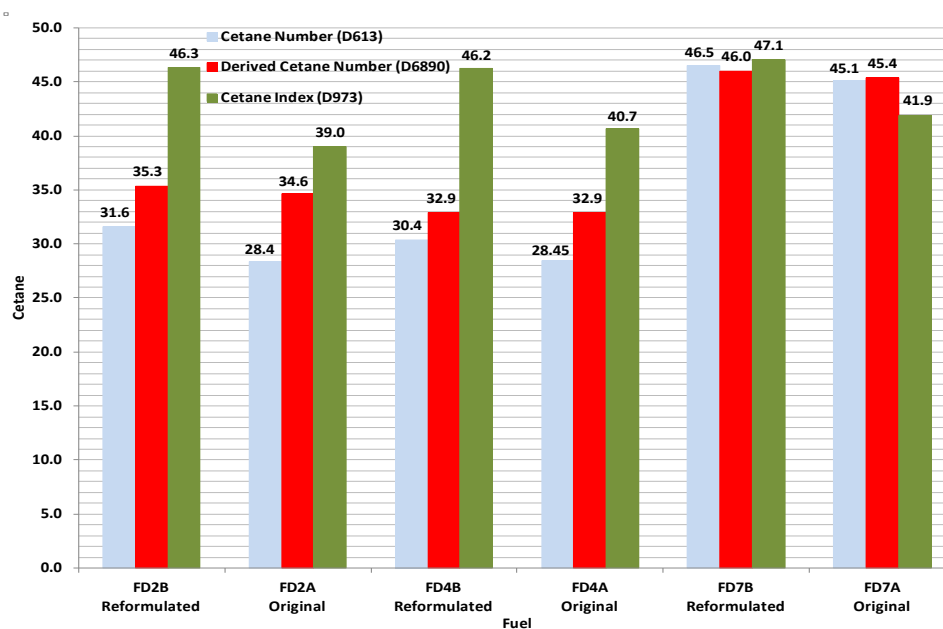
Figure 2.4 Cetane Values from Various ASTM Tests

2.2.2 Distillation

Two different ASTM methods were used to characterize the distillation properties of the fuels: D86 and D2887 (7). The D86 values obtained from four different labs were very close. The average values are plotted in Figure 2.5, and the detailed data are tabulated in Table 2.9. The temperature corresponding to a given recovery fraction X is designated as TX (i.e., T90 indicates the temperature at which 90% of the fuel has been vaporized and recovered). The reformulated fuels are indicated by solid point connectors while the original fuels are indicated by dashed point connectors. As expected based on T90's for the reformulated fuels, FD7B has a higher back end volatility (lower T60-T100 boiling points) than FD2B and FD4B. However, FD4B has a higher front end volatility (lower T0-T30 boiling points) than FD7B.
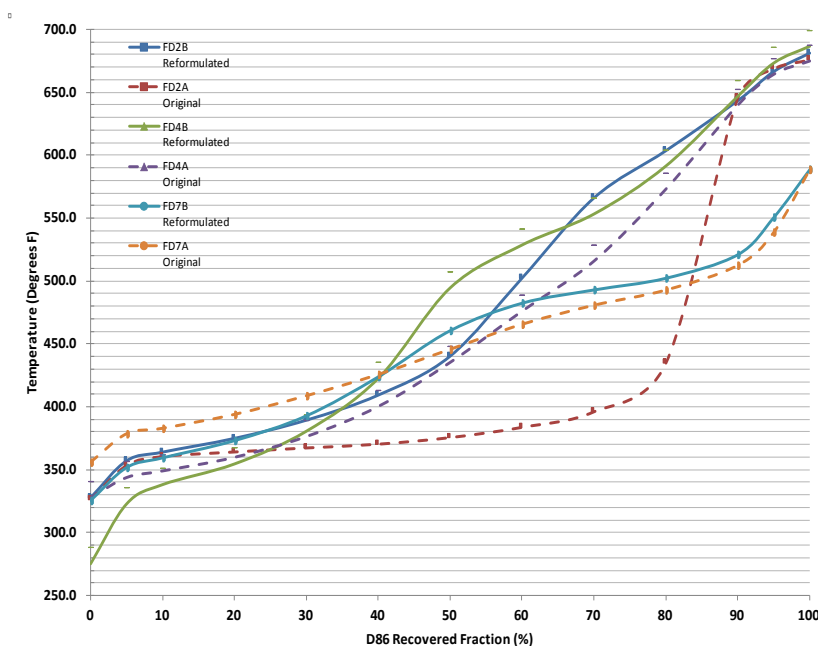
Figure 2.5   Distillation curves from ASTM D86 analyses

For a given pair of reformulated and original fuels, although the heavy ends (T90, T95, and EP) are extremely close due to having T90 as one of the matrix design targets, other parts of the distillation curve are different. The most noticeable difference is in the middle portion (T30-T70) of the distillation curves for the FD2 fuels. The original fuel FD2A has a very flat profile in this region, while the reformulated fuel FD2B has a much steeper profile, more characteristic of market diesel fuels. The flat profile of FD2A indicates that this fuel has a significant fraction (~75%) of hydrocarbons that boil below 400˚F. The maximum temperature difference (170˚F) between the two fuels occurs in the T70-T80 region. For the FD4 fuels, the reformulated fuel has a lower initial boiling region (47˚F difference at the initial boiling point and 20˚F difference at T5), but a higher mid boiling region (T40-T80), with the largest difference of 53˚F at T60. For the FD7 fuels, the front end boiling points of the reformulated fuel are somewhat lower than those of the original fuel (maximum difference of 30 ˚F occurs at the initial boiling point, T0), but slightly higher boiling points in the middle (maximum difference of 17˚F at T60).

The second method used to evaluate the volatility characteristics of the fuels was ASTM D2887 (7). In this method, the boiling range distribution is simulated by the use of a gas chromatograph (GC) where a nonpolar column is used to elute the components of the sample in order of increasing boiling point. The column temperature is raised at a reproducible linear rate and the area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of n-paraffins covering the boiling range expected in the sample. The results of these analyses are plotted in Figure 2.6 and the detailed data is included in Table 2.2. The reformulated fuels are indicated by solid point connectors while the original fuels are indicated by dashed point connectors. Although the exact values are different (and the results are reported in terms of wt% rather than vol%), the trends are very similar to those obtained from the ASTM D86 analyses. The original fuel FD2A has a very flat profile in the middle (T30-T70) region, while the reformulated fuel FD2B has a much steeper profile. FD7B has a higher back end volatility (lower T60-T100 boiling points) than FD2B and FD4B. However, FD4B has a higher front end volatility (T0.5) than FD7B.
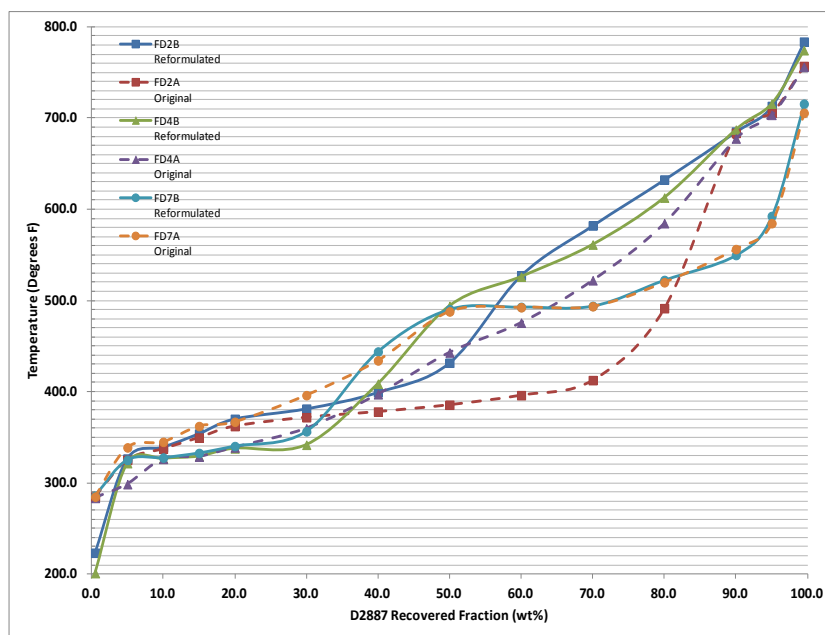
Figure 2.6   Distillation curves from ASTM D2887 analyses

2.2.3 Specific Gravity

The specific gravities of the fuels were measured using ASTM method D4052 (8). The lab-to-lab reproducibility was excellent, and the individual values are reported in the Summary Table 2.9 at the end of this chapter. The average values are listed in Table 2.1 below.   For fuels FD2 and FD4, the specific gravities of the reformulated fuels are slightly higher (1.3-2%) than those of the original fuels while for FD7 the values are within 0.2% of each other.

Table 2.1   Fuel Specific Gravities (ASTM D4052)

	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Specific Gravity	0.8195	0.8035	0.8461	0.8355	0.8356	0.8372

2.2.4 Kinematic Viscosities

Kinematic viscosity measurements were made at 40˚C using ASTM method D445 (9). The average values are listed in Table 2.2. Values for the reformulated versions of fuels FD2 and FD4 were slightly higher than for the original fuels, while for FD7 fuels, the values for the reformulated version were slightly lower than the values for the original version. Lab-to-lab reproducibility was better for the reformulated fuels than for the previously measured original fuels.

Table 2.2   Fuel Kinematic Viscosities (ASTM D445)

	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Kinematic Viscosity (cSt)	2.472	1.806	2.014	1.783	1.504	1.670

2.2.5 Cloud Point

ASTM Method D2500 (10) was used to measure cloud points. As shown below in Table 2.3, the cloud points of the reformulated fuels appear to be very close to those of the original fuels. Values for fuels FD2 and FD4 were <-54˚C while values for the FD7 fuels were in the -18 to -22˚C range.

Table 2.3   Fuel Cloud Points (ASTM D2500)

	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Cloud Point (˚C)	<-54	<-54	<-54	<-54	-18.4	-21.5

2.2.6 Flash Point

Flash points were measured using the ASTM closed cup method D93 (11). Lab-to-lab differences were <9˚F, well within the ASTM reproducibility guidelines, and lab-averaged values are reported below.   The most noticeable difference between the reformulated and original fuels was for FD4 where the flash

point was significantly lower for the reformulated fuel. The flash point for FD4B is slightly below the US ULSD#2 minimum specification of 125.6˚F (52˚C) (although ULSD specs don't apply to these fuels, diesel engine testers should take note).

Table 2.4   Fuel Flash Points (ASTM D93)

	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Flash Point (˚F)	134.7	128.0	112.3	134.7	140.3	149.7

2.2.7   Net Heat of Combustion (NHC)

ASTM method D240 (12) was used to measure net heats of combustion. Tests were run in two labs for the reformulated fuels vs. one lab previously for the original fuels. Lab-to-lab reproducibility for the reformulated fuels was excellent with all values within 0.6% or better. Values for the reformulated fuels were within <0.35 % of the original fuels. Average measured values are reported below in Table 2.5. The higher aromatics FD4 and FD7 fuels have lower gravimetric heats of combustion than FD2, consistent with the lower gravimetric (but higher volumetric) energy content of aromatics.

Table 2.5   Fuel Net Heats of Combustion (ASTM D240)

	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
NHC (BTU/lb)	18512	18553	18255	18269	18272	18211

2.2.8   Lubricity

Because the lubricity of diesel fuels (i.e. , their ability to reduce friction between moving parts) can impact the wear of components of diesel engines, several ASTM test methods have been developed to measure lubricity. In the ASTM D6079 (13) high frequency reciprocating test rig method used here, lubricity is characterized by the diameter of the wear scar (WSD) that is formed on a hardened steel ball when it is oscillated across a hardened steel plate immersed in the fuel: the smaller the WSD, the better the lubricity.   The reformulated versions of FD2 and FD4 have better lubricities than the original versions. However, it should be noted, with the exception of FD4B, that all of the values are higher than the US ULSD#2 maximum specification of 520 microns. So users of these FACE Diesel Fuels may want to consider adding a lubricity additive when performing engine tests.

Table 2.6   Fuel Lubricity (ASTM D6079)

	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
WSD (microns)	540	673	464	636	641	625

10

2.3   MEASUREMENTS OF CHEMICAL PROPERTIES BY ASTM METHODS

The various types of hydrocarbons in the fuels were characterized by several ASTM techniques, including: fluorescent indicator adsorption (FIA), supercritical fluid chromatography (SFC), and mass spectrometry (MS). In addition, the carbon, hydrogen, nitrogen, and sulfur contents and bromine number were measured.

2.3.1   Hydrocarbons by Fluorescent Indicator Adsorption (FIA)

The FIA method of ASTM D1319 (3) characterizes the fuel composition in terms of vol.% of three classes of hydrocarbons: saturates (also known as alkanes or paraffins); aromatics; and olefins (or alkenes). The saturates category includes not only normal (or straight chain) alkanes, but also isoparaffins (or branched alkanes) and cycloparaffins (or fully saturated ring structures/naphthenes).

FIA tests were run in four labs (including the manufacturer's). The average results for the three hydrocarbon classes are presented in Figure 2.7.   The ranges of results are included in parentheses. The fuels components are predominantly characterized as saturates or aromatics, with significantly smaller amounts of olefins. The smallest ranges (indicating best lab-to-lab reproducibility) were obtained for the FD7 fuels. The poorest reproducibility was obtained for FD4B.
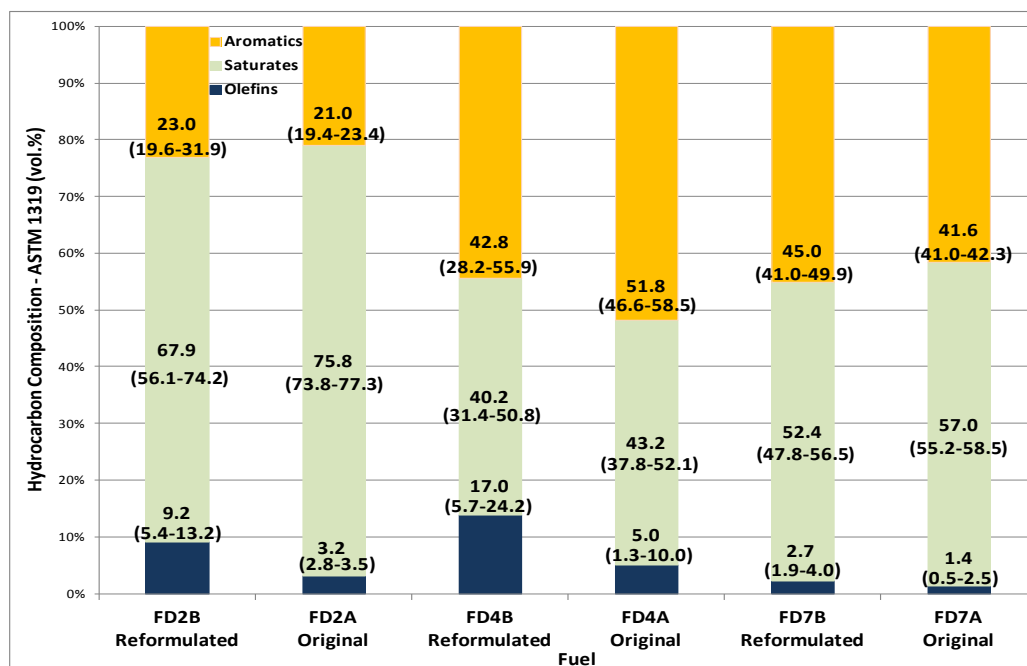
Figure 2.7   Fuel compositions by fluorescent indicator absorption (ASTM D1319 analyses)

As mentioned in the discussion of the aromatics FIA results in Section 2.1, the larger reproducibility range may possibly be attributed to the fact that the FACE Diesel Fuel formulations fall somewhat outside the envelope of conventional fuel formulations for which the ASTM tests were designed. Furthermore, many compounds that can be present in the fuels exhibit characteristics of more than one of these hydrocarbon classes. A good example of this is tetralin (also known as tetrahydronaphthalene

11

or benzocyclohexane). The resulting molecule has the appearance of a benzene ring fused to a cyclohexane ring. So tetralin could be identified either as an aromatic or a saturate, depending on the characterization technique used. For ASTM D1319, the separation of these classes of compounds is dependent upon the affinity of adsorption of the compounds on silica gel. This may introduce some ambiguity into the interpretation of results. For this reason, other ASTM methods were additionally used to provide more information about the hydrocarbon makeup of the fuels.

2.3.2   Aromatics by Supercritical Fluid Chromatography (SFC)

The SFC method of ASTM D5186 (14) is reported to be statistically more precise than D1319 for determination of aromatic content of diesel fuels (3). This method separates the hydrocarbons into three fractions: monoaromatics, polyaromatics, and nonaromatics and characterizes the composition in terms of mass %.   The reformulated fuel samples were analyzed by four labs. The original samples were previously analyzed by two labs. Bar graphs of the average results are presented in Figure 2.8. Also included in the figure are the range of values obtained from the different labs (in parentheses below the average values) and average values for total aromatics determined by summing the average values for the mono- and polyaromatics (displayed to the right of each bar graph).
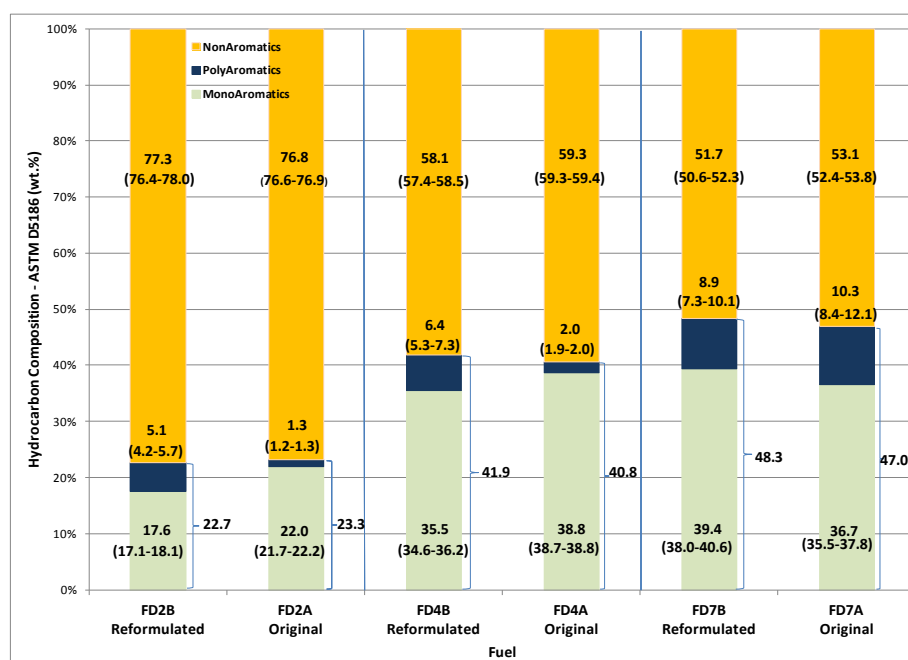
Figure 2.8 Fuel compositions by supercritical fluid chromatography (ASTM D5186 analyses)

The lab-to-lab reproducibility is excellent as evidenced by the very narrow range of values that were obtained for each hydrocarbon class for each fuel. The results indicate that the FD7 fuels have the highest total aromatics and polyaromatics contents while the FD2 fuels have the lowest.   The total aromatics content of all three reformulated fuels are very close to those of the original fuels, although the polyaromatics content of reformulated fuels FD2B and FD4B are slightly higher than their original fuel counterparts, FD2A and FD4A, respectively.

2.3.3 Hydrocarbons by Mass Spectrometry (MS)

This analysis by ASTM method D2425 (15) enables a significantly greater degree of fuel composition determination than either ASTM D1319 or D5186. In this method, samples are separated into saturate and aromatic fractions which are then further characterized by MS. The amounts of eleven different hydrocarbon classes can be determined: paraffins (normal + isoparaffins); mono- and other noncondensed cycloparaffins; condensed dicycloparaffins; condensed tricycloparaffins; monoaromatics; indanes + tetralins; C_nH_{2n-10} compounds (indenes, etc.); naphthalenes (or diaromatics); C_nH_{2n-14} compounds (acenaphthenes, i.e. two fused aromatic rings joined by a saturated C5 ring); C_nH_{2n-14} compounds (acenaphthylenes, i.e two fused aromatic rings joined by an unsaturated C5 ring); and triaromatics. The results from a single set of analyses by one lab are summarized in Figure 2.9. To the right of each bar graph are the mass % of the individual hydrocarbon classes constituting 0.5% or more of the fuel.
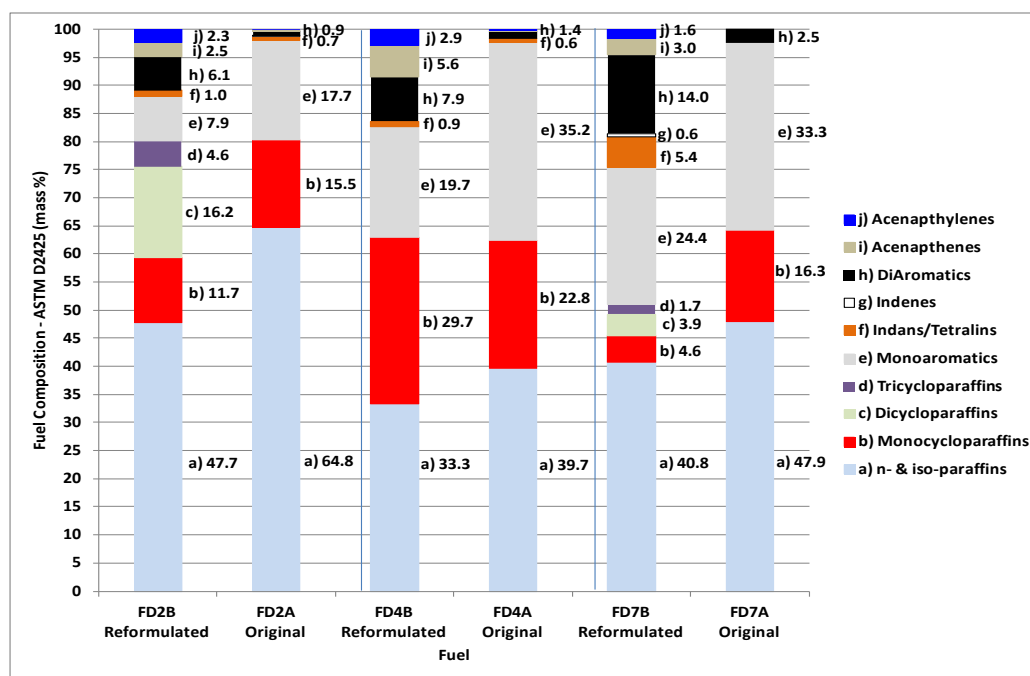
Figure 2.9 Fuel compositions by mass spectrometry (ASTM D2425 analyses)

Not all of the hydrocarbon classes were detected in all of the fuels. Triaromatics were not detected in any of the fuels. The analyses indicate that all of the fuels contain components from the paraffinic (normal and iso); monocycloparaffinic; monoaromatic; and diaromatic hydrocarbon classes. These results are consistent with the types of compounds present in commercial ULSD's. Of the reformulated fuels, FD2B has the highest amount of normal-, iso- and dicyclo-parafffins; FD4B has the highest amount of monocycloparaffins; FD7B has the highest amount of aromatic compounds. Compared to the original fuels, the reformulated fuels appear to contain a wider variety of hydrocarbon classes, especially in the polyaromatics classes. Also, the reformulated fuels appear to have a lesser quantity of monoaromatics and a greater quantity of polyaromatics.

2.3.4 Elemental Analyses

Carbon and hydrogen contents were measured by three labs for the reformulated fuels and two labs for the original fuels using ASTM method D5291 (16). The results are listed below in Table 2.7. Values for the reformulated fuels and the original versions are very close to each other.   The slightly lower carbon values and higher hydrogen values for the FD2 fuels compared to the other fuels are consistent with the slightly lower aromatics content of the FD2 fuels.

Sulfur content was measured by three labs using a variety of methods: ASTM D5453 (17), D5623 (18), and D7039 (19). The results were very close to each other and so average values are reported below in Table 2.7. All fuels had sulfur contents of 7 ppm (wt) or lower, thus falling into the ultra-low sulfur category.   Nitrogen content was measured by one lab using ASTM D4629 (20). All fuels had nitrogen contents below 2 ppm (wt).

Note that the CHSN total has an allowable range of 100 +/- 2 wt.%.

Table 2.7   Elemental Analyses Results

	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
C (wt.%)	85.7	85.7	86.8	86.8	87.1	86.7
H (wt.%)	13.7	13.9	12.6	13.0	12.6	12.8
S (ppmw)	3.4	0.4	4.4	<0.5	7.0	1.3
N (ppmw)	0.2	1.7	0.5	0.9	0.6	0.9

2.3.5 Bromine Number Analyses

Bromine number is a measure of the aliphatic unsaturation (olefin content) of petroleum distillates. Results measured by one lab using ASTM method D1159 (21) are tabulated below. All of the fuels had bromine contents <0.75 g Br/100 g sample. This indicates that all of the fuels had a very low level of olefinic-type unsaturation. For comparison, pure mono-olefins have values >60 (the fewer the number of carbon atoms, the greater the value) and di-olefins have values >200. The method is essentially insensitive to the unsaturation of aromatics, as mono- and di-aromatics have values at or very close to 0.

Table 2.8 Bromine Number Results

	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Br No.	0.72	0.15	0.61	0.29	0.53	0.25

Table 2.9 Summary Data for ASTM Standard Tests

Specific Tests	FACE Fuels (by FD/CPChem Designation)					
	FD2B Reformulated	**FD2A** Original	**FD4B** Reformulated	**FD4A** Origina1	**FD7B** Reformulated	**FD7A** Original
Design Variable Levels						
Cetane Number	Low	Low	Low	Low	High	High
Aromatic Content (vol %)	Low	Low	High	High	High	High
T_{90} (F)	High	High	High	High	Low	High
Cetane Number by Engine Method (ASTM D613)						
-Lab 1	31.2	28.7	31.3	28.5	47.1	45.9
-Lab 2	28.8		28.5		44.7	
-CPChem C of A	34.6	28.0	31.4	28.4	47.8	44.3
-Average	31.6	28.4	30.4	28.45	46.5	45.1
Cetane Index (calculated)ASTM D976						
-Lab 1	47.4	39.0	46.3	40.7	44.9	41.9
-Lab 3	45.2		46.1		49.2	
-Average	46.3	39.0	46.2	40.7	47.05	41.9
Derived Cetane Number (ASTMD689						
-Lab 2	34.6		32.5		44.9	
-Lab 4	35.9		33.1		46.0	
-Lab 5	35.5	34.6	33.0	32.9	47.0	45.4
-Average	35.3	34.6	32.9	32.9	46.0	45.4
Hydrocarbons by FIA (ASTM D1319)						
Aromatics, Volume %						
-Lab 1 (& repeat)	31.9	23.4		51.2(49.1)	49.9	41.6
-Lab 3 (& repeat)	20.1	20.2	55.9	57.0 (60.0)	45.8	41.0
-Lab 4	20.4		28.2		41.0	
-CPChem C of A	19.6	19.4	44.4	46.6	43.2	42.3
-Average	23.0	21.0	42.8	51.8	45.0	41.6
Olefins (vol %)						
-Lab 1 (& repeat)	12.0	2.8		12.4 (7.7)	2.3	1.2
-Lab 3 (& repeat)	6.0	3.5	5.7	3.6 (3.7)	1.9	0.5
-Lab 4	5.4		21.0		2.5	
-CPChem C of A	13.2	3.3	24.2	1.3	4.0	2.5
-Average	9.2	3.2	13.4	5.0	2.2	1.4
Saturates (Vol %)						
-Lab 1 (& repeat)	56.1	73.8		36.4 (43.2)	47.8	57.2
-Lab 3 (& repeat)	73.9	76.3	38.4	39.4 (36.2)	52.4	58.5
-Lab 4	74.2		50.8		56.5	
-CPChem C of A	67.2	77.3	31.4	52.1	52.8	55.2
-Average	67.9	75.8	40.2	43.2	52.4	57.0

Table 2.9 Summary Data for ASTM Standard Tests

| Specific Tests | FACE Fuels (by FD/CPChem Designation) | | | | | |
	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Origina1	FD7B Reformulated	FD7A Original
Aromatics by SFC [ASTM D5186]						
-Total Aromatics (mass %)						
-Lab 1	22.0	23.1	41.5	40.7	48.2	46.2
-Lab 2	23.6		42.6		47.8	
-Lab 3	22.2	23.4	41.5	40.6	47.9	47.6
-Lab 4	22.8		41.9		49.5	
-Average	22.7	23.3	41.9	40.7	48.3	46.9
-Monoaromatics (mass %)						
-Lab 1	17.2	21.7	35.4	38.8	39.8	37.8
-Lab 2	18.1		35.7		38.0	
-Lab 3	18.0	22.2	36.2	38.7	40.6	35.5
-Lab 4	17.1		34.6		40.6	
-Average	17.6	22.0	35.5	38.8	39.4	36.7
-Polynuclear Aromatics (mass %)						
-Lab 1	4.8	1.3	6.2	2.0	8.4	8.4
-Lab 2	5.6		6.9		9.8	
-Lab 3	4.2	1.2	5.3	1.9	7.3	12.1
-Lab 4	5.7		7.3		10.1	
-Average	5.1	1.25	6.4	1.95	8.9	10.25
-Non Aromatics: Calculated by difference (mass %)						
-Lab 1	78.0	76.9	58.5	59.3	51.8	53.8
-Lab 2	76.4		57.4		52.3	
-Lab 3	77.8	76.6	57.4	59.4	52.1	52.4
-Lab 4	77.2		58.1		50.5	
Hydrocarbon Types By Mass Spectrometry (mass %) (ASTM D2425) (Lab 1)						
Paraffins	47.7	64.8	33.3	39.7	40.8	47.9
Monocycloparaffins	11.7	15.5	29.7	22.8	4.6	16.3
Dicycloparaffins	16.2	0	<0.1	0	3.9	0
Tricycloparaffins	4.6	0	<0.1	0	1.7	0
Total Napthenes	32.5	15.5	29.7	22.8	10.2	16.3
Total Saturates	80.2	80.3	63.0	62.5	51.0	64.2
Alkylbenzenes	7.9	17.7	19.7	35.2	24.4	33.3
Indans/Tetralins	1.0	0.7	0.9	0.6	5.4	0
Indenes (CnH2n-10)	<0.1	0.1	<0.1	0	0.6	0
Napthalene	<0.1	0.3	<0.1	0.5	0.2	2.5
Alkylnapthalenes	6.1	0.6	7.9	0.9	13.8	0
Acenapthenes (CnH2n-14)	2.5	0.2	5.6	0.1	3.0	0
Acenapthylenes (CnH2n-16)	2.3	0.1	2.9	0.2	1.6	0
Tricyclic Aromatics (CnH2n-18)	<0.1	0	<0.1	0	<0.1	0
Total PNAs	10.9	1.2	16.4	1.7	18.6	2.5
Total Aromatics	19.8	19.7	37.0	37.5	49.0	35.8

16

Table 2.9 Summary Data for ASTM Standard Tests

Specific Tests	FACE Fuels (by FD/CPChem Designation)					
	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Origina1	FD7B Reformulated	FD7A Original
Elemental Analysis (ASTM D5291)						
Carbon, wt%						
-Lab 1	86.18	86.12	87.26	86.90	87.38	86.57
-Lab 2	84.61		86.01		86.73	
-Lab 3	86.26	85.29	87.10	86.68	87.21	86.88
-Average	85.68	85.71	86.79	86.79	87.11	86.73
Hydrogen, wt%						
-Lab 1	13.65	13.64	12.56	12.77	12.51	12.59
-Lab 2	13.76		12.70		12.54	
-Lab 3	13.76	14.23	12.63	13.23	12.59	12.93
-Average	13.72	13.94	12.63	13.00	12.55	12.76
Sulfur by Ultraviolet Fluorescence (ppm) (ASTM D5453)						
-Lab 1	3.3	0.4	4.0	0.1	5.9	1.4
-CPChem C of A	3.1	0.3	3.8	<1	8.1	2.0
Sulfur (ppm) (ASTM D5623) (Lab 3)	4.0	<0.5	5.7	<0.5	6.9	<0.5
Sulfur (ppmw) (ASTM D7039) (Lab 2)	3		4		7	
Nitrogen (mg/L) (ASTM D4629) (Lab 3)	0.2	1.68	0.5	0.87	0.6	0.9
Bromine No. (g Br/100g) (ASTM D1159)	0.72	0.15	0.61	0.29	0.53	0.25
Specific Gravity (ASTM DD4052)						
-Lab 1	0.8207	0.8037	0.8468	0.8359	0.8361	0.8375
-Lab 2	0.8204		0.8468		0.8361	
-Lab 3	0.8200	0.8030	0.8460	0.8352	0.8354	0.8366
-CPChem C of A	0.8173	0.8037	0.8454	0.8355	0.8357	0.8375
-Average	0.8195	0.8035	0.8461	0.8355	0.8356	0.8372
Flash Point (°F) (ASTM D93)						
-Lab 1	138.2	128.0	114.8	139.0	140.0	149.0
-Lab 2	135.5		115.7		140.9	
-CPChem C of A	130.4	134.4	106.4	130.4	140.1	150.3
-Average	134.7	131.2	112.3	134.7	140.3	149.7
Net Heat of Combustion (BTU/lb) [ASTM D240]						
-Lab 1	18,456	18,553	18,231	18,269	18,253	18,211
-Lab 4	18,568		18,278		18,291	
Kinematic Viscosity at 40°C (cSt) [ASTM D445]						
-Lab 1	2.469	1.960	2.001	1.785		1.759
-Lab 2	2.488		2.025		1.505	
-Lab 3		1.652		1.781		1.581
-Lab 4	2.459		2.017		1.502	
-Average	2.472	1.806	2.014	1.783	1.504	1.670
Cloud Point (°C) (ASTM D2500)						
-Lab 1	<-54	-51	<-54	-50	-18.3	-21
-Lab 2	<-72		-61		-19	
-Lab 3	-59	-59	-49.2	-59	-17.8	-22
HFRR Lubricity[WSD (µm)](ASTM D6079)	540	673	464	636	641	625

Specific Tests		FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original1	FD7B Reformulated	FD7A Original
Distillation (°F) [ASTM D86]							
Lab 1:	IBP	330	345	277	324	327	357
	5%	355	354	322	342	351	377
	10%	363	358	336	348	358	380
	15%	368	360	344	353	364	387
	20%	374	363	351	359	373	392
	30%	389	368	379	376	393	408
	40%	411	374	418	400	424	425
	50%	440	380	491	433	460	445
	60%	497	388	527	474	482	465
	70%	563	402	552	513	493	480
	80%	602	454	589	571	502	492
	90%	638	654	643	640	520	512
	95%	663	672	670	664	548	538
	FBP	680	679	684	674	595	583
Recovered (mL)		97.9	98.3	97.8	97.7	98.1	97.5
Residue (mL)		1.1	1.2	1.3	1.4	1.3	1.7
Loss (mL)		1.0	0.5	0.9	0.9	0.6	0.8
Lab 2:	IBP	318		270		316	
	5%	357		326		351	
	10%	363		339		359	
	20%	373		355		372	
	30%	387		380		392	
	40%	406		425		423	
	50%	439		498		460	
	60%	504		528		482	
	70%	566		552		493	
	80%	604		592		502	
	90%	643		648		521	
	95%	668		674		552	
	FBP	677		684		579	
Recovered (mL)		97.7		97.9		97.7	
Residue (mL)		1.6		1.7		2.0	
Loss (mL)		0.7		0.4		0.3	
Lab 4:	IBP	335		281		332	
	5%	357		323		354	
	10%	365		338		362	
	20%	376		359		376	
	30%	392		382		395	
	40%	410		424		426	
	50%	441		497		462	
	60%	503		531		483	
	70%	568		555		494	
	80%	605		593		503	
	90%	643		648		523	
	95%	668		674		551	
	FBP	683		690		603	
Recovered (mL)		97.7		97.7		98.1	
Residue (mL)		1.4		1.5		1.3	
Loss (mL)		0.9		0.8		0.6	

Table 2.9. Summary Data for ASTM Standard Tests

Specific Tests		FACE Fuels (by FD/CPChem Designation)					
		FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Origina1	FD7B Reformulated	FD7A Original
Distillation (°F) [ASTM D86]							
CPChem CofA:	IBP	328	307	273	332	327	355
	5%	358	353	321	346	351	380
	10%	365	363	336	350	359	386
	20%	376	365	355	361	372	396
	30%	389	367	383	377	392	409
	40%	409	367	423	401	423	426
	50%	440	371	493	438	460	446
	60%	505	379	528	478	482	466
	70%	567	390	554	518	493	481
	80%	604	416	591	575	502	494
	90%	642	637	647	639	521	513
	95%	666	666	674	664	552	539
	FBP	685	673	688	675	579	594
Recovered (mL)		97.6	97.9	97.9	98.5	97.7	98.3
Residue (mL)		1.4	1.0	1.5	1.0	2.0	1.0
Loss (mL)		1.0	1.1	0.6	0.5	0.3	0.7
Average:	IBP	328	326	276	328	325	356
	5%	357	353	323	344	352	378
	10%	34	360	338	349	359	383
	20%	375	364	355	360	373	394
	30%	389	367	381	376	393	409
	40%	409	370	423	400	424	426
	50%	440	376	495	435	461	446
	60%	502	384	529	476	482	466
	70%	566	396	553	516	493	481
	80%	604	435	591	573	502	493
	90%	643	646	647	640	521	512
	95%	666	669	673	664	551	539
	FBP	681	676	686	675	589	589
Simulated Distillation (°F) (mass %) [ASTM D2887]							
0.50%		223.2	284.7	200.8	283.3	285.8	284.7
5%		326.5	325.0	321.4	298.4	325.0	338.7
10%		339.1	337.3	326.5	326.1	327.6	344.8
15%		353.8	349.5	329.0	328.6	332.6	362.1
20%		370.0	362.1	337.6	338.7	340.2	366.8
30%		381.2	371.8	341.6	359.6	356.4	396.0
40%		399.2	378.0	408.6	397.0	443.8	434.1
50%		431.6	385.5	493.9	442.8	490.3	487.8
60%		527.4	396.0	525.9	475.5	492.8	492.4
70%		582.1	412.5	561.2	522.0	493.9	493.5
80%		632.5	491.4	612.7	584.6	522.3	519.8
90%		685.0	683.6	687.2	677.5	549.7	556.2
95%		713.1	705.6	715.6	703.4	592.5	584.6
99.50%		783.7	757.0	774.3	756.0	715.6	705.6

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3. 1D GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) ANALYSIS

The 1-D GC-MS analyses were conducted by Oak Ridge National Laboratory (ORNL). The resulting chromatograms show the compounds that make up significant portions of the fuel. Minor compounds (at parts-per-million concentrations) that do not make up significant portions of the fuel are neglected in this visualization of the fuel hydrocarbons. Figures 3.1 through 3.6 show the results of GC-MS analysis for the reformulated and original fuels. The plots show the abundance of the compounds (in arbitrary units). The analyses for the original fuels were conducted when those fuels were manufactured.
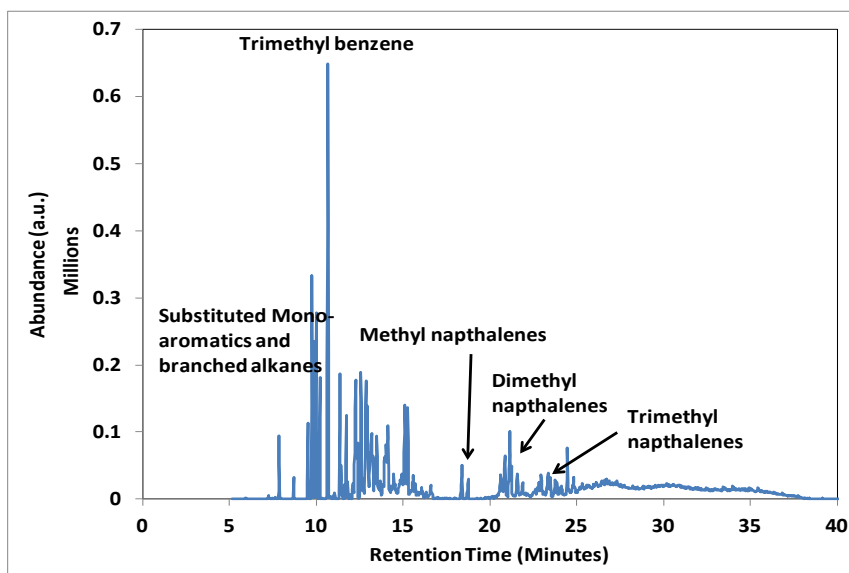
Figure 3.1 1D GC-MS Chromatogram of Reformulated Fuel FD2B
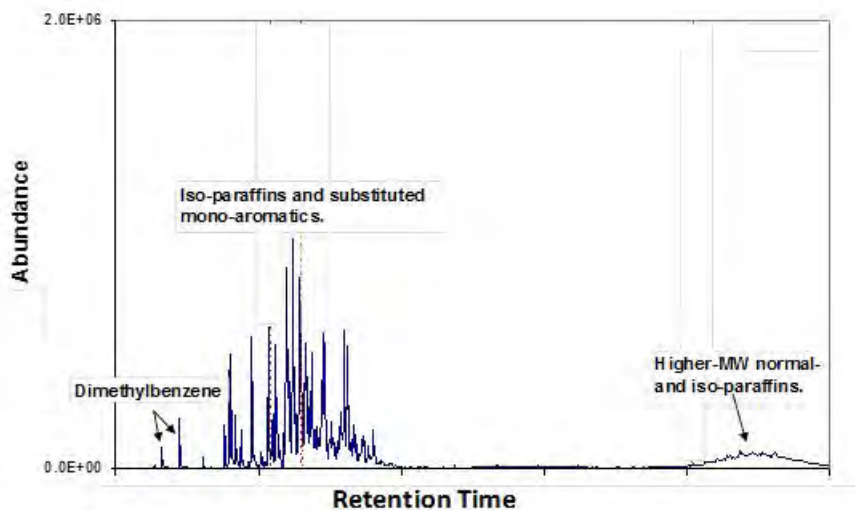
Figure 3.2 1D GC-MS Chromatogram of Original Fuel FD2A
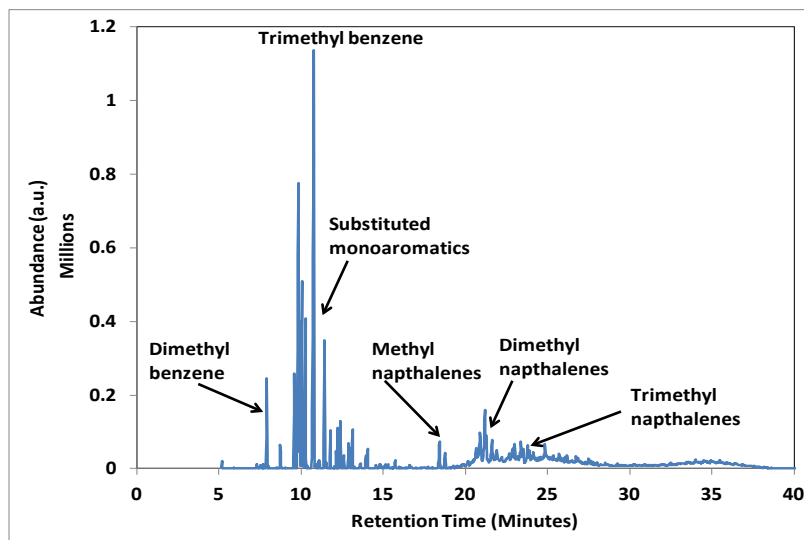
Figure 3.3   1D GC-MS Chromatogram of Reformulated Fuel FD4B
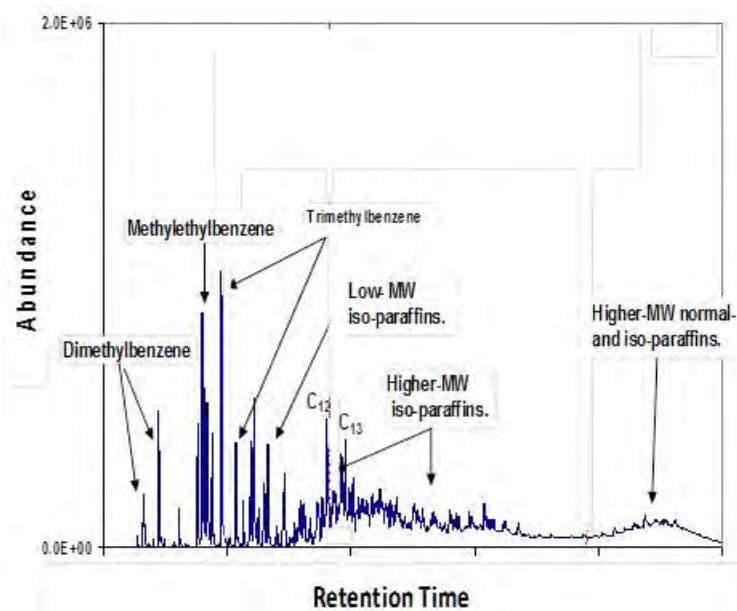
Figure 3.4   1D GC-MS Chromatogram of Original Fuel FD4A

The FD2 and FD4 fuels are the high-T_{90}, low-CN fuels. The original FD2A has a bimodal distribution of hydrocarbons, with most of the fuel mass made up of very volatile monoaromatics and isoparaffins plus some paraffins at boiling points between 650 and 750°F. There is essentially no hydrocarbon in the boiling point range of middle distillates. This is consistent with the flat portion in the middle section of the distillation curve for this fuel. The reformulated FD2B fuel has components similar to those in FD2A, but also appears to have mono-, di-, and tri-naphthalenes in the intermediate range. FD4A has a similar hydrocarbon distribution as FD2A, but with the addition of isoparaffins in the intermediate boiling range. FD4B has similar components as FD4A, but also includes mono-, di-, and tri-methyl naphthalenes in the intermediate region.

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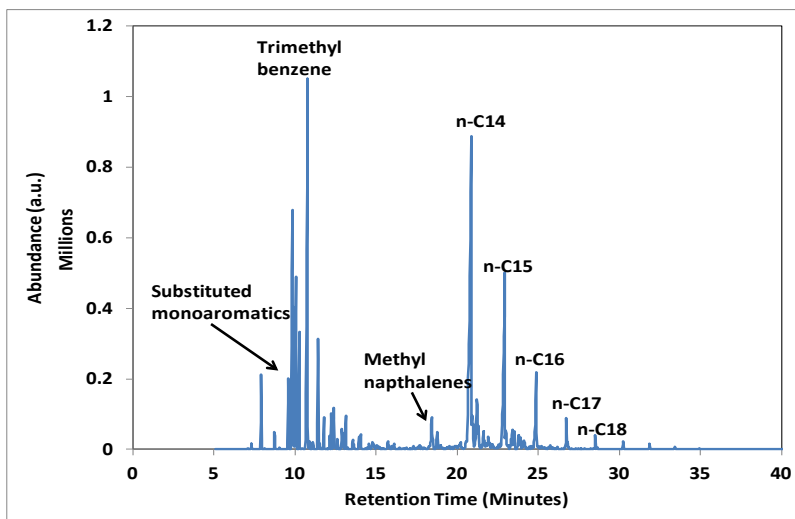
Figure 3.5   1D GC-MS Chromatogram of Reformulated Fuel FD7B
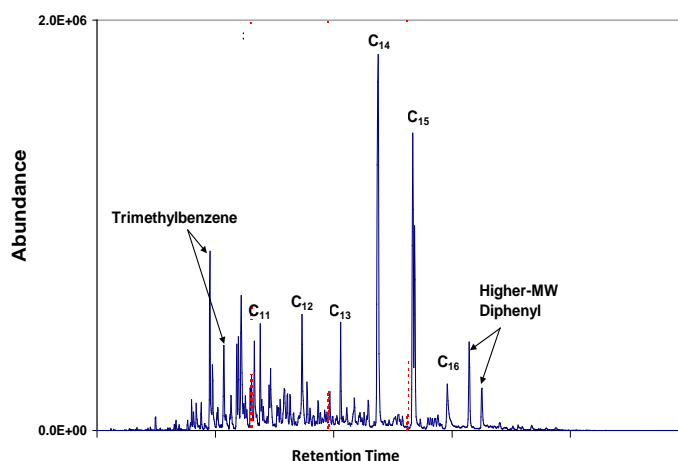
Figure 3.6 1D GC-MS Chromatogram of Original Fuel FD7A

The FD7 fuels are the low-T_{90}, high-aromatics fuels. Both the reformulated, FD7B, and original, FD7A, fuels exhibit the characteristic monoaromatic blending stream at the low end of the distillation, again suggesting that the most volatile components of the fuels can be thought of as having a low CN.   Both fuels also exhibit n-paraffins and isoparaffins from C_{11}–C_{16}, but not in a normal distribution. FD7B appears to contain relatively more of the n-paraffins and less of the monaromatics than FD7A. FD7A contains higher-molecular weight diphenyl compounds near the end of the distillation which FD7B does not appear to have.

4. HYDROCARBON CHARACTERIZATION FOR FRACTIONS BOILING UP TO 392°F

4.1 PIONA

4.1.1 Introduction

The PIONA analysis described in ASTM D5443 (1) and ASTM D6839 (2) is intended to determine the carbon number ($C_5 - C_{11}$) distribution of **p**araffins, **i**soparaffins, **o**lefins, **n**aphthenes and **a**romatics for samples which boil at less than 392°F(200°C). The PIONA technique uses complex multidimensional gas chromatography to separate the compounds to appropriate hydrocarbon groups (3).

CanmetENERGY uses PIONA to complement other advanced hydrocarbon characterization methods such as GC-FIMS and SPE-GC-MS which have no capability to completely characterize hydrocarbon streams which consist of compounds boiling below 392°F. The combination of those techniques with PIONA enables composition determination over the whole carbon number range. The combined GC-FIMS/PIONA and SPE-GC-MS/PIONA data results can be found in sections 4.2 and 4.3, respectively. Two assumptions were made for the PIONA results: cycloparaffins (naphthenes) were all monocycloparaffins and aromatic group includes all identified monoaromatic peaks, especially alkylbenzenes.

Technical details of PIONA analysis and instrumentation used in CanmetENERGY was described in details in the CRC report on the original FACE Diesel Fuels (4)

4.1.2 Results and Discussion

A summary of the SOAP (<u>S</u>aturates, <u>O</u>lefins, <u>A</u>romatics, <u>P</u>olars) contents determined by PIONA analyses and presented as weight percents for the original and reformulated FACE fuels is given in Table 4.1 and Figure 4.1. The detailed PIONA carbon number distribution of hydrocarbon types for the reformulated and original FACE fuels are presented in Tables A.1 to A.6 in Appendix A. (Note that due to rounding some of the sums appear to be off by +/- 0.01)

Table 4.1 Summary of PIONA hydrocarbon composition (wt %) that boils below 392°F

Hydrocarbon Type	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Saturates	8.04	7.10	4.72	2.99	2.43	9.30
Olefins	0.15	2.50	0.26	0.08	0.61	0.10
Aromatics	27.81	46.22	34.14	36.19	32.39	19.76
Polars	0.00	0.00	0.00	0.00	0.00	0.00
Total	**36.00**	**55.83**	**39.12**	**39.26**	**35.43**	**29.15**

The hydrocarbon composition for the reformulated FACE fuel 4B is similar to the original FD4A. The other two reformulated fuels (FD2B and FD7B) show meaningful changes in aromatic content as compared to originally designed blends. FD7B has more monoaromatic compounds than FD7A. Reformulated FD2B has less aromatic hydrocarbons than FD2A that boil at less than 392°F. The majority of aromatic compounds presented in the fuels are focused around C9.
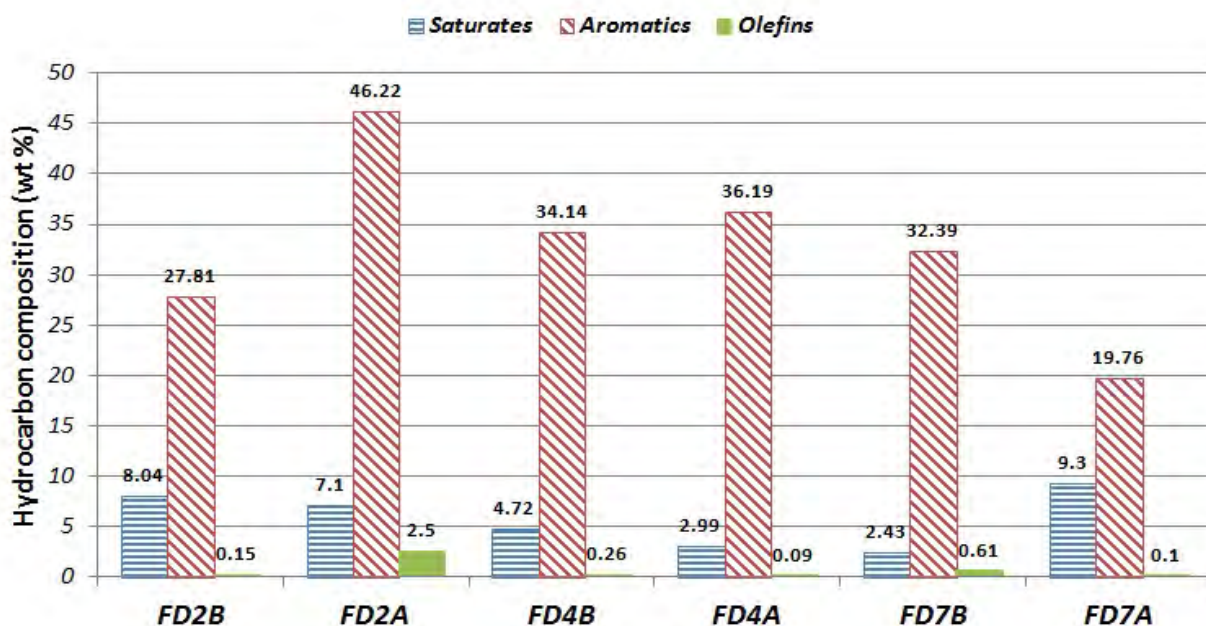
Figure 4.1 PIONA data for hydrocarbons boiling below 392°F/200°C

The original PIONA technique was developed for hydrocarbon samples having final boiling points of no higher than 392°F/200°C. The CanmetENERGY PIONA instrument was equipped with a prefractionator to remove fractions of sample that boil above 392°F/200°C. Theoretically, the fractionation cut occurs just before elution of dodecane (boiling point of 417-424 °F (214-218°C)). However, in actuality, as discussed in section 7 of the previous FACE fuels report (4), when the sample contains a large amount of paraffins around C12 the aromatic content will be overestimated and the saturates will be underestimated. Authors of this report did not notice this phenomenon in previous work on determination of the hydrocarbon content for regular diesel fuels, but did see it in the case of some prepared blends. For the original and reformulated versions of FD2 which have significant amounts of paraffins in this problematic region, the PIONA analyses significantly under-report the saturates and over-report the aromatics. This is evident later in section 5.1 when these results are compared with those from the 2D GC techniques that do not require sample fractionation.

4.1.3   References

1. ASTM International, Standard Test Method for Paraffin, Naphthene, and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates Through 200°C by Multi-Dimensional Gas Chromatography, ASTM D5443-04 (ASTM International, Pennsylvania, 2004).

2. ASTM International, Test Method Hydrocarbon Types, Oxygenated Compounds and Benzene in Spark Ignition Engine Fuels by Gas Chromatography, ASTM D6839-02 (ASTM International, PA, 2002).

3. Hsu, Ch.S., Analytical Advances for Hydrocarbon Research

4. Alnajjar, M.; Cannella, B.; Dettman, H.; Fairbridge, C.; Franz, J.; Gallant, T.; Gieleciak, R.; Hager, D.; Lay, C.; Lewis, S.; Ratcliff, M.; Sluder, S.; Storey, J.; Yin, H.; Zigler, B.; "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1 (2010).

4.2   DETAILED HYDROCARBON ANALYSIS

4.2.1   Introduction

Because of the issues with PIONA outlined in the previous section, detailed hydrocarbon analysis (DHA) was performed on the three reformulated FACE fuel diesel blends.

The DHA technique according to ASTM D6729 (1) covers the determination of individual hydrocarbon species in naphtha fractions with boiling ranges up to 392°F(200°C). Generally the DHA method is based on separation of individual components after running samples using a single, long (100 m) capillary column and quantification based on the flame ionization detector (FID). The DHA instrument operates with a prefractionator (used in the PIONA analyses) to remove fractions that boil above 392°F.

Good practice shows that for most cases the best solution is to use a better optimized PIONA technique.

4.2.2   Results and Discussion

The data after DHA analysis were transformed and recorded as carbon number (Appendix B, Tables B.1 to B.3) or boiling point distributions of selected hydrocarbon types (Appendix B, Tables B.4-B.6). Results in Table 4.2 and Figure 4.2 summarize data from Appendix B and present total values for saturates, olefins and aromatics. The DHA bulk hydrocarbon profiles are very similar to those obtained from PIONA analyses, suggesting that the same fractionation issues are also affecting the DHA results, especially for the FD2 fuels. Further, the accuracy of the DHA is reduced significantly due to fact that olefins, paraffins and aromatics tend to overlap in the region above C7. (Note that due to rounding some of the sums appear to be off by +/- 0.01).

Table 4.2 Summary of DHA hydrocarbon composition (wt %) that boils below 392°F

Hydrocarbon Type	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Saturates	3.40	6.91	7.30	3.42	5.17	8.07
Olefins	1.59	0.29	0	0.19	0.22	0.8
Aromatics	31.0	45.31	31.73	35.35	29.89	19.41
Unknown	0.01	3.32	0.08	0.31	0.15	0.88
Total	36.00	55.83	39.12	39.26	35.43	29.15
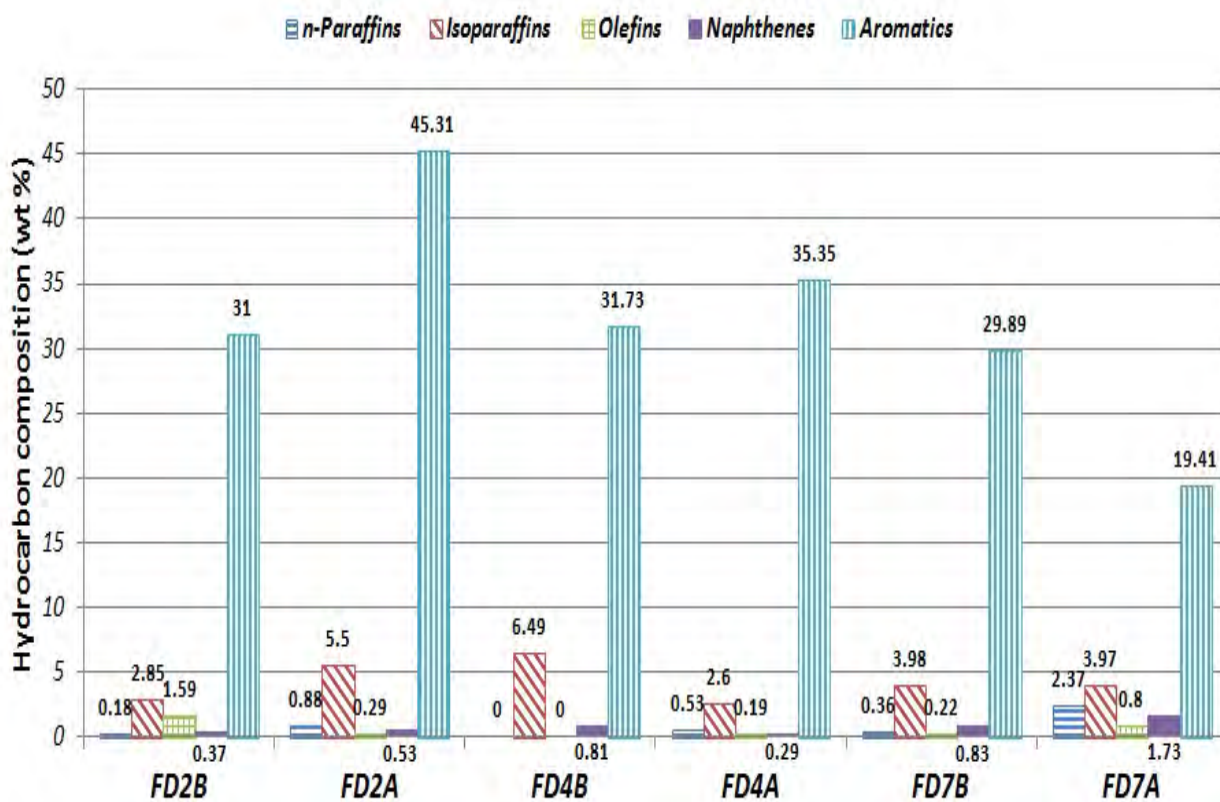
Figure 4.2   DHA data for hydrocarbons boiling below 392°F/200°C

4.2.3   References

1. ASTM International, *Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High Resolution Gas Chromatography,* ASTM D6729-01(2006)e1 (ASTM International, Pennsylvania, 2001).

5. HYDROCARBON CHARACTERIZATION FOR PETROLEUM FRACTIONS BOILING ABOVE 392°F

5.1 SOAP-SOLID PHASE EXTRACTION ANALYSIS

5.1.1 Introduction

Solid Phase Extraction (SPE) is an extraction technique based on selective partitioning of sample components between solid and liquid phase. The SPE analysis was used to separate petroleum samples with low polar content into **S**aturate, **O**lefin, **A**romatic, and **P**olar (SOAP) fractions (1). The SPE method is time efficient and environmentally friendly due to less solvent usage compared to other methods used for class separations such as ASTM D2007 (2) and/or ASTM D2549 (3). The SPE procedure with quantification of sample fractions boiling above 392°F(200°C) is outlined in Figure 5.1. The sample elutes through a cartridge filled with silica-based stationary phase using different solvents and/or solvent mixtures. The eluted fractions are concentrated to a known volume before being quantified using GC-FID (Agilent 6890). The FID's response is considered universal for hydrocarbons and is directly proportional to the mass flow rate of reduced carbon atoms. Saturate and aromatic fractions can be further investigated using GC-MS to identify and quantify their individual hydrocarbon components (ASTM D2786 for saturates, ASTM D3239 for aromatics). The detailed description of SPE procedure performed by CanmetENERGY in Devon can be found in a previous report (4).
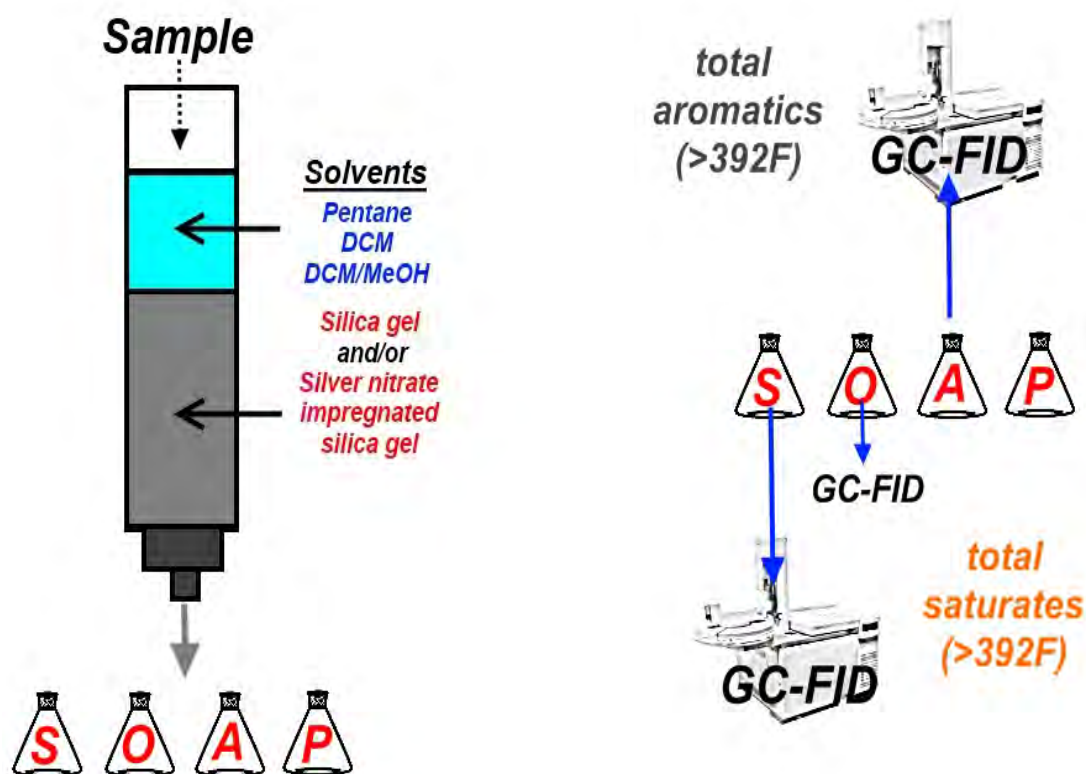
Figure 5.1   SPE procedure with quantification of sample Saturates (S), Olefins (O), Aromatics (A) and Polar (P) fractions boiling above 392°F (200°C). Saturates, Olefins and Aromatics contents determined by GC-FID. Polars concentration is estimated by subtracting the sum of S, O and A from 100%.

5.1.2   Results and Discussion

The data from SOAP-SPE analysis for the original and reformulated FACE fuel samples are shown in Table 5.1 and Figure 5.2. The amounts of material boiling above 392°F (200°C) were taken from simulated distillation (ASTM D2887) data. To get the full boiling point range report, the PIONA/DHA data has to be combined with SOAP-SPE data. Such information is presented in section 6.3.

Table 5.1 Summary of SPE hydrocarbon composition (wt %) that boils above 392°F/200°C

Hydrocarbon Type	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Saturates	54.8	34.9	51.7	56.5	47.3	42.5
Olefins	0.2	0.2	0.2	0.3	0.3	0.6
Aromatics	9.1	9.1	9.0	4.0	17.0	27.8
Polars	0.0	0.0	0.0	0.0	0.0	0.0
Total	**64.1**	**44.2**	**60.9**	**60.8**	**64.6**	**70.9**

One observation is that the total content of material boiling above 392°F (200°C) for reformulated FD2B is significantly higher than in the original FD2A. The FACE diesel #2B has more saturates than FD2A. Reformulated FD7B has less aromatic hydrocarbons than FD7A.
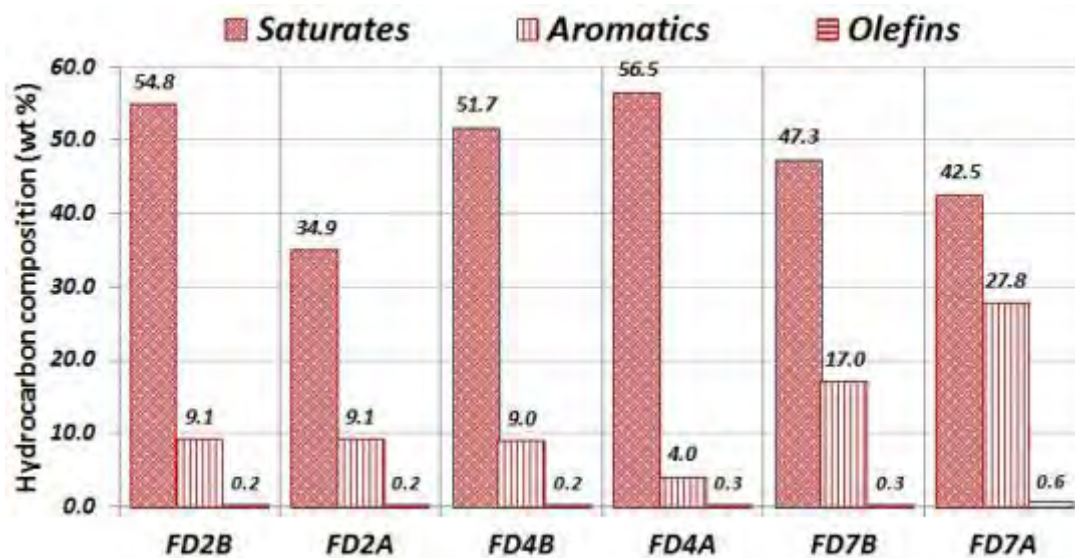
Figure 5.2 SOAP-SPE data for sample fraction boiling above 392°F/200°C

5.1.3 References

1. Fairbridge, C., et al., "Comparison of the characteristics of oil sands-derived diesel fuels and their blends with conventional diesel fuels," IASH 2000, 7th International Conference on Stability and Handling of Liquid Fuels, October 2000, Graz, Austria, Edited by Harry N. Giles (U.S. Department of Energy, Washington D.C., 2001).

2. ASTM International, *Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method,* ASTM D2007-03(2008) (ASTM International, Pennsylvania, 2008).

3. ASTM International, *Standard Test Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography*, ASTM D2549-02(2007) (ASTM International, Pennsylvania, 2008).

4. Alnajjar, M.; Cannella, B.; Dettman, H.; Fairbridge, C.; Franz, J.; Gallant, T.; Gieleciak, R.; Hager, D.; Lay, C.; Lewis, S.; Ratcliff, M.; Sluder, S.; Storey, J.; Yin, H.; Zigler, B.; "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1 (2010).

5.2   SOLID PHASE EXTRACTION - GAS CHROMATOGRAPHY-MASS SPECTROMETRY

5.2.1 Introduction

The purpose of hydrocarbon-type analyses such as ASTM D2786 (1) or D3239 (2) is to estimate the detailed hydrocarbon profiles of sample fractions boiling above 392°F (200°C). In the ASTM method D2786, the relative concentrations of noncyclic alkanes and six carbon naphthenic hydrocarbon types in the fuel **saturate** fraction is determined by mass spectrometry. The ASTM D3239 method uses mass spectrometry to determine 18 aromatic hydrocarbon types in the fuel **aromatic** fraction.

At CanmetENERGY, both ASTM procedures were built-in to the GC-MS system and used to perform the detailed hydrocarbon analysis of petroleum streams boiling above 392°F (200°C). The aromatic and saturate GC-MS data were combined with PIONA or DHA data (see sections 4.1 and 4.2) providing the total hydrocarbon type contents in full boiling range (IBP-FBP). Neat diesel samples were separated into saturate and aromatic fractions by a modified solid phase extraction (SPE) method developed by CanmetENERGY (formerly known as NCUT) (3). The resulting fractions were analyzed by capillary gas chromatography with flame ionization detector (GC-FID) to estimate total saturate and total aromatic content. The scheme of SPE-GC-MS is provided in Figure 5.3.
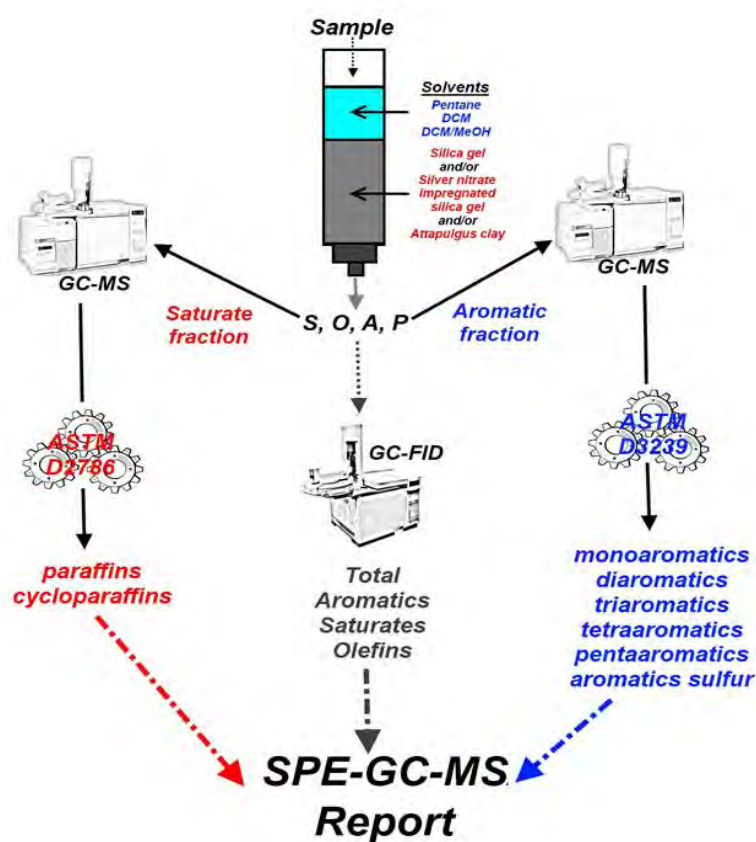
Figure 5.3 Hydrocarbon class separations by combining solid phase extraction and gas chromatography with mass spectrometry

5.2.2 Results and discussion

The SPE-GCMS analysis is an extension of the SOAP-SPE method presented earlier and offers a more detailed breakdown of the hydrocarbon classes composing the saturates and aromatic hydrocarbon types. Table 5.2 presents SPE-GCMS hydrocarbon composition for fraction boiling in range 392°F – FBP for reformulated and original FACE Diesel fuels. The complete SPE-GC-MS/PIONA report valid for full boiling point range is provided in tabular form in Appendix C.

It was previously mentioned in section 4.1.2 that the reformulated FD2B sample has more saturated hydrocarbons than the original FD2A sample. With the SPE-GCMS analyses, we observe that the main difference appears for the cycloparaffinic hydrocarbons where the concentrations are double those of the reformulated FD2B sample (see Figure 5.4).

According to Table 5.2 and Figure 5.5, the monoaromatic content is composed predominantly of alkylbenzenes and is lower for reformulated FD7B in comparison to original FD7A. The total diaromatics content is similar (~10 %) for both FD7B and FD7A fuels; however, there were differences within diaromatic types such as naphthocycloalkanes. Naphthocycloalkane content was decreased almost 10 times its original amount found in FD7A fuel (see Figure 5.6).

There is a relatively high correlation coefficient (R^2=0.9755) between FD2B and FD4B hydrocarbon composition (see figure 5.7), which suggests that the same feedstock source was used for both fuels in the 392˚F (200˚C) and higher temperature range. The correlation with FD7B is poorer (Figure 5.8).

Table 5.2 Summary of SPE-GCMS hydrocarbon composition (wt %) that boils above 392°F

Hydrocarbon Type	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Boiling range	392˚F (200°C)-FBP					
SATURATES	54.80	34.92	51.72	56.50	47.29	42.50
Total paraffins	24.66	22.15	17.45	28.00	31.59	32.60
Cycloparaffins	30.14	12.78	34.27	28.50	15.70	9.90
Monocycloparaffins	12.49	5.69	11.44	13.00	3.26	5.20
Dicycloparaffins	9.15	3.65	9.01	8.50	6.24	4.30
Tricycloparaffins	4.82	2.00	7.82	4.90	4.63	0.40
4-Rings cycloparaffins	3.67	1.37	6.01	2.10	1.56	0.00
5-Rings cycloparaffins	0.00	0.07	0.00	0.00	0.00	0.00
AROMATICS	9.06	9.08	9.02	4.00	17.01	27.80
Monoaromatics	3.23	8.53	3.93	3.10	8.94	15.90
Alkylbenzenes	2.34	8.43	3.28	2.80	5.31	9.30
Benzocycloalkanes	0.62	0.10	0.50	0.30	2.67	4.50
Benzodicycloalkanes	0.27	0.00	0.15	0.00	0.95	2.00
Diaromatics	5.82	0.53	5.08	0.90	8.07	10.70
Naphthalenes	4.95	0.45	4.51	0.80	7.00	4.10
Naphthocycloalkanes	0.31	0.00	0.24	0.00	0.61	5.90
Fluorenes	0.56	0.07	0.32	0.00	0.46	0.70
Triaromatics	0.00	0.00	0.00	0.00	0.00	0.30
Phenanthrenes	0.00	0.00	0.00	0.00	0.00	0.30
Phenanthrocycloalkanes	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Sulfur	0.00	0.00	0.00	0.00	0.00	1.00
Benzothiophenes	0.00	0.00	0.00	0.00	0.00	0.90
Dibenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.10
OLEFINS	0.15	0.20	0.15	0.30	0.27	0.60
TOTAL	64.01	44.20	60.89	60.70	64.57	70.80
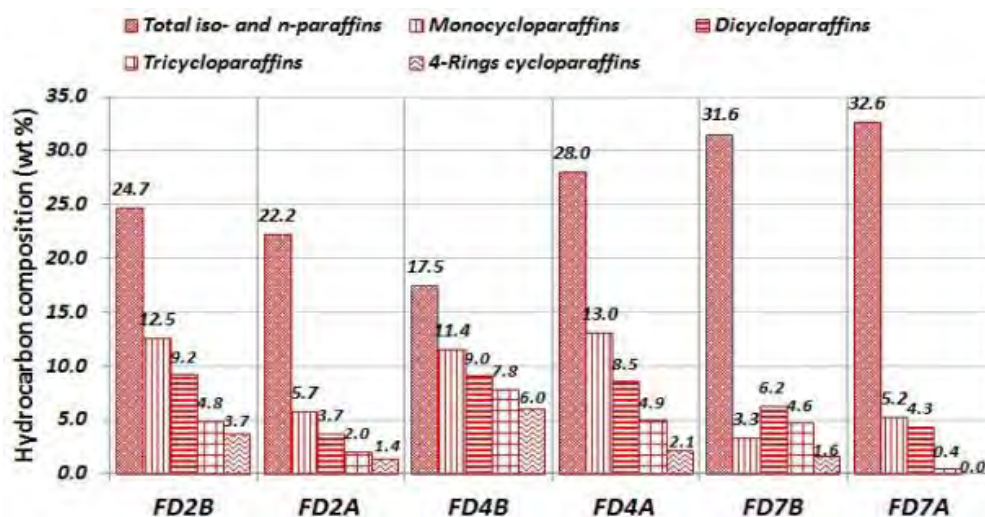
Figure 5.4 SPE-GCMS data for saturates in reformulated and original FACE diesel fuels
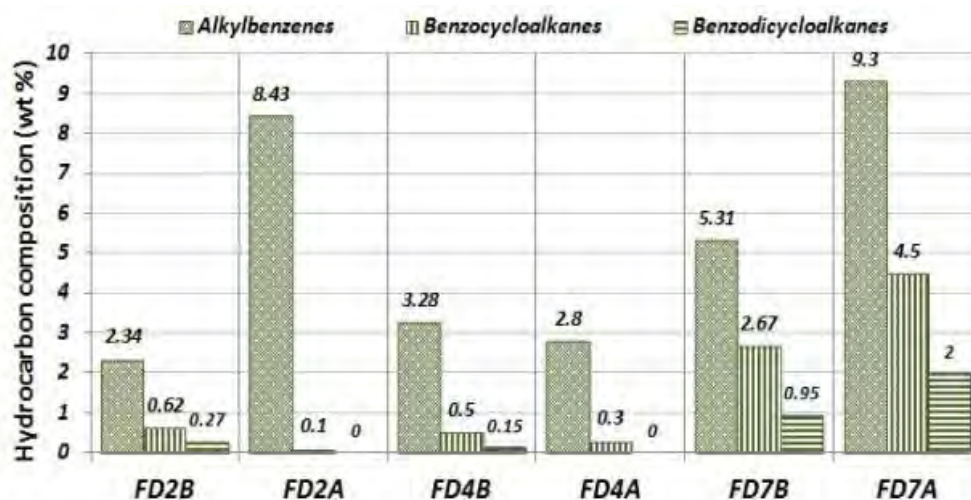
Figure 5.5 SPE-GCMS data for monoaromatics in reformulated and original FACE diesel fuels
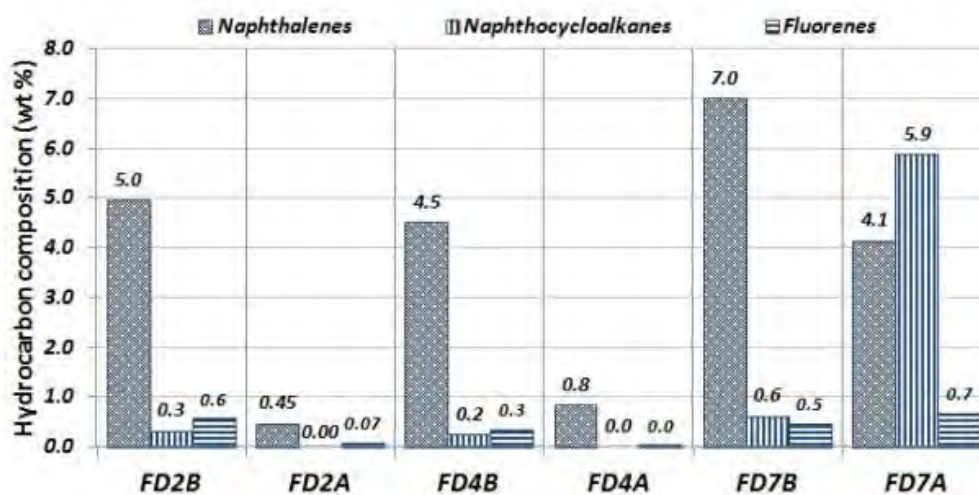
Figure 5.6 SPE-GCMS data for diaromatics in reformulated and original FACE diesel fuels
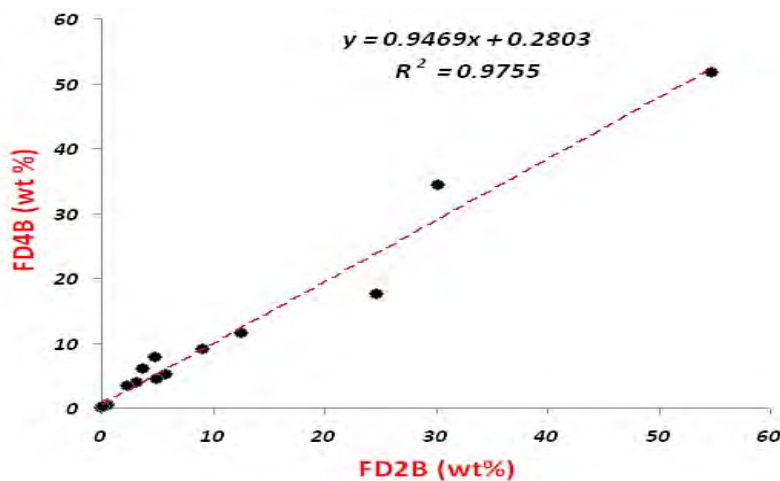
Figure 5.7 Correlation between FD4B and FD2B hydrocarbon components boiling above 392˚F.
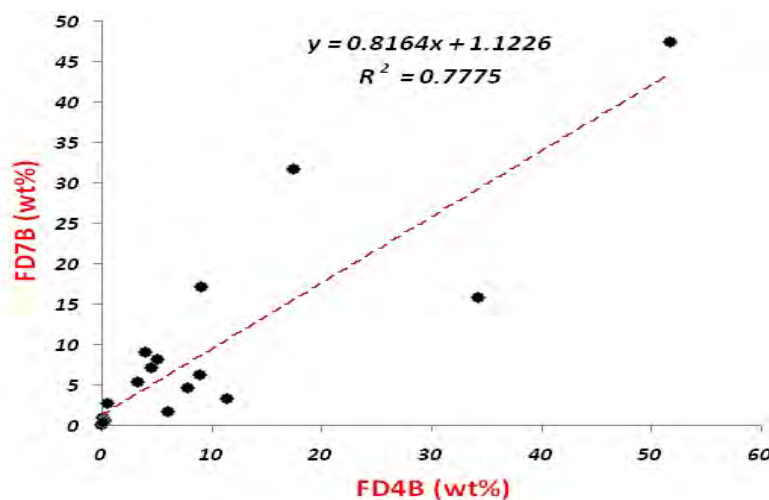
Figure 5.8 Correlation between FD7B and FD4B hydrocarbon components boiling above 392˚F.

5.2.3   References

1.   ASTM International, *Standard Test Method for Hydrocarbon Types Analysis of Gas-Oil Saturates Fractions by High Ionizing Voltage Mass Spectrometry,* ASTM D2786-91(2006) (ASTM International, Pennsylvania, 1991).

2.   ASTM International, *Standard Test Method for Aromatic Types Analysis of Gas-Oil Aromatic Fractions by High Ionizing Voltage Mass Spectrometry,* ASTM D3239-91(2006) (ASTM International, Pennsylvania, 1991).

3.   Bundt, J., et al., "Structure-type separation of diesel fuels by solid phase extraction and identification of the two- and three-ring aromatics by capillary GC-mass spectrometry," *Journal of High Resolution Chromatography,* **14**, 91–98 (1991).

5.3   GAS CHROMATOGRAPHY – HIGH RESOLUTION FIELD IONIZATION MASS SPECTROMETRY

5.3.1   Introduction

GC-FIMS was used to perform a detailed breakdown analysis of saturated and aromatic hydrocarbons (1). GC-FIMS was originally developed for diesel middle distillates in the boiling range of 392-649°F (200-343°C). This method covers the determination of five saturated, ten aromatic and three sulfur containing hydrocarbon types. The saturates group include: n-paraffins, iso-paraffins and mono-, di- and polycycloparaffins. The aromatic group consists of: monoaromatics (alkylbenzenes, indanes/tetralins, indenes), diaromatics (naphthalenes, acenaphthenes/biphenyls, acenaphthalenes/fluorenes), triaromatics (phenanthrenes/anthracenes, cyclopentanophenanthrenes), tetraaromatics (pyrenes/fluoranthenes, chrysenes/benzoanthracenes). The aromatic sulfur containing compounds are divided into three subgroups: benzothiophenes, dibenzothiophenes, naphthobenzothiophenes.

5.3.2   Results and Discussion

GC-FIMS does not require that the sample be separated into saturate and aromatic fractions prior to analysis, in contrast to SPE-GCMS. The results are reported by carbon number starting from C10 up to C21. Table 5.3 presents GC-FIMS hydrocarbon composition for fractions boiling in range 392°F – FBP for reformulated and original FACE Diesel fuels. The complete GC-FIMS/PIONA report valid for full boiling point range is provided in tabular form in Appendix D.

For the reformulated FD2B and FD4B fuels, the monocycloparaffins are significantly higher and the n- and iso-paraffins are significantly lower than in the original FD2A and FD2B fuels.

The total diaromatics content is higher for FD7B than for FD7A fuel. However, in case of FD7A the two aromatic ring hydrocarbons are evenly distributed into two diaromatic types: naphthalene and biphenyls. In reformulated FD7B fuel, biphenyls were almost completely replaced by naphthalenes (see Figure 5.9).

In contrast to SPE-GCMS, GC-FIMS can determine iso- and normal paraffins as separate hydrocarbon groups (see Figure 5.10).

Table 5.3 Summary of GC-FIMS hydrocarbon composition (wt %) that boils above 392°F/200°C

Hydrocarbon Type	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
Boiling range	392°F-FBP					
Saturates	48.66	31.14	48.57	40.48	39.97	45.93
Paraffins	8.43	16.74	13.11	18.02	25.43	36.43
IsoParaffins	6.40	16.53	11.02	18.00	7.26	3.71
N-paraffins	2.03	0.20	2.09	0.03	18.17	32.73
Cycloparaffins	40.23	14.40	35.47	22.45	14.54	9.49
Monocycloparaffins	28.51	8.86	18.11	12.98	5.49	5.72
Dicycloparaffins	3.13	2.63	5.16	4.00	5.43	3.14
Polycycloparaffins	8.59	2.92	12.20	5.48	3.62	0.63
Aromatics	15.34	13.03	12.33	20.26	24.63	24.87
Monoaromatics	9.81	8.88	7.82	14.42	9.23	12.95
Benzenes	3.41	5.60	3.41	11.37	2.91	8.05
Indanes/tetralins	4.35	2.93	3.12	2.92	4.71	3.98
Indenes (benzocycloalkane)	2.04	0.35	1.29	0.13	1.60	0.93
Diaromatics	5.27	3.59	4.22	5.47	15.07	11.91
Naphthalenes	4.18	2.97	3.37	4.77	11.93	5.40
Acenaphthenes/biphenyls	1.09	0.37	0.86	0.39	0.73	6.25
Acenaphthalenes/fluorenes	0.00	0.26	0.00	0.31	2.41	0.27
Triaromatics	0.11	0.01	0.12	0.01	0.11	0.00
Phenanthrenes/anthracenes	0.11	0.01	0.12	0.01	0.10	0.00
Cyclopentanophenanthrenes	0.00	0.01	0.00	0.00	0.01	0.00
Tetraaromatics	0.01	0.00	0.01	0.00	0.01	0.00
Pyrenes/fluoranthenes	0.01	0.00	0.01	0.00	0.01	0.00
Chrysenes/benzoanthracenes	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Sulfur	0.13	0.54	0.16	0.37	0.21	0.01
Benzothiophenes	0.04	0.47	0.03	0.30	0.03	0.01
Dibenzothiophenes	0.09	0.07	0.12	0.07	0.18	0.00
Naphthobenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.00
Total	64.00	44.17	60.90	60.74	64.60	70.80
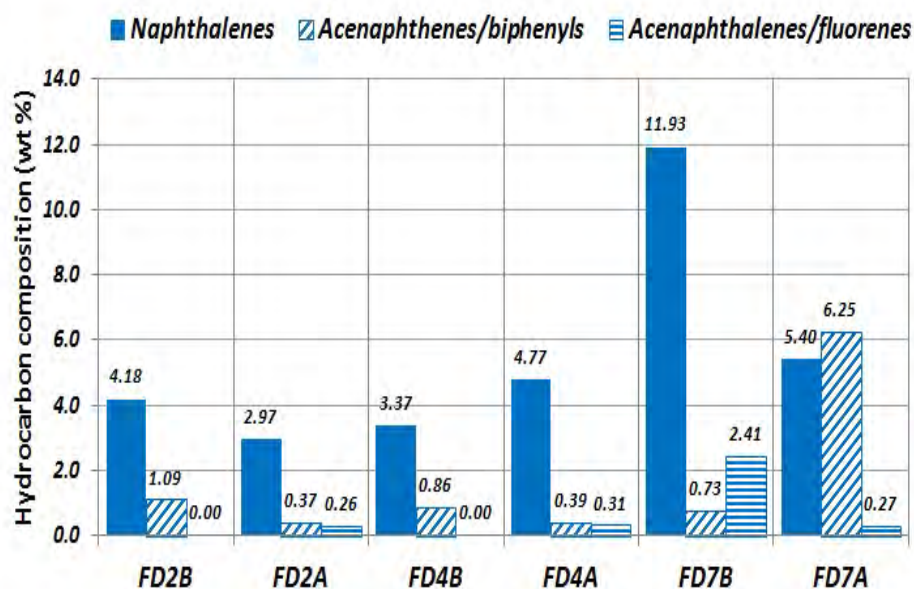
Figure 5.9 GC-FIMS data for diaromatics in reformulated and original FACE diesel fuels
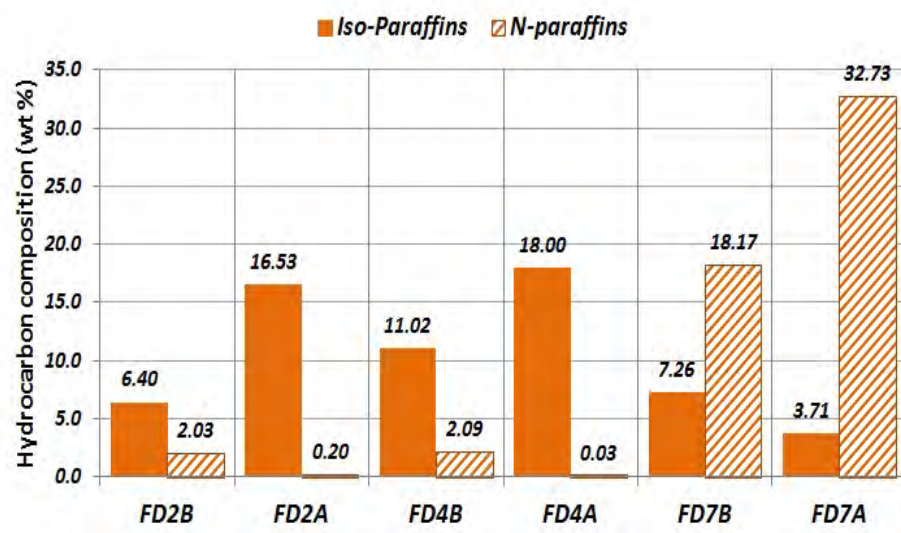
Figure 5.10 GC-FIMS data for iso- and n-paraffins in reformulated and original FACE diesel fuels

5.3.3 References

1. Briker, Y., et al., "Diesel fuel analysis by GC-FIMS—normal paraffins, isoparaffins and cycloparaffins," *Energy & Fuels,* **15**, 996–1002 (2001).

2. Briker, Y., et al., "Diesel fuel analysis by GC-FIMS—aromatics, n-paraffins and isoparaffins," *Energy & Fuels,* **15**, 23–37 (2001).

6.   HYDROCARBON CHARACTERIZATION FOR HYDROCARBONS IN FULL BOILING POINT RANGE

6.1   TWO DIMENSIONAL GAS CHROMATOGRAPHY WITH FLAME IONIZATION DETECTOR

6.1.1 Introduction

Comprehensive two-dimensional gas-chromatography (GCxGC) is a hybrid technique where the sample is separated on two chromatographic columns connected in series with a modulator placed between them. Selection of columns for GCxGC separation is based on their selectivity and orthogonality. The main factors influencing usefulness of this method are: high chromatographic resolution, high peak capacity and chemically structured two-dimensional chromatograms.

Detectors used in this system must be characterized by small internal volumes, short retention times and high data acquisition rates. Among detectors meeting these demands is the Flame Ionization Detector (FID). The FID detector is considered a general hydrocarbon detector. It response is linear over a very wide range of concentrations and proportional to the mass flow rate of carbon. All quantitative analyses regarding hydrocarbon classification provided in this section were based on FID response. The detailed description of the two-dimensional chromatographic systems used in recent analyses is provided in the next section titled "Experimental conditions for 'normal' and 'reversed' GCxGC-FID".

To facilitate side by side comparison of the original and new reformulated FACE fuels, GCxGC-FID analyses were repeated for the original FACE fuels rather than relying on the results previously obtained for those fuels.

6.1.2   Experimental Conditions for 'Normal' and 'Reversed' GCxGC-FID

The CanmetENERGY GCxGC-FID instrument (Agilent 680 GC with a LECO thermal modulator and secondary oven) is equipped both with a 'normal' and 'reversed' column set combination. In the former case the first column is non-polar and the second column is polar. The column features and the operating conditions for 'normal' GCxGC-FID experiment are listed in Table 6.1.

Table 6.1 – Chromatographic conditions for 'normal' GCxGC-FID analysis

1st column	*Varian Factor 4 VF5-HT, 30 m x 0.32 mm DF:0.1*
Main oven program	*50 ℃ (1) to 350 ℃ (0) at 3 ℃/min*
2nd column	*BPX-50, 1.0 m x 0.1 DF:0.1*
Secondary oven program	*10 ℃ offset from main oven*
Inlet Temperature	*350 ℃*
Injection size	*0.2 μL*
Split ratio	*100:1*
Carrier gas	*He, constant flow, 1.5 mL/min*
Modulator temperature	*55 ℃ offset from main oven*
Detector	*FID, 350 °C with SCD adapter, 800 °C*
Acquisition rate	*100 Hz*
Modulation period	*6 s*

The 'normal' two-dimensional GC technique provides typical chromatograms (see Figure 7.1) where the chemical compounds are first separated according to volatility which can be easily transformed to the

boiling point. The second separation is governed by polarity, which in practice for these fuels means separation according increasing number of aromatic rings.

Classification regions were created and the hydrocarbon typing template which was used in this work is shown in Figure 6.1. Selected representatives of compounds assigned to hydrocarbon classes from hydrocarbon template are shown in Figure 6.2.
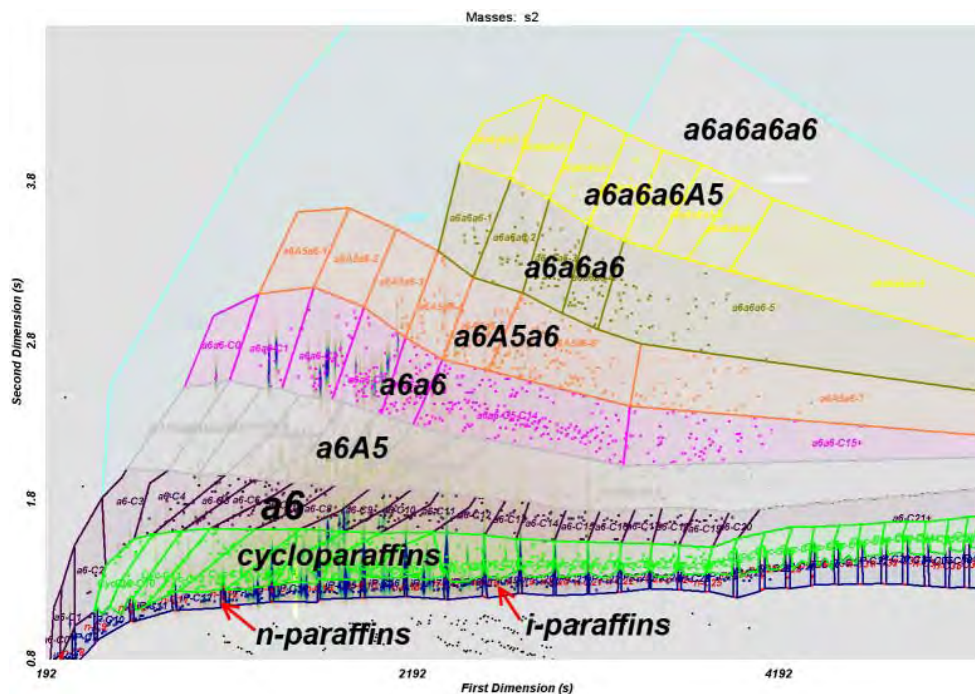
Figure 6.1. Schematic example of compound class distribution used during hydrocarbon typing on 'normal' GCxGC-FID. (a6 = 6 carbon aromatics; A5 = 5 carbon ring aliphatic)
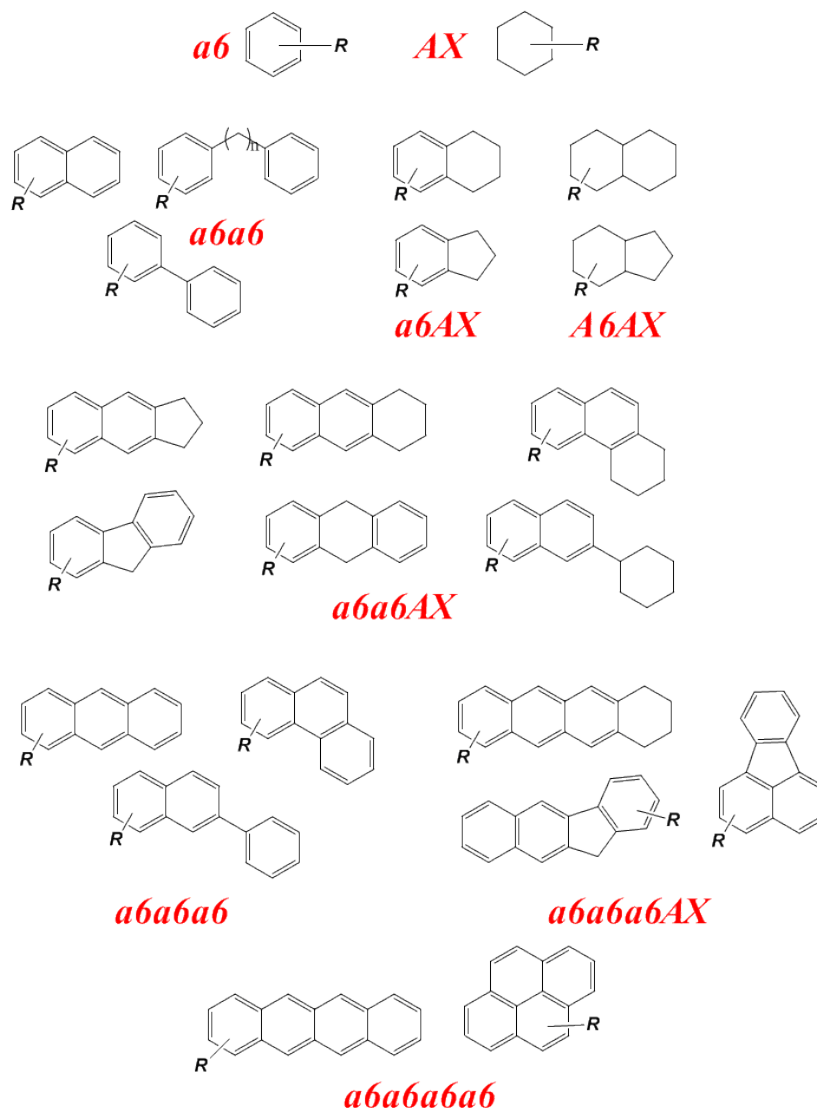
Figure 6.2 Examples of compounds assigned to groups used in 'normal' GCxGC-FID system.
(a6 = 6 carbon aromatic ring; AX = aliphatic ring, where X – number of carbons (usually 5 or 6);
R=aliphatic group)

In addition to the 'normal' column setup, FACE fuel samples were subjected to GCxGC experiment with 'reversed' column setup. In 'reversed' mode, the first column is a long polar column and the second one is a short non-polar column. The reversed polarity column setup has been shown by CanmetENERGY to improve the separation between saturates, olefins/ cycloparaffins and aromatics, and potentially to increase capacity utilization. The consequence of using the 'reverse' column setup is to extend the cross-border and thus improve the separation between saturates and aromatics as well as paraffinic and cycloparaffinc hydrocarbon types, which allows the accurate integration of these regions. The structural organization of hydrocarbon groups was observed for 'reverse' GCxGC, however the hydrocarbon types are in reverse order compared to a 'normal' column setup (Figure 6.3).
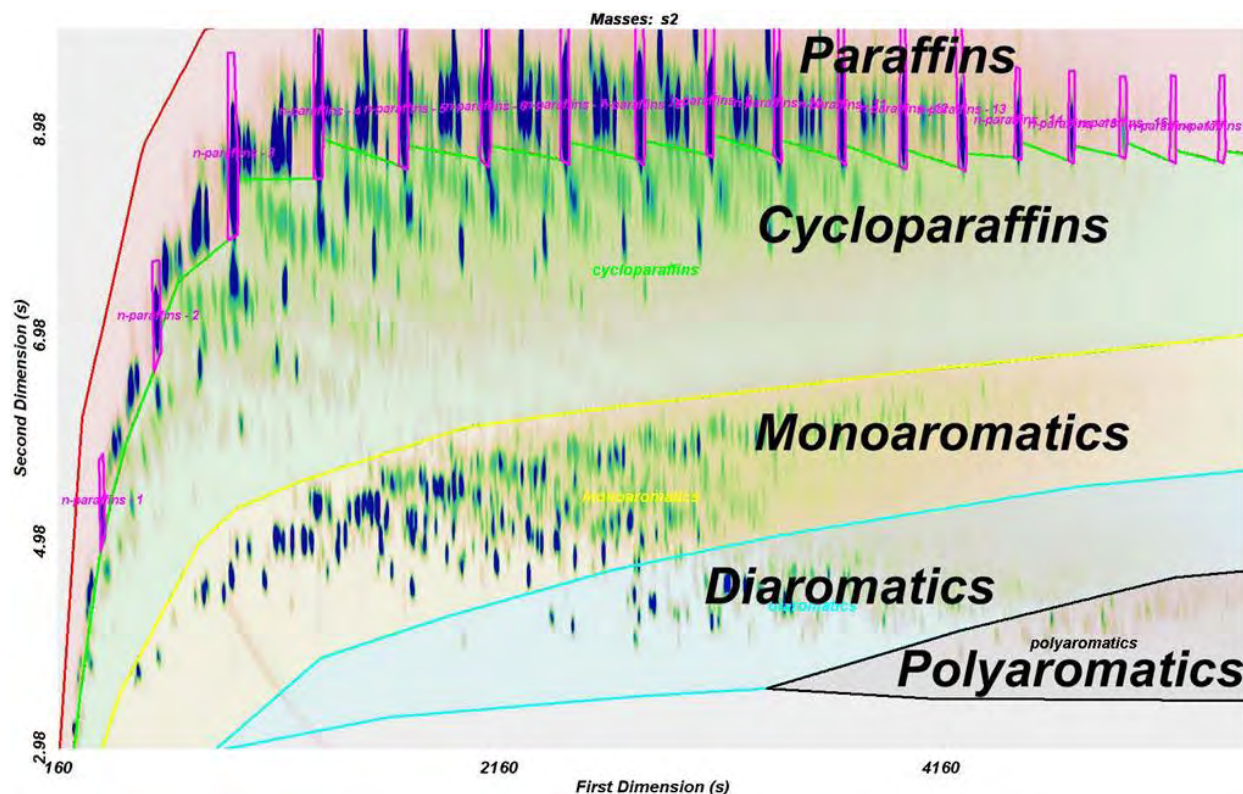
Figure 6.3 Schematic example of compound class distribution using 'reverse' column set combination and separation conditions from Table 6.2

Despite the unquestionable advantages of using the '*reverse*' system, the authors of this report noticed a few disadvantages, such as: loss of correlation between retention time and boiling point, and poorer separation between aromatic hydrocarbons types compared to a 'normal' column setup. The details of column features and the operating conditions for the '*reverse*'-GCxGC-FID experiment are listed in Table 6.2.

Table 6.2 Chromatographic conditions for 'reverse' GCxGC-FID analysis

1st column	*Varian Factor 17 VF17-MS, 30 m x 0.32 mm DF:0.15*
Main oven program	*40 ℃ (5) to 350 ℃ (1) at 2 ℃/min*
2nd column	*RTX-5, 1.5 m x 0.18 DF:0.2*
Secondary oven program	*20 ℃ offset from main oven*
Inlet Temperature	*350 ℃*
Injection size	*0.1 μL*
Split ratio	*500:1*
Carrier gas	*He, constant flow, 1.5 mL/min*
Modulator temperature	*70 ℃ offset from main oven*
Detector	*FID, 350 °C*
Acquisition rate	*100 Hz*
Modulation period	*10 s*

6.1.3 Results and Discussion from 'Normal' GCxGC-FID Experiment

Figure 6.4 presents general hydrocarbon compositions based on a 'normal'-GCxGC-FID system. Detailed tabulated GCxGC-FID class-by-class results are listed in Appendix E.

Comparing the reformulated fuels to each other:
- FD2B has about one-half of the total aromatics as FD4B and FD7B (which is consistent with the design targets of 20% aromatics for FD2B and 45% aromatics for FD4B and FD7B);
- FD2B has 2-3 times more cycloparaffins than FD4B and FD7B;
- FD2B and FD4B have about 5 times more isoparaffins and 7 times less n-paraffins than FD7B.

Compared to the original FACE #2 fuel, FD2A, the reformulated fuel, FD2B, appears to have:
- about the same amount of total saturates (n-paraffins + iso-paraffins + cycloparaffins);
- about the same amount of total aromatics (alkylbenzenes + indanes/tetralins + diaromatics);
- significantly less isoparaffins;
- significantly more cycloparaffins;
- less alkylbenzenes;
- more diaromatics.

Compared to the original FACE #4 fuel, FD4A, the reformulated fuel, FD4B, appears to have:
- about the same amount of total saturates (n-paraffins + iso-paraffins + cycloparaffins);
- about the same amount of total aromatics (alkylbenzenes + indanes/tetralins + diaromatics);
- slightly less alkylbenzenes;
- slightly more diaromatics.

Compared to the original FACE #7 fuel, FD7A, the reformulated fuel, FD7B, appears to have:
- about the same amount of total saturates (n-paraffins + iso-paraffins + cycloparaffins);
- about the same amount of total aromatics (alkylbenzenes + indanes/tetralins + diaromatics);
- more alkylbenzenes;
- less diaromatics
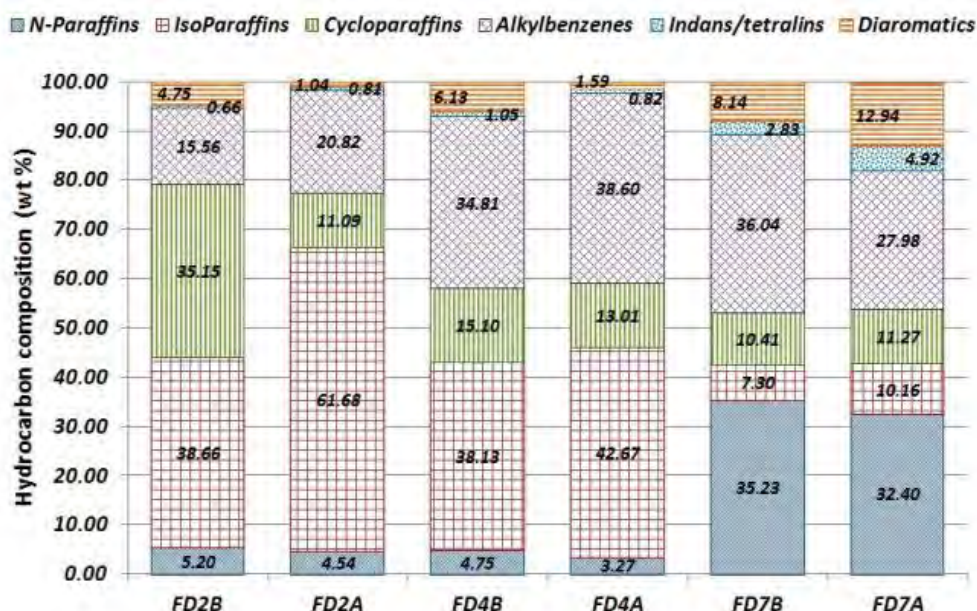
Figure 6.4 Hydrocarbon composition by 'normal' GCxGC-FID system

Simulated distillation by gas chromatography (ASTM D2887) is commonly used in the petroleum industry for determining the boiling point behavior of refinery streams. Comprehensive two-dimensional gas chromatography with 'normal' column setup can also provide distillation curves very similar (if not the same) as those derived from the D2887 technique. To achieve that, the first dimension retention time has to be translated into boiling point using a relationship established with n-paraffins. The FID signal response is converted to weight percentage of sample analyzed, by normalizing the relative signal intensity. Figure 6.5 shows a comparison of distillation curves obtained from ASTM D2887 and 'normal'-GCxGC-FID analyses for both original and reformulated FACE fuels. As can be seen from the plots, GCxGC SimDis is in good agreement with conventional D2887 SimDis. This suggests GCxGC-SimDis could be used as an equivalent to the ASTM approved simulated distillation technique.
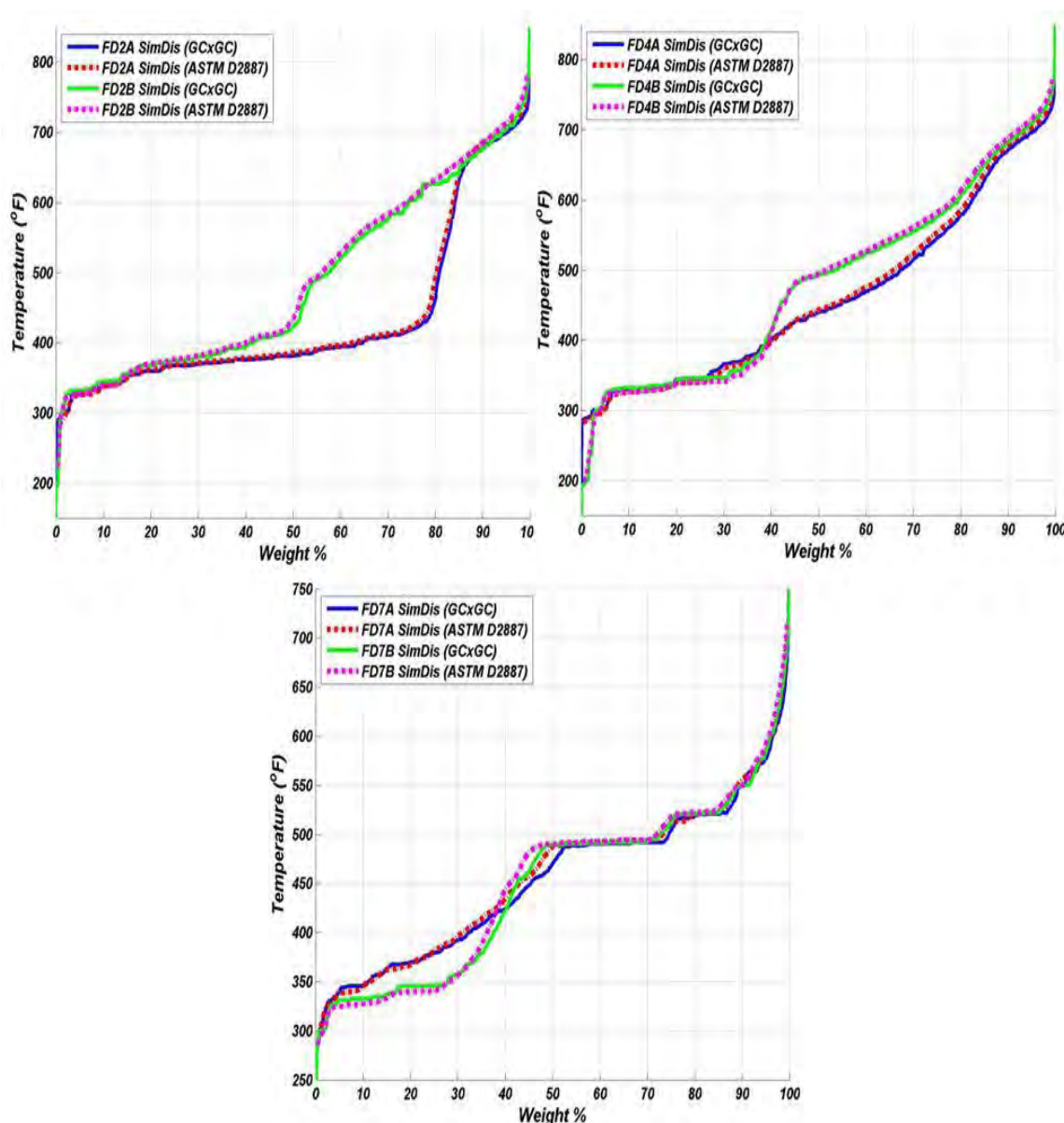
Figure 6.5 Comparison of distillation curves obtained from ASTM D2887 and GCxGC-FID experiment for original and reformulated FACE fuels.

44

Two-dimensional gas chromatography as a comprehensive technique can be used to provide more sophisticated 'advanced simulated distillation' curves. In addition to aforementioned total liquid distillation curves, it is possible to plot very specific SimDis curves based on each hydrocarbon class found during the classification process. Figures 6.6 to 6.8 present the proposed approach applied to the original and reformulated FACE fuels. The specific hydrocarbon class SimDis curves showed in these figures was restricted to two main hydrocarbon groups namely: saturates and aromatics.
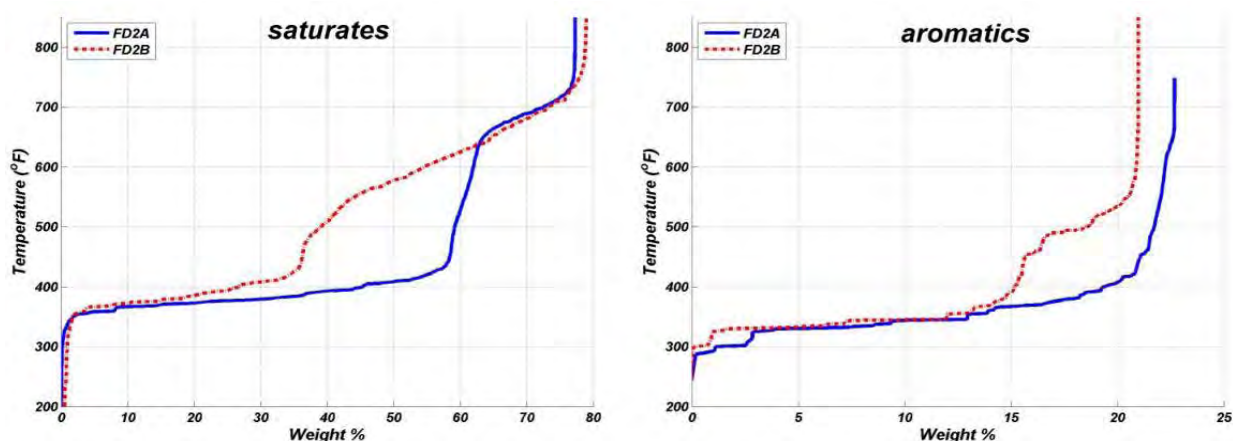
Figure 6.6 'Group type' SimDis based on saturate and aromatic GCxGC-FID classification region for FACE Fuels #2
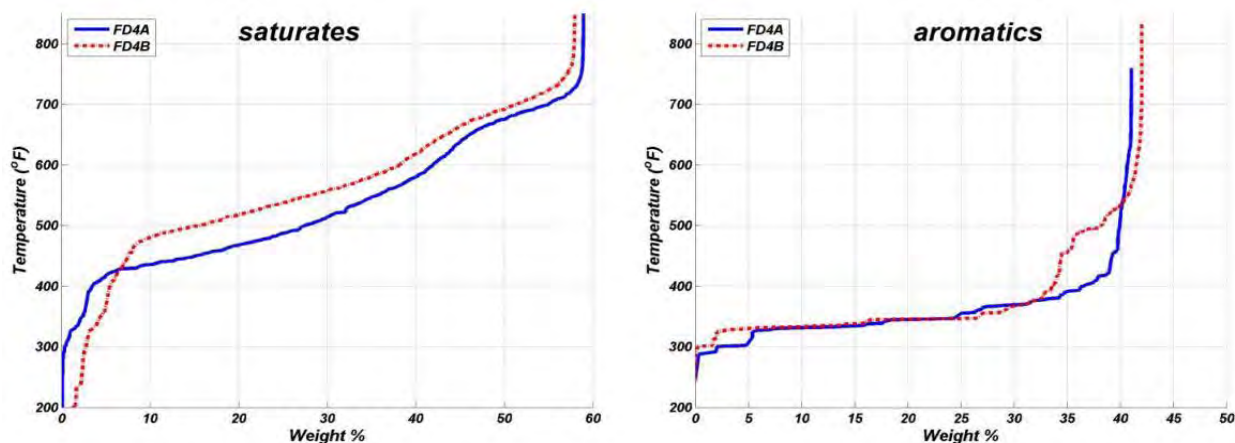
Figure 6.7 'Group type' SimDis based on saturate and aromatic GCxGC-FID classification region for FACE Fuels #4.
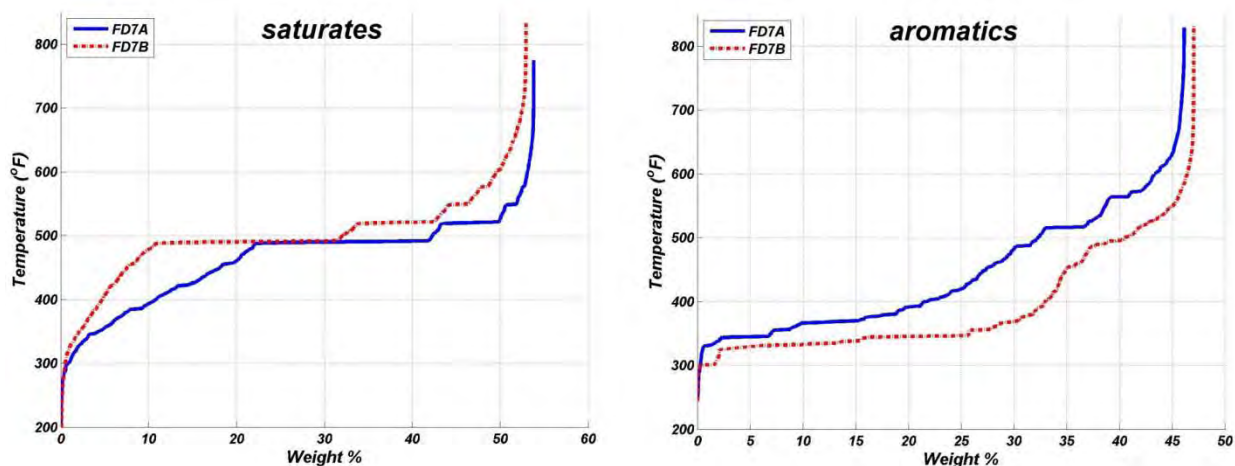
Figure 6.8 'Group type' SimDis based on saturate and aromatic GCxGC-FID classification region for FACE Fuels #7.

It is possible to expand this type of analysis to the subclasses such as diaromatics, isoparaffins or n-paraffins. The n-paraffinic SimDis curves presented in Figure 6.9 are always characterized by stair shape profile because of the significant difference in boiling points between consecutive n-paraffins. The figure shows that there is significant amount of hydrocarbons boiling at around 488° F and 518°F. These correspond to n-tetradecane (n-$C_{14}H_{30}$) and n-pentadecane (n-$C_{15}H_{32}$), respectively.
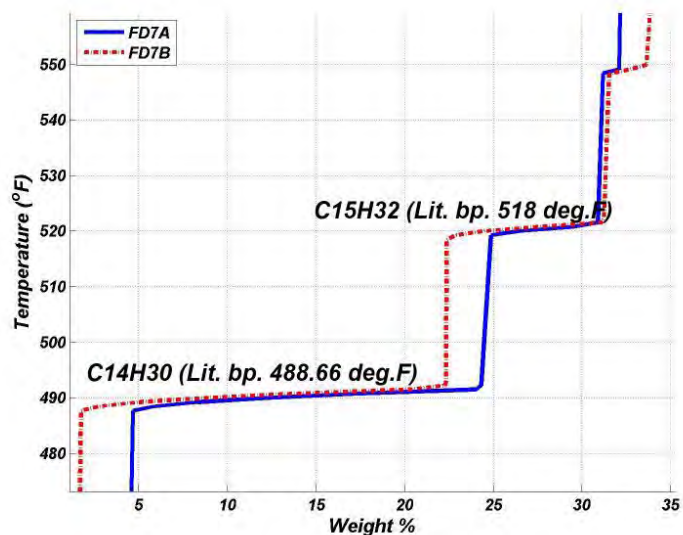
Figure 6.9 'Group type' SimDis based on n-paraffinic GCxGC-FID classification region for FACE fuels #7

The SimDis results presented above reveal different aspects of the volatility behavior of the analyzed fuels. However, very often this information alone is insufficient for complete description of fuel characteristics in processes like upgrading or combustion. On the other hand distinct structure of GCxGC chromatograms allows for detailed hydrocarbon characterization of analyzed samples. Merging GCxGC structural information with distillation profiles allows for creation of an enhanced view of chemical composition in boiling point domain.

To achieve this, peak information (position and area) after preprocessing with ChromaTOF software was further processed in MATLAB® software (2). The first-dimension retention time was converted into a temperature scale using a correlation established between boiling point of n-paraffins and their retention time. This exercise allowed for presentation of GC×GC-FID maps in the D2887 distillation temperature domain. Additionally, peaks found in chromatograms were presented in bubble plot form, where the size of the bubble is related to the compound concentration. Figures 6.10–6.15 presents the upgraded chromatograms for each of the FACE fuels. The Simdis curve obtained from ASTM D2887 analysis was superimposed on chromatogram as dashed magenta line. Black dashed vertical lines on the pictures show the SimDis regions T10, T50 and T90, respectively. This type of GCxGC data presentation should assist in interpretation of chromatograms and help readers to visually distinguish the compositional fingerprints between the reformulated and original FACE fuels.

The discussion provided in section 2.2.2, concerning the most significant differences in Simdis profiles for original FD2A and reformulated FD2B, stay valid in light of the new recent data presentation (Figure 6.10 and Figure 6.11). Moreover, this type of presentation of GCxGC information offers the possibility for deeper insight into hydrocarbon structure of the questionable regions.
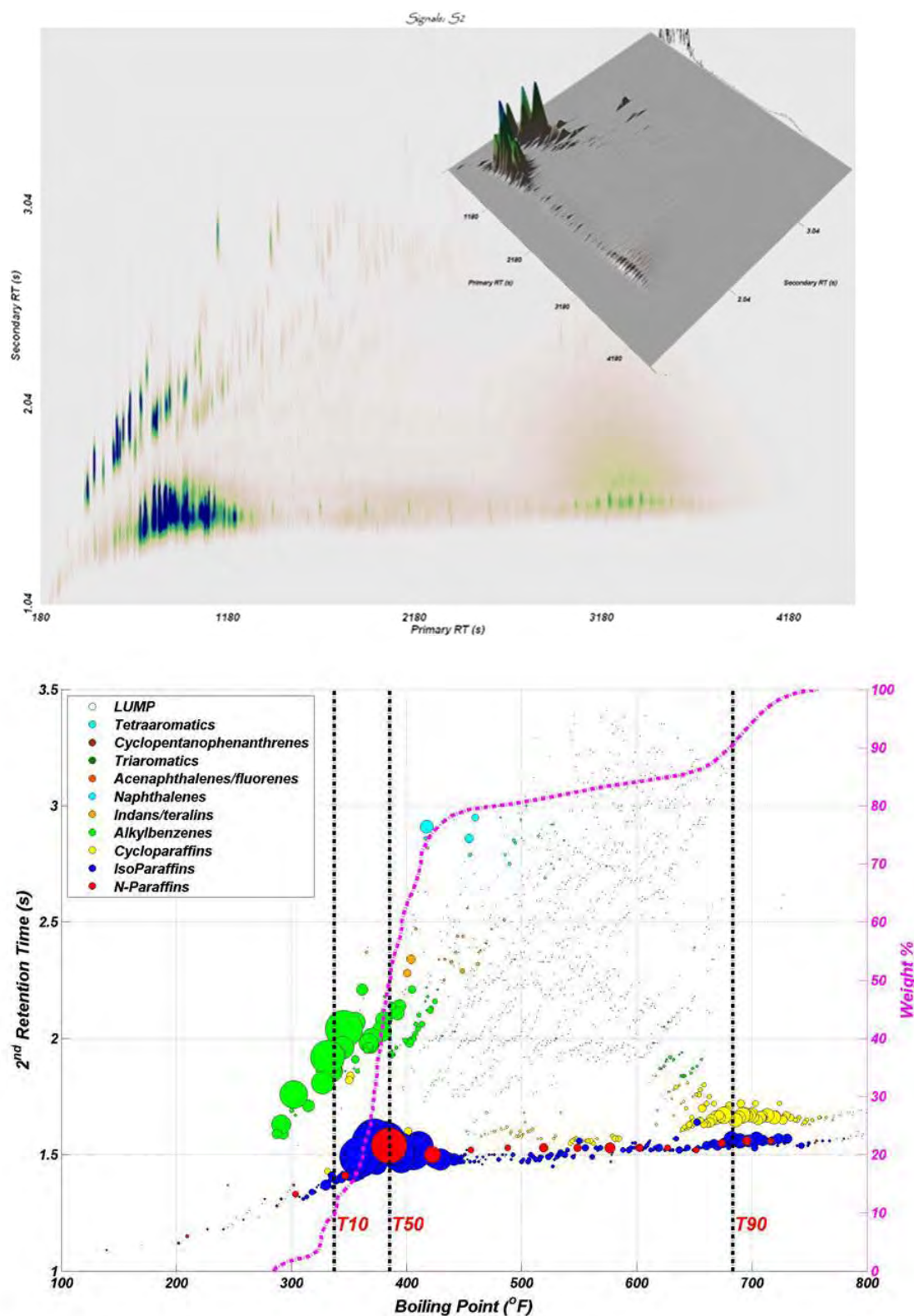
Figure 6.10 Original FD2A. 'Normal' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a function of boiling point presented as a bubble plot (bottom plot). Simdis curve from ASTM D2887 analysis was superimposed on chromatograms as magenta, dashed line. The dashed vertical lines, left to right, represent T_{10}, T_{50} and T_{90} based on Simdis (ASTM D2887).
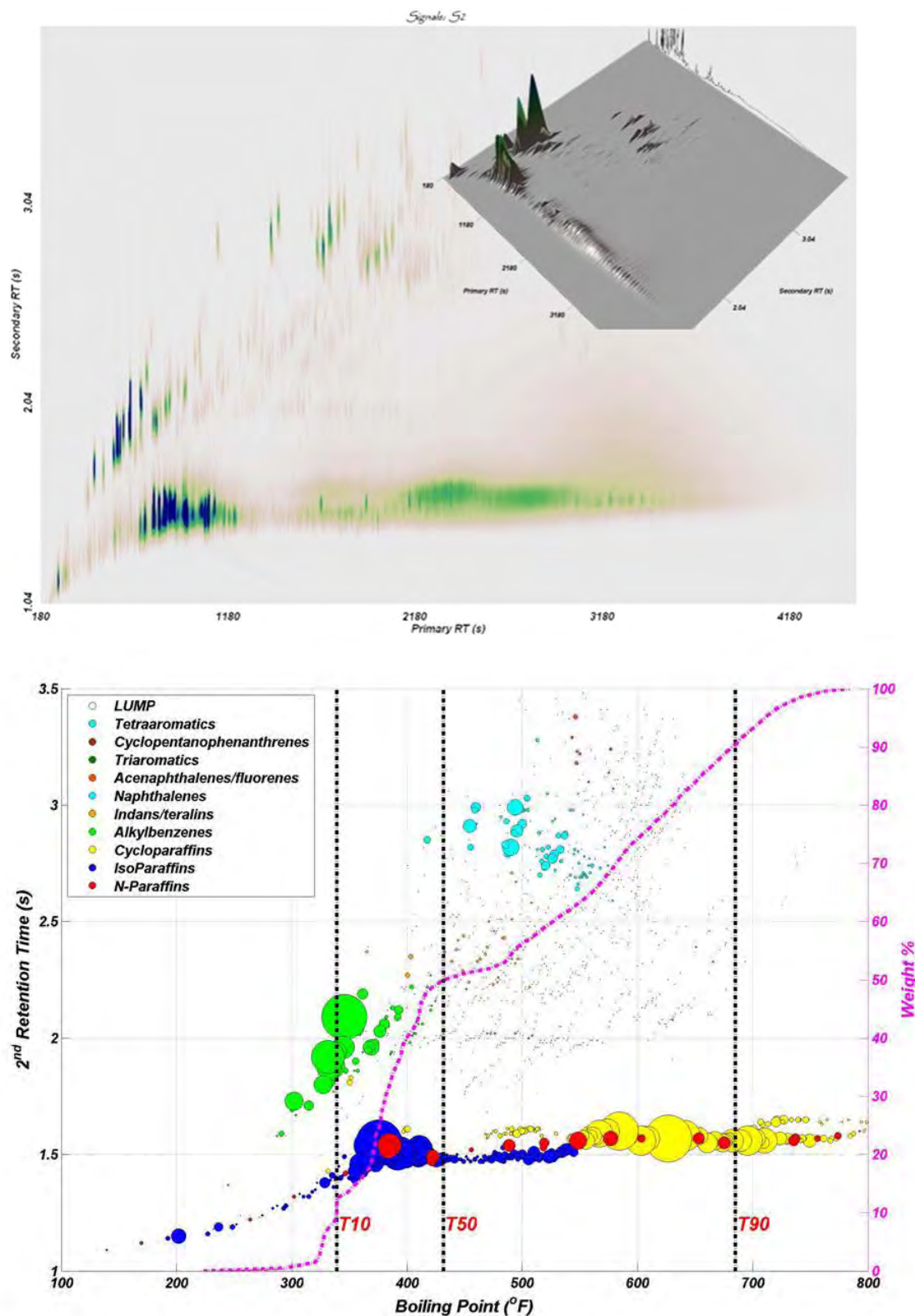
Figure 6.11   Reformulated FD2B. 'Normal' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a function of boiling point presented as a bubble plot (bottom plot). Simdis curve from ASTM D2887 analysis was superimposed on chromatograms as magenta, dashed line. The dashed vertical lines, left to right, represent T_{10}, T_{50} and T_{90} based on Simdis (ASTM D2887).
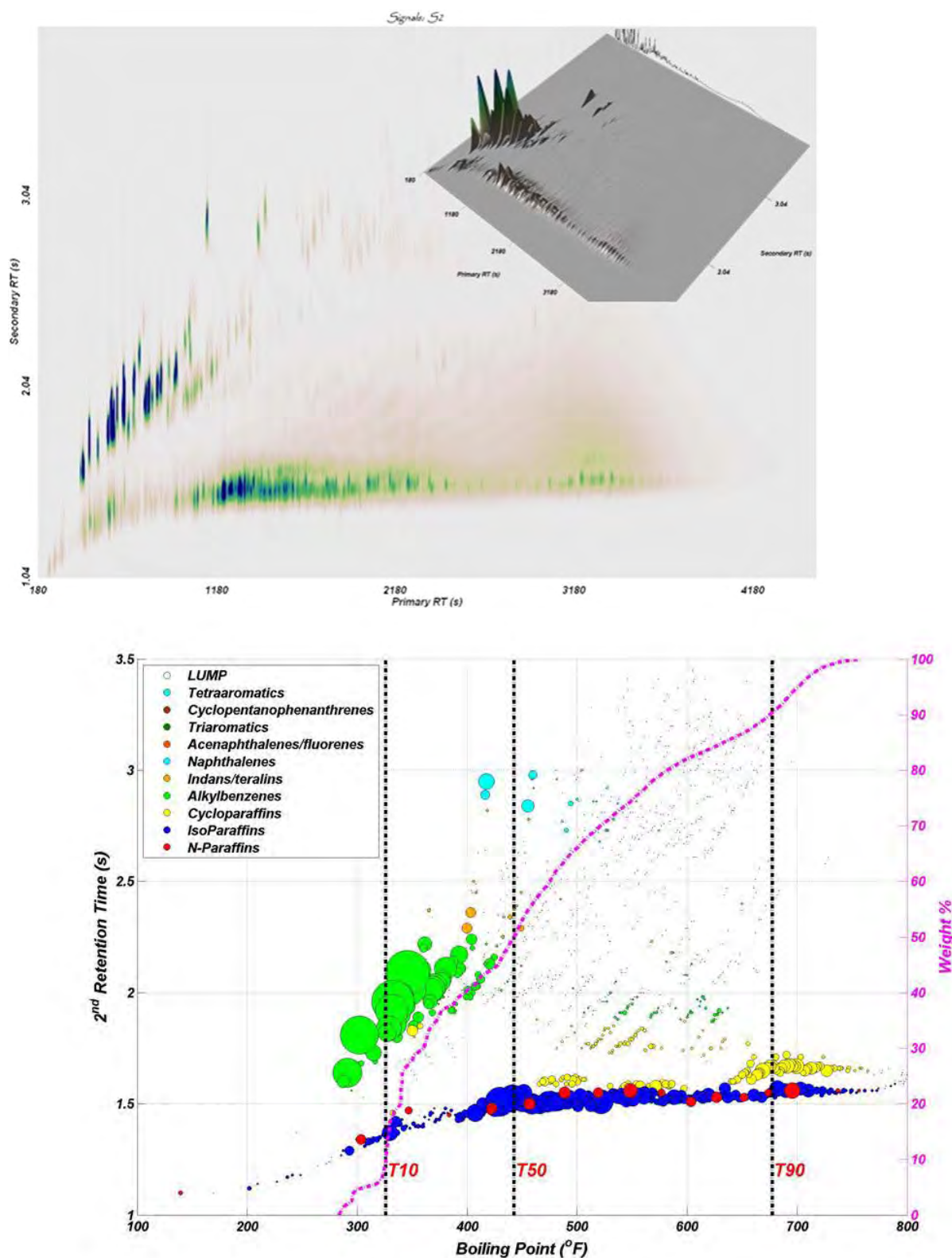
Figure 6.12 Original FD4A. 'Normal' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a function of boiling point presented as a bubble plot (bottom plot). Simdis curve from ASTM D2887 analysis was superimposed on chromatograms as magenta, dashed line. The dashed vertical lines, left to right, represent T_{10}, T_{50} and T_{90} based on Simdis (ASTM D2887).
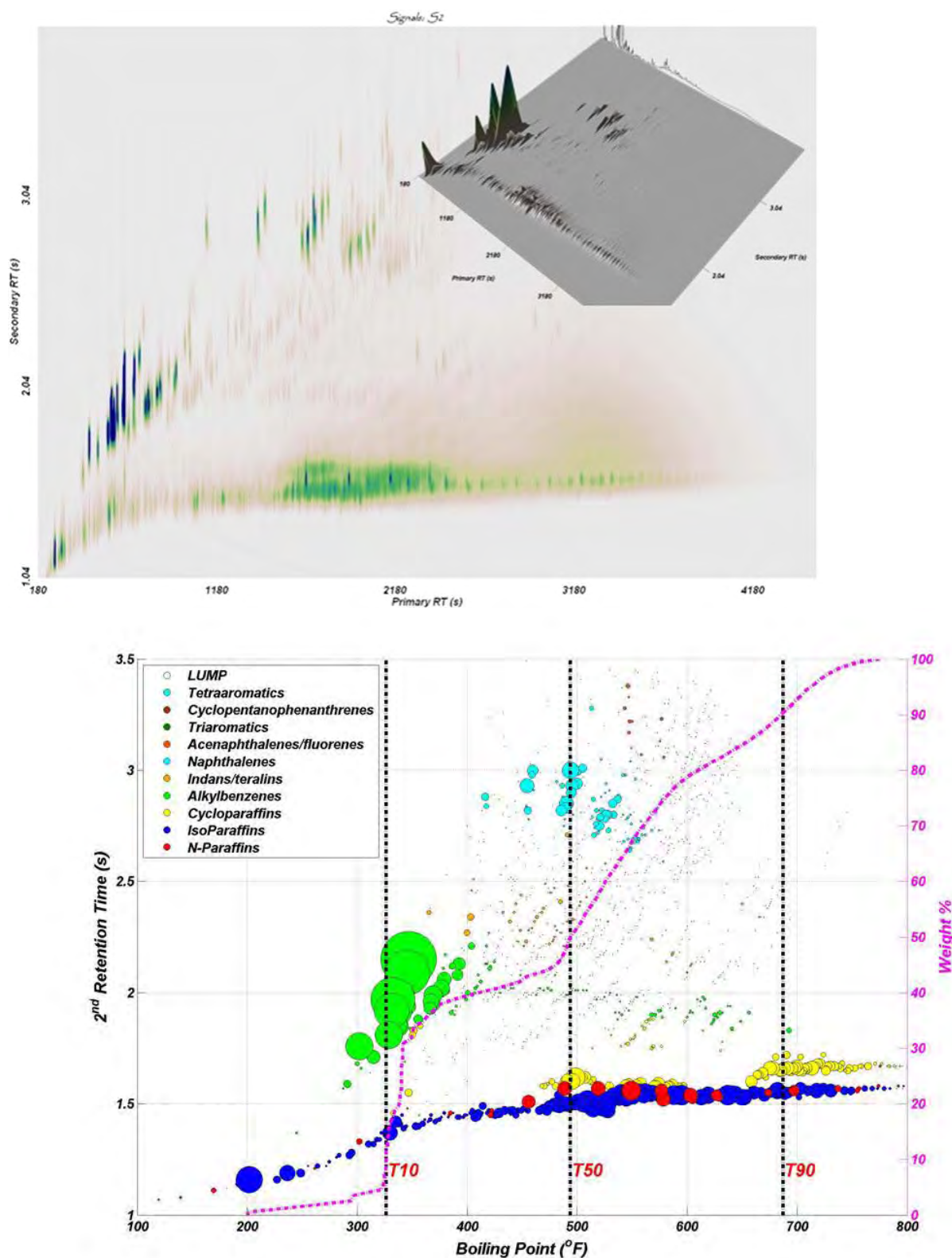
Figure 6.13 Reformulated FD4B. 'Normal' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a function of boiling point presented as a bubble plot (bottom plot). Simdis curve from ASTM D2887 analysis was superimposed on chromatograms as magenta, dashed line. The dashed vertical lines, left to right, represent T_{10}, T_{50} and T_{90} based on Simdis (ASTM D2887).
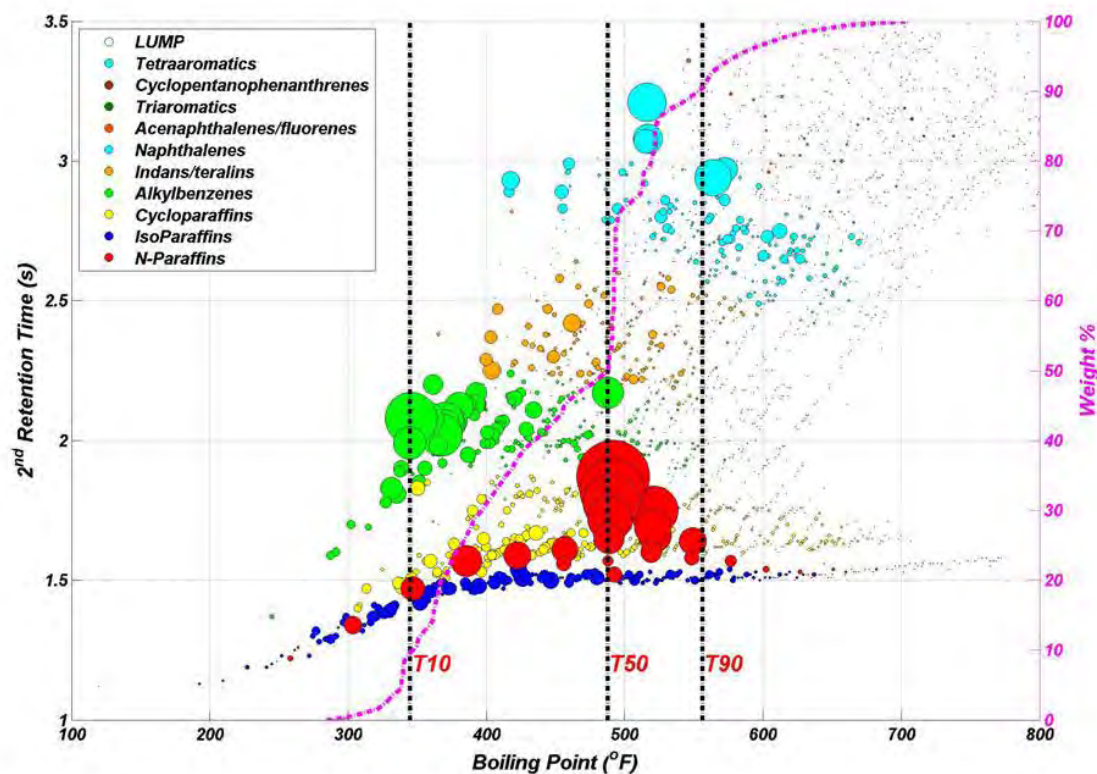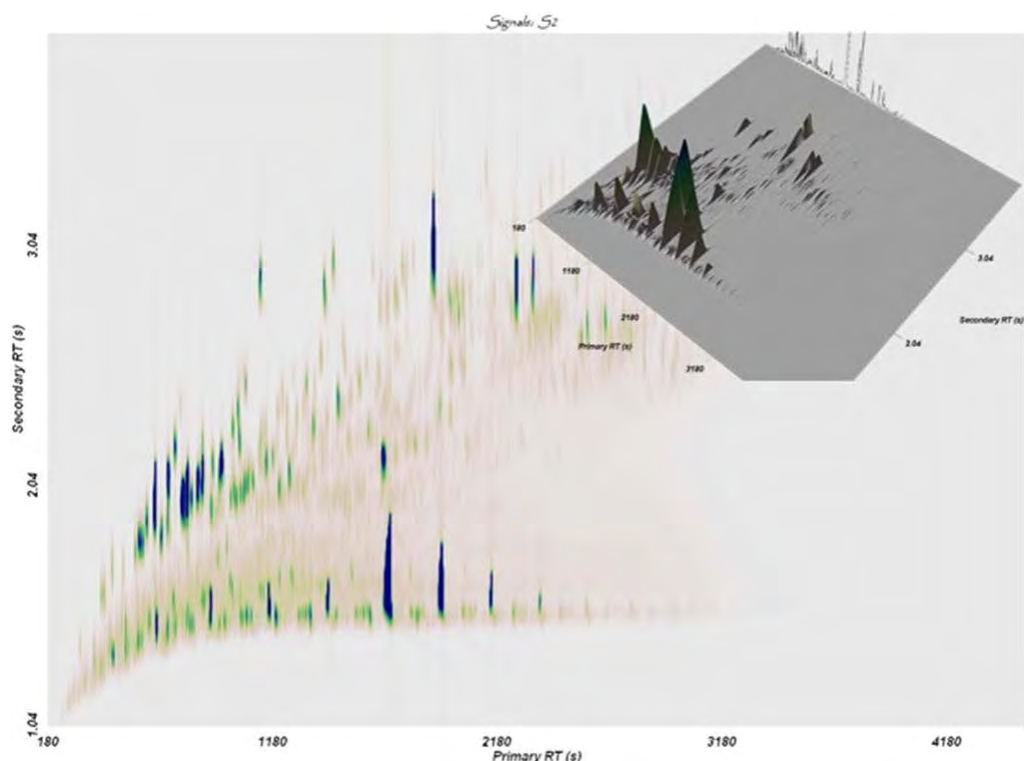
Figure 6.14 Original FD7A. 'Normal' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a function of boiling point presented as a bubble plot (bottom plot). Simdis curve from ASTM D2887 analysis was superimposed on chromatograms as magenta, dashed line. The dashed vertical lines, left to right, represent T_{10}, T_{50} and T_{90} based on Simdis (ASTM D2887).
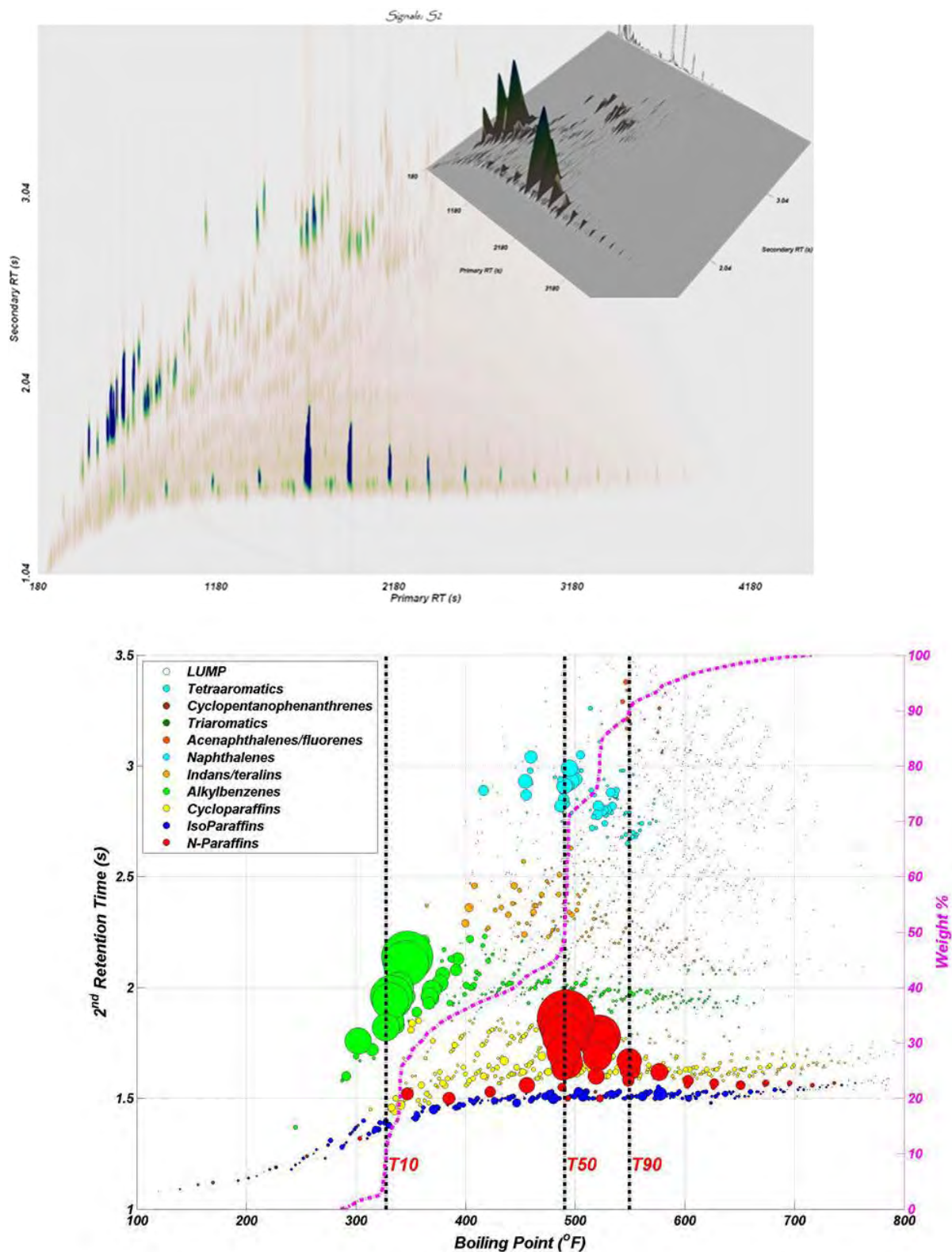
Figure 6.15 **Reformulated FD7B. 'Normal' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a function of boiling point presented as a bubble plot (bottom plot). Simdis curve from ASTM D2887 analysis was superimposed on chromatograms as magenta, dashed line. The dashed vertical lines, left to right, represent T_{10}, T_{50} and T_{90} based on Simdis (ASTM D2887).**

Figure 6.16 shows the distribution of hydrocarbons by carbon number for n-paraffins (left figures) and iso-paraffins (right figures) of the reformulated (dark bars) and original (light bars) FACE diesel fuels. Figure 6.17 shows the carbon number distribution for the cycloparaffins. Figure 6.18 shows the carbon number distribution for the alkylbenzenes (left figure) and naphthalenes (right figures).
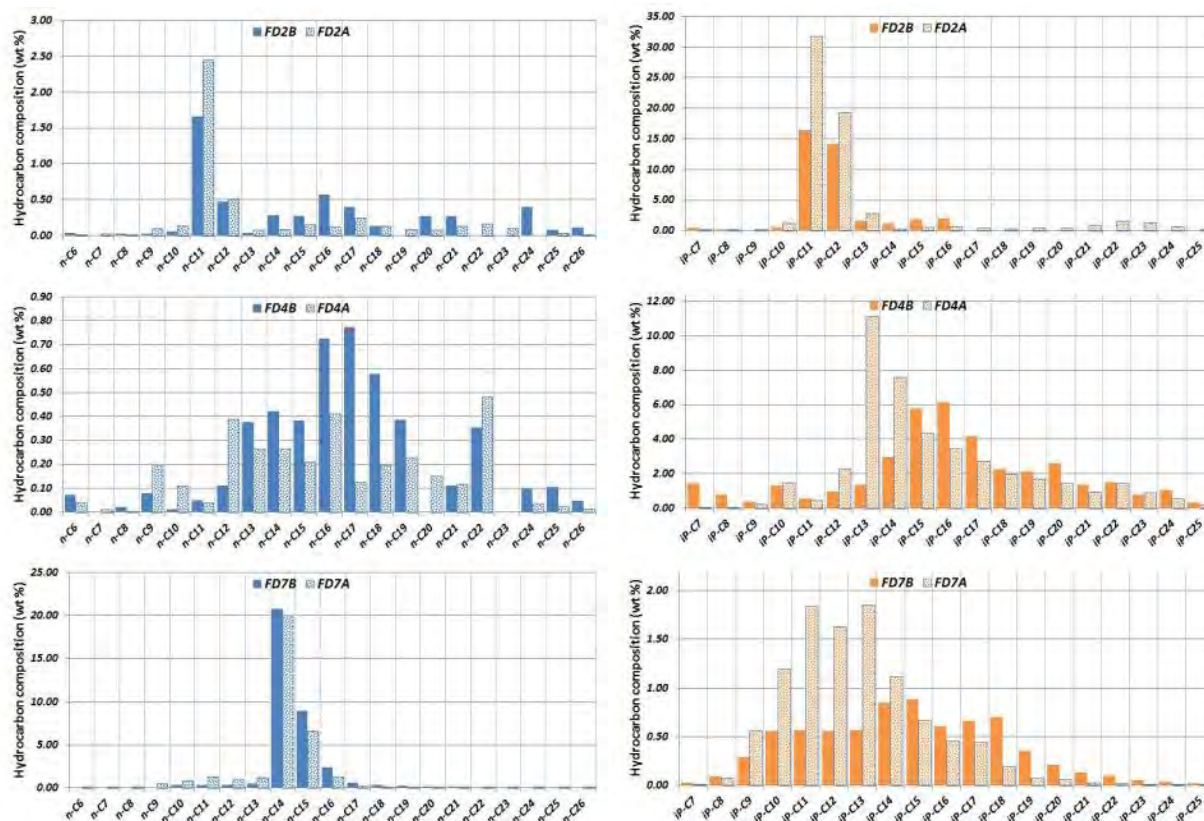
Figure 6.16 Distribution of n-paraffins (left side) and iso-paraffins (right side) by carbon number
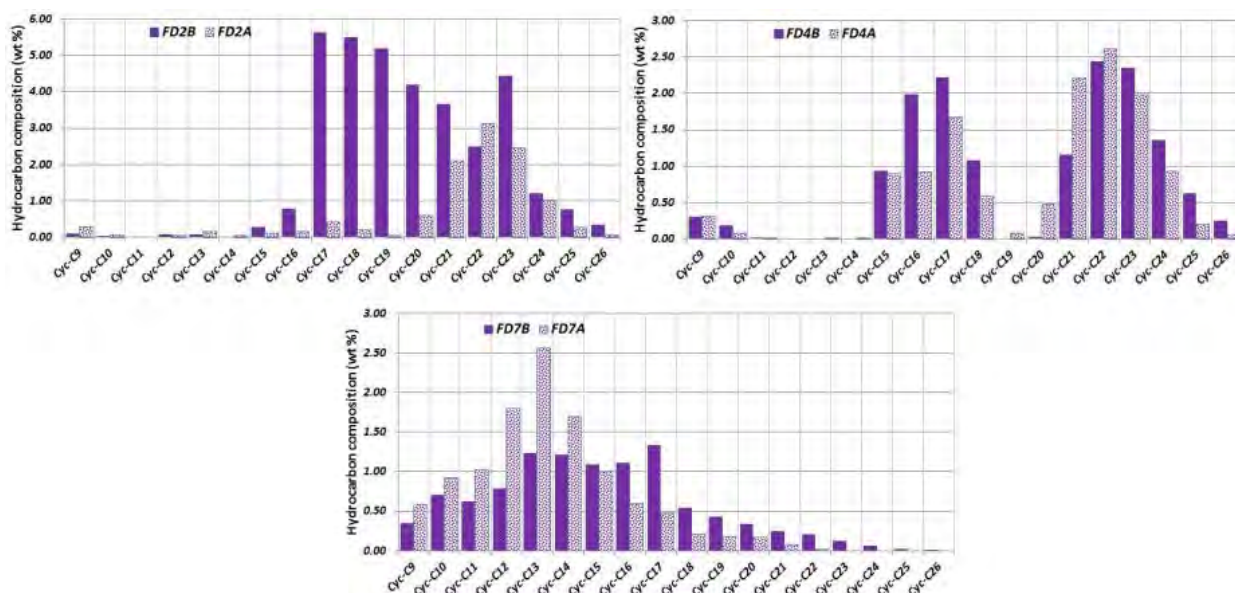
Figure 6.17 Distribution of cycloparaffins by carbon number
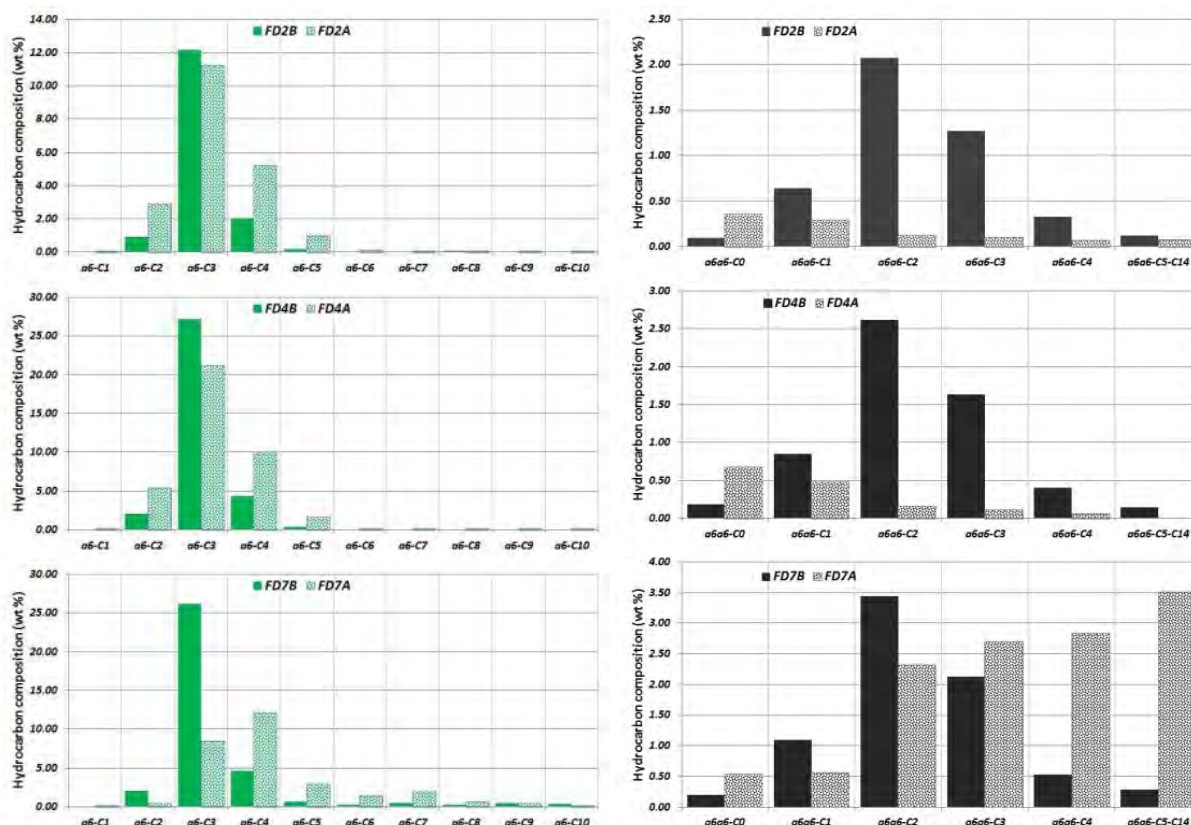
Figure 6.18 Distribution of alkylbenzenes (left side) and naphthalenes (right side) by carbon number

These charts demonstrate:
- The presence of more higher carbon number paraffins in the FD2 and FD4 fuels compared to the FD7 fuels, consistent with the lower target boiling point for the FD7 fuels;
- The more symmetric carbon number distribution for the n-paraffins of FD4B fuel vs. the FD2B and FD7B fuels;
- The diversified cycloparaffinic profile for all fuels;
- The predominance of C9 Aromatics in the alkylbenzenes of all 3 reformulated fuels

Upon calculating the ratio between two consecutive alkylbenzene and naphthalene isomeric groups taken from Figure 6.18 we found very interesting trends shown in Figure 6.19. For both the original and reformulated fuels the ratios of consecutive alkylbenzenes and naphthalenes appears to be about the same for the FD2 and FD4 fuels, although the ratios are different for the reformulated vs. original fuels. This suggests that the same aromatic feedstocks were used to prepare the FD2 and FD4 fuels, but different blendstocks were used to prepare the reformulated vs. the original fuels.
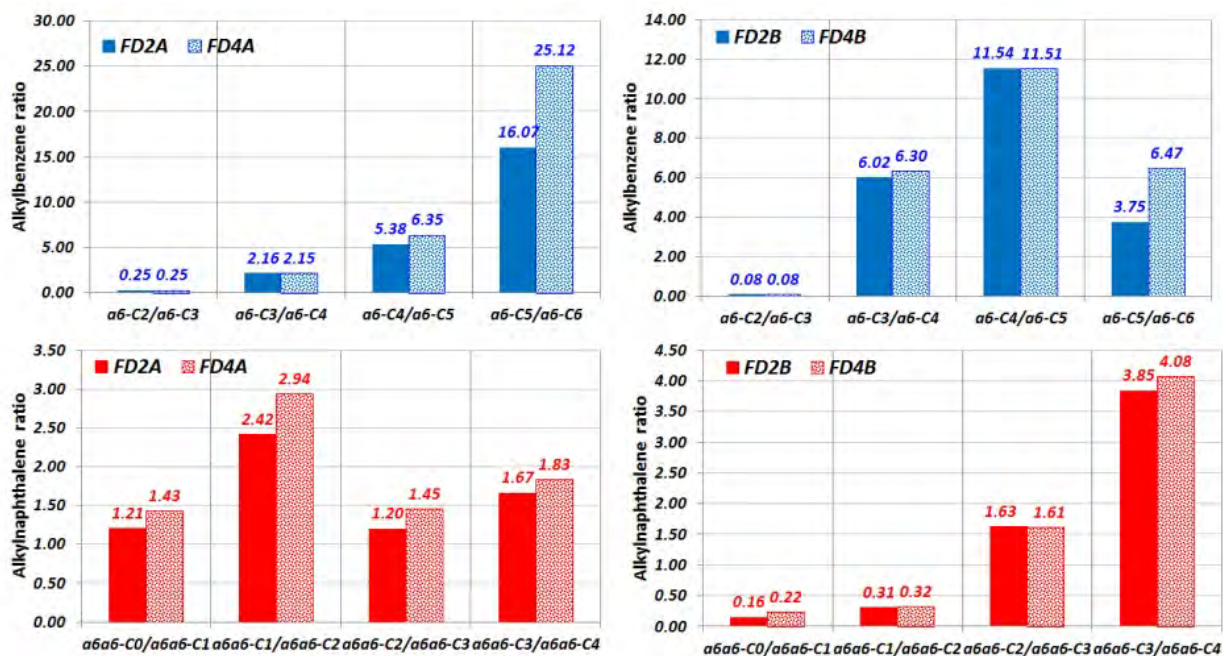
Figure 6.19 Isomeric ratio calculated by dividing successive alkylbenzenes (top figures) and alkylnaphthalenes (bottom figures) concentration: a6-C(N)/a6-C(N+1) and a6a6-C(N)/a6a6-C(N+1), respectively

6.1.4 Results and Discussion from 'Reversed' GCxGC-FID Experiment

Two-dimensional gas chromatography of fuels is usually performed using 'normal'-GCxGC mode (as discussed in Section 6.1.3). To achieve better separation between paraffins, cycloparaffins and aromatics, the 'reverse'-GCxGC-FID system was also utilized in this work. As expected, the selected column combination (Table 6.2) provided good separation of individual components and excellent separation between saturates and aromatic classes. Six hydrocarbon classes (n-Paraffins, iso-Paraffins, cycloparaffins, monoaromatics, diaromatics and polyaromatics) were identified and quantified using an FID detector. GCxGC-FID hydrocarbon compositions are presented in Figure 7.20. The trends obtained are similar to those reported in Section 6.1.3 for the 'normal' analysis, namely:

Comparing the reformulated fuels to each other:
- FD2B has about one-half of the total aromatics as FD4B and FD7B (which is consistent with the design targets of 20% aromatics for FD2B and 45% aromatics for FD4B and FD7B);
- FD2B has more cycloparaffins that FD4B and FD7B;
- FD2B and FD4B have about 5-7 times more isoparaffins and 10-15 times less n-paraffins than FD7B.

Compared to the original FACE #2 fuel, FD2A, the reformulated fuel, FD2B, appears to have:
- about the same amount of total saturates (n-paraffins + iso-paraffins + cycloparaffins);
- about the same amount of total aromatics (alkylbenzenes + indanes/tetralins + diaromatics);
- significantly less isoparaffins;
- significantly more cycloparaffins;
- less monoaromatics;
- more diaromatics.

Compared to the original FACE #4 fuel, FD4A, the reformulated fuel, FD4B, appears to have:
- about the same amount of total saturates;
- about the same amount of total aromatics;
- slightly less monoaromatics;
- slightly more diaromatics.

Compared to the original FACE #7 fuel, FD7A, the reformulated fuel, FD7B, appears to have:
- about the same amount of total saturates;
- about the same amount of total aromatics;
- more monoaromatics;
- less diaromatics

Comparing the results of the "normal" and "reverse" analyses:
- the amounts for total saturates and total aromatics from both methods are very close to each other for all fuels, with the largest absolute difference of 3.2% for the total saturates of FD2B (75.8% for "normal" and 79.0% for "reverse");
- the amounts in the individual aromatic classes are very close to each other;
- the biggest differences are in the cycloparaffin and isoparaffin hydrocarbon classes. The cycloparaffin values are higher from the "reverse" method for all fuels except FD2B. Correspondingly, the isoparaffin values are lower from the "reverse" method for all fuels except FD2B.
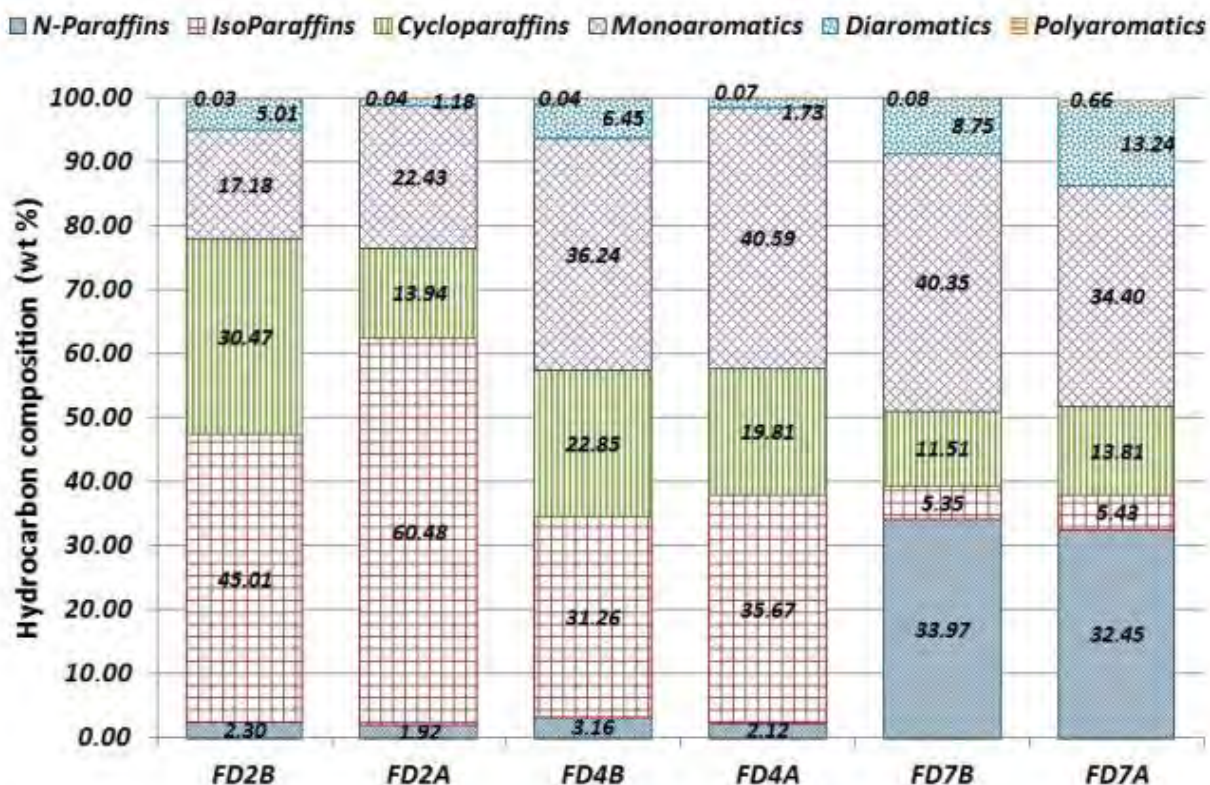
Figure 6.20 Hydrocarbon composition by 'reverse' GCxGC-FID system

One drawback of the 'reverse' system is poorer separation in the aromatic part of the chromatogram, especially for diaromatic and higher polyaromatic species. In this case, it was observed that partially hydrogenated aromatic compounds tend to coelute with corresponding unsaturated aromatic hydrocarbons to a greater extent than in the 'normal' mode GCxGC. As a results, it is difficult to split the diaromatic region into naphthalenes and hydrogenated three ring aromatics. The other disadvantage is connected with the inability to set the correlation between the retention time and the boiling point and thereby present GCxGC-results as volatility vs. polarity plots. 'Reverse' GCxGC-FID chromatograms obtained from the analysis of supplied samples are shown in Figures 6.21 – 6.26. Retention time in the first dimension is shown on the x-axis, and retention time in the second dimension is shown on the y-axis. To enhance visibility of hydrocarbon group speciation, peak areas and peak position were transferred into MATLAB and converted to bubble plots.

Most of the bubble plots show peaks on the bottom of the figure. These peaks are so-called 'wrap-arounds'. The second retention time for those compounds is longer than the assumed modulation period, so they elute later as a first peaks, during the next modulation period. The 'wrap-around' effect is undesirable especially in case of a 'normal' *non-polar x polar* column setup mode, where such peaks may affect the quantification. In this work, using 'reverse'-GCxGC-FID system, 'wrap-around' did not affect the separation, identification and quantification, since the more strongly-retained iso- and n-paraffins did not overlap any other peaks. Wrap-around can be avoided by using a longer modulation period. However, a longer modulation period leads to a lower resolution on the first column, so it was decided to not change the modulation time.
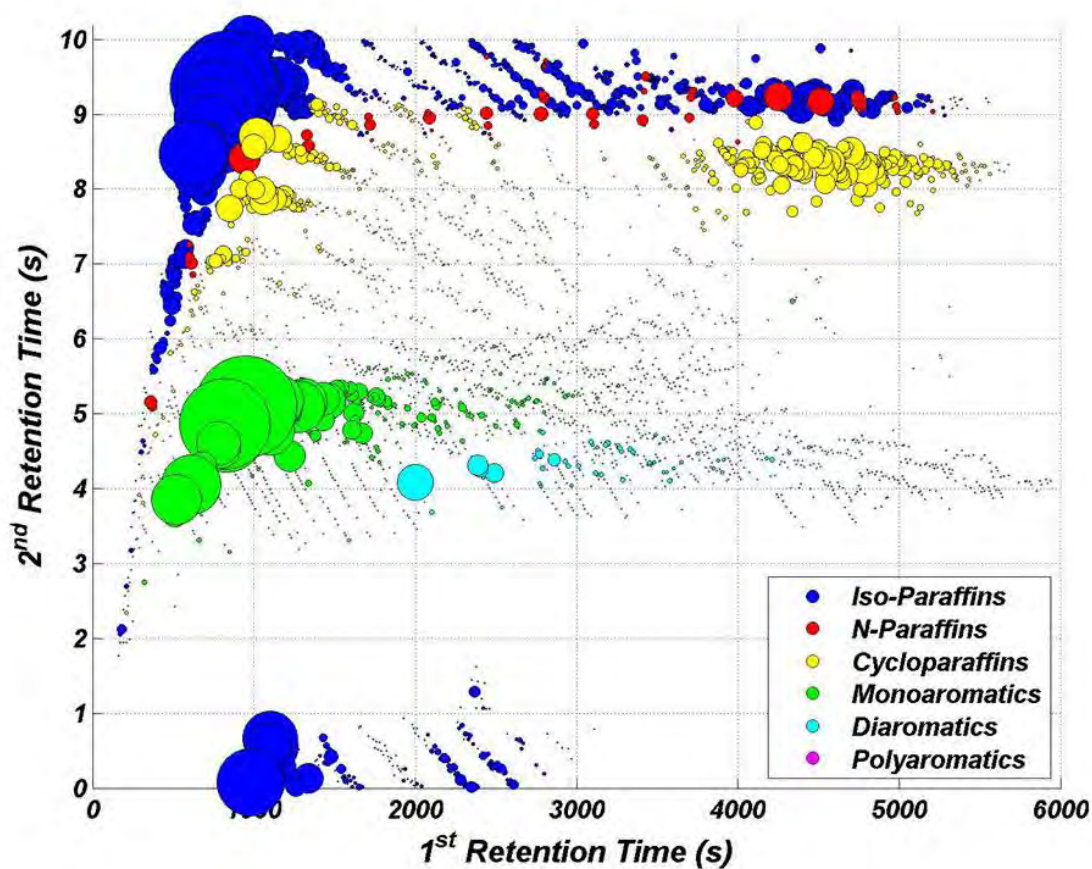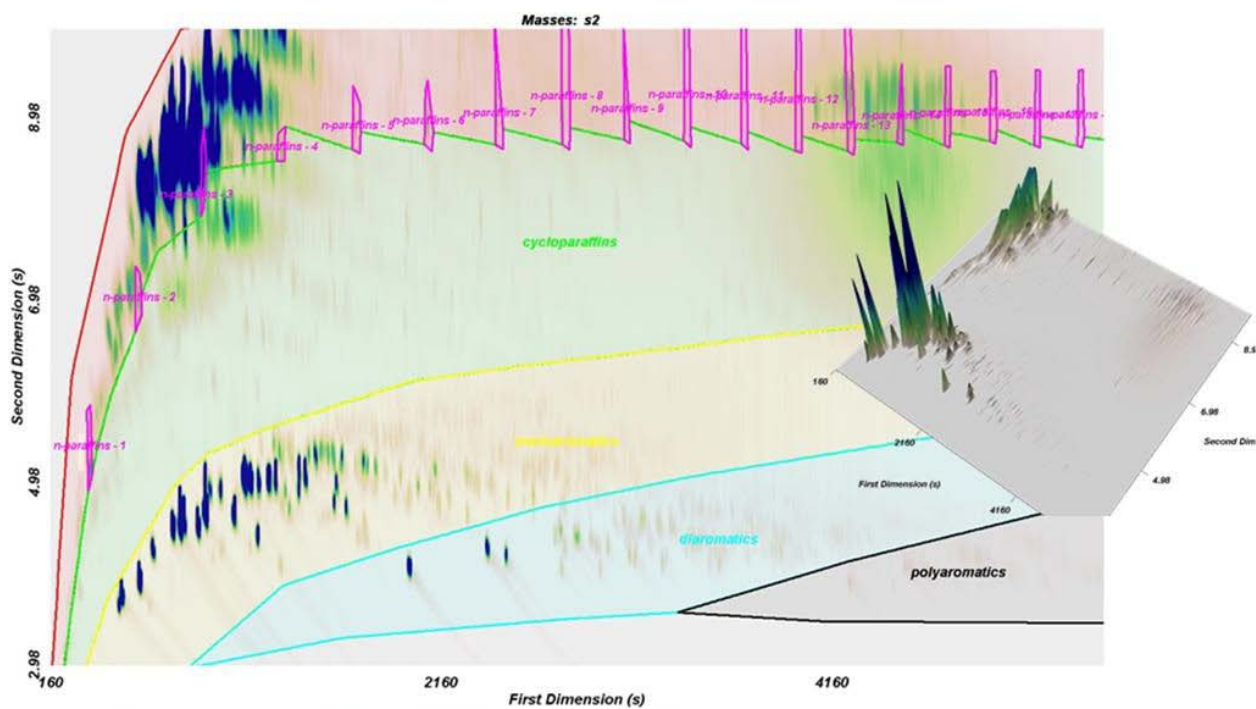
Figure 6.21 Original FD2A. 'Reverse' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a bubble plot (bottom plot).
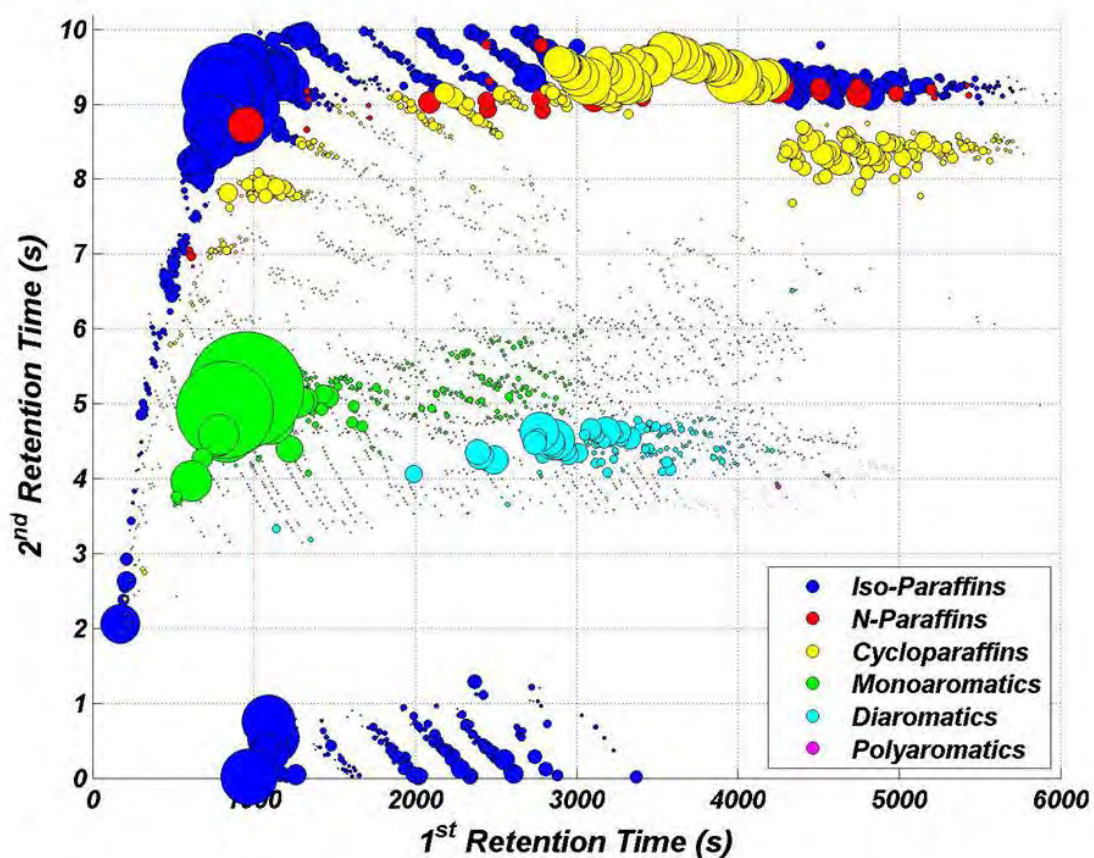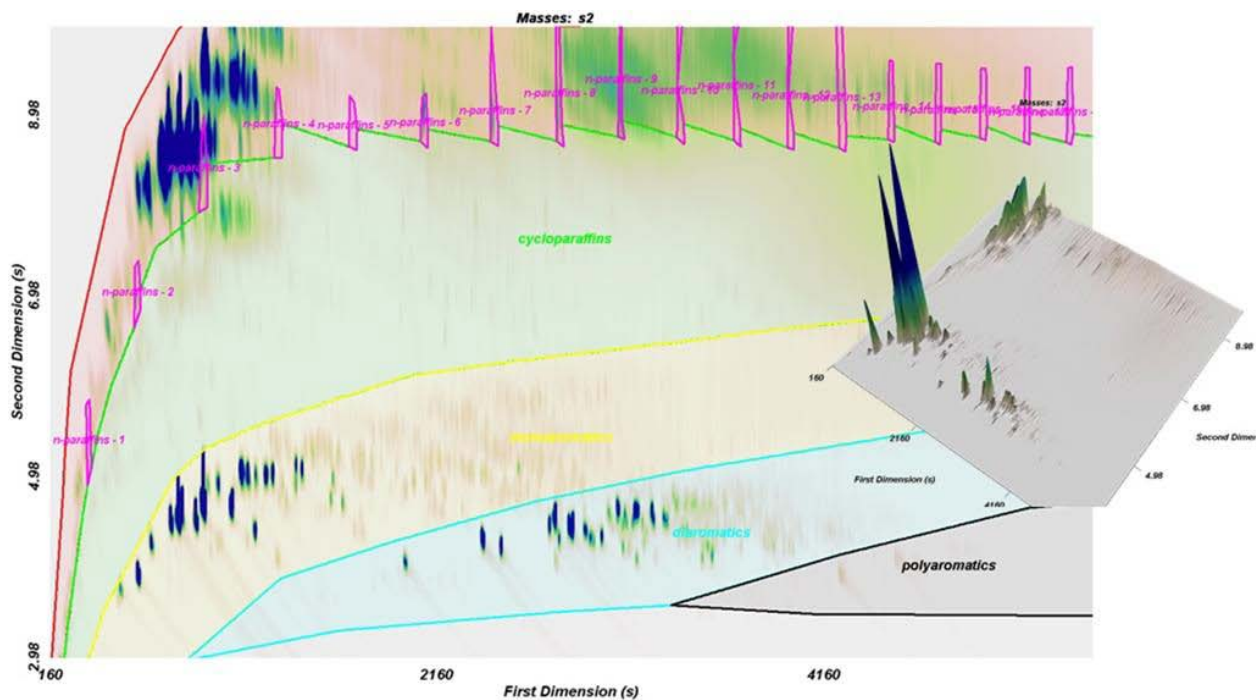
Figure 6.22 Reformulated FD2B. 'Reverse' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a bubble plot (bottom plot).
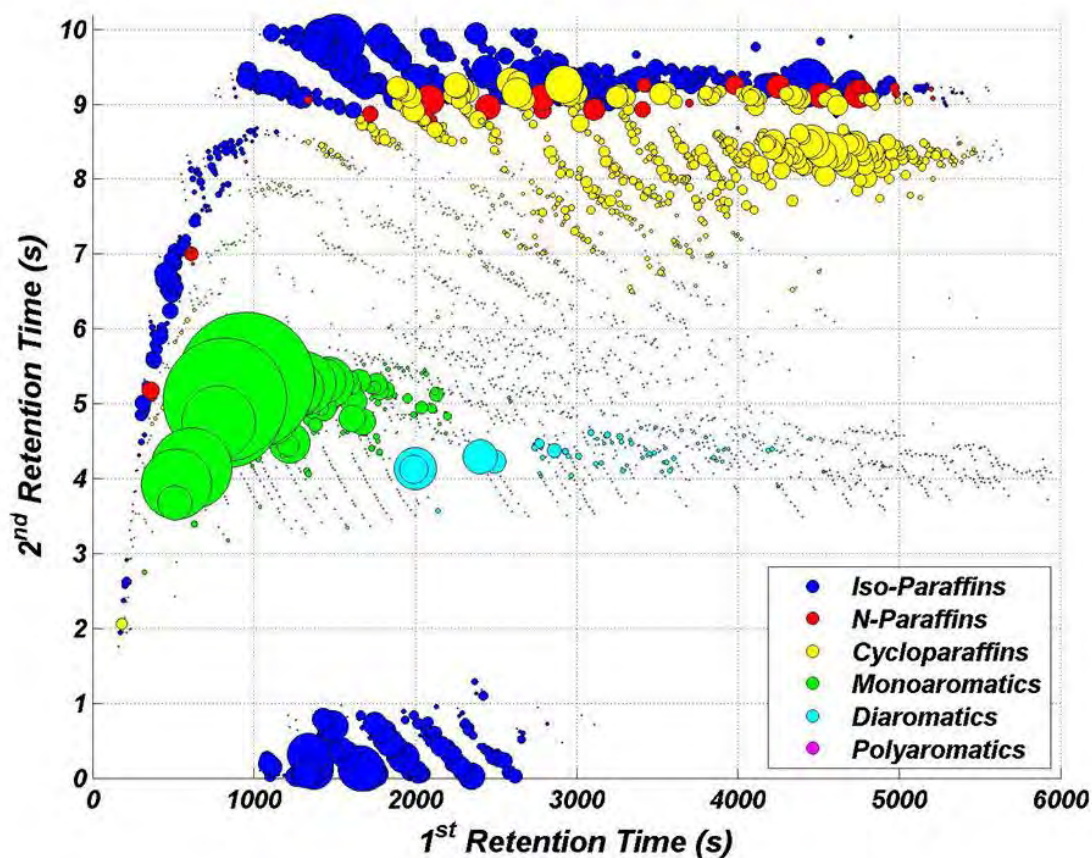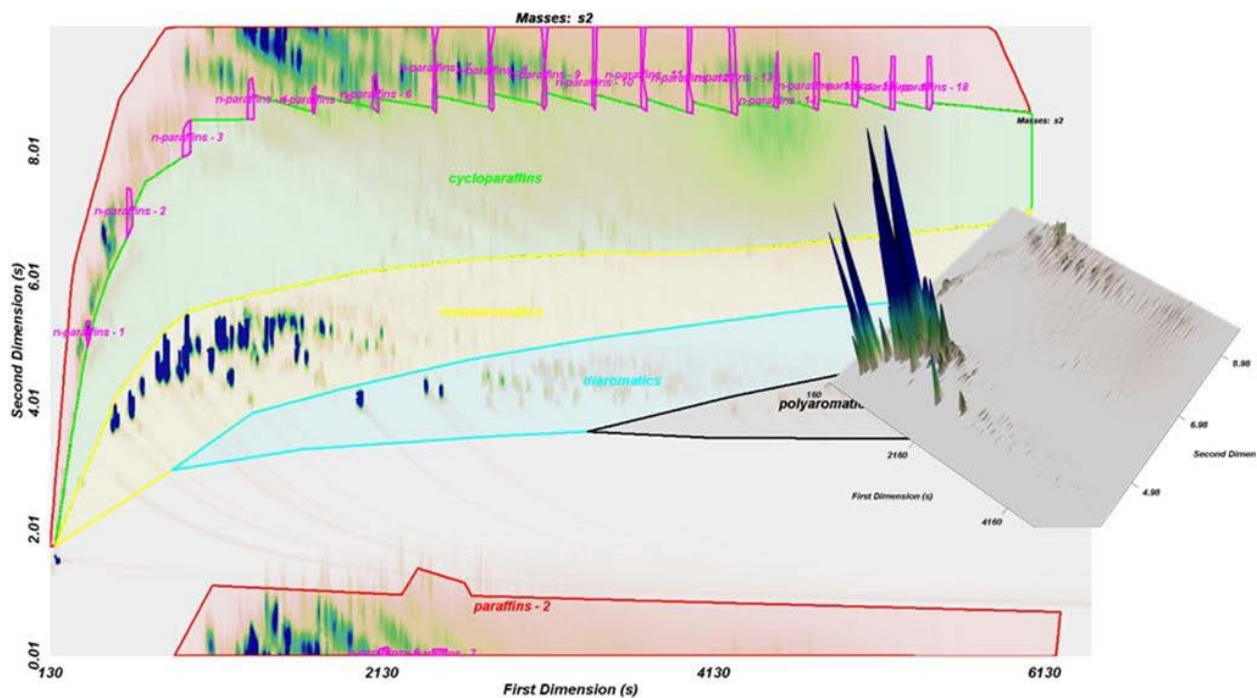
Figure 6.23 Original FD4A. 'Reverse' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a bubble plot (bottom plot).
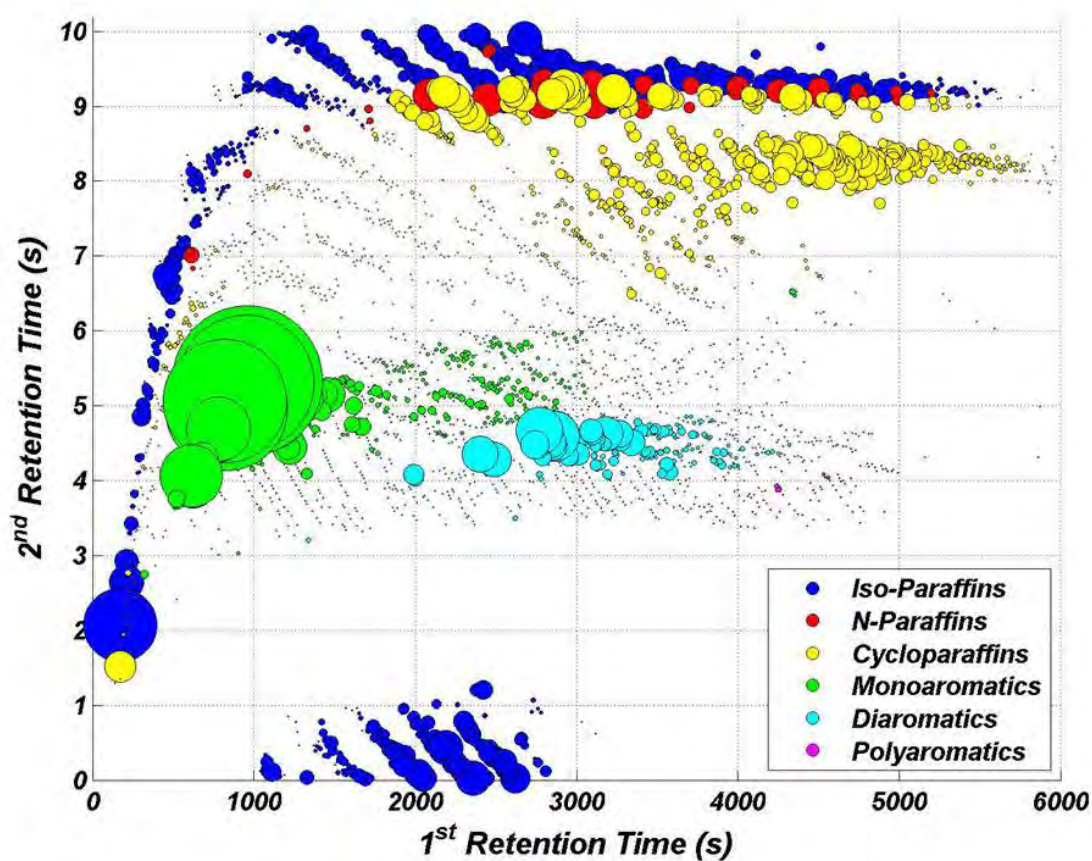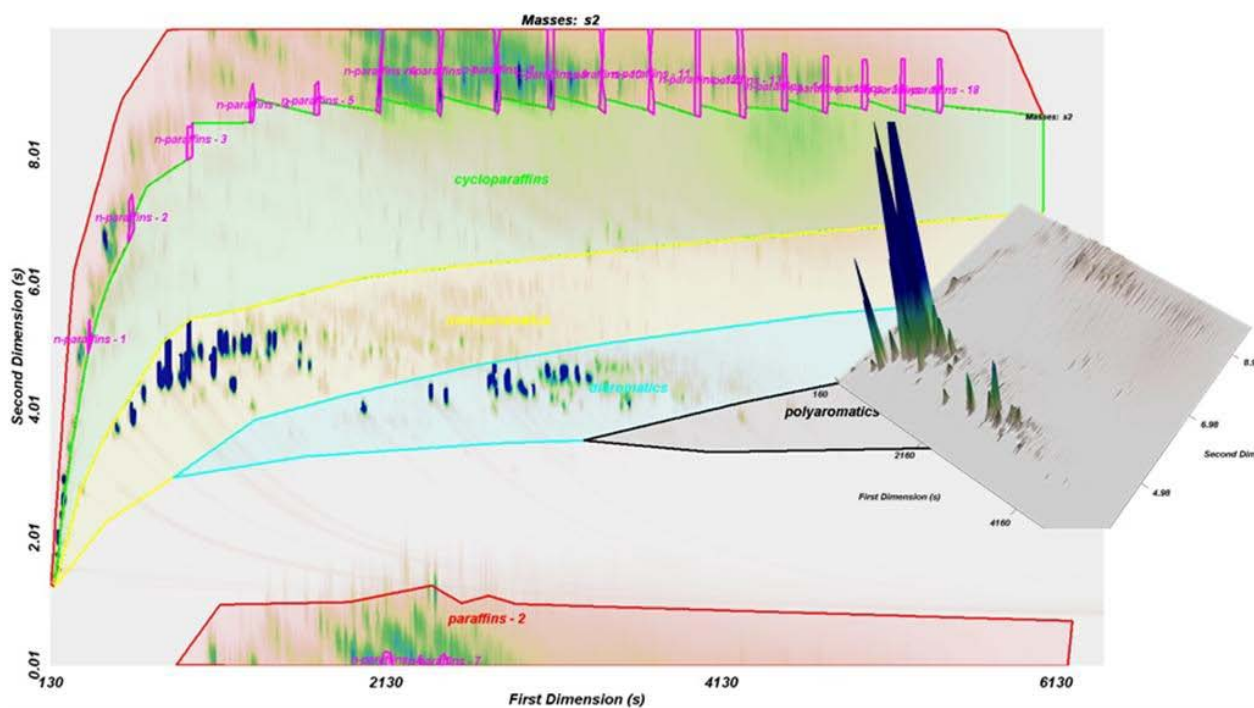
Figure 6.24 Reformulated FD4B. 'Reverse' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a bubble plot (bottom plot).
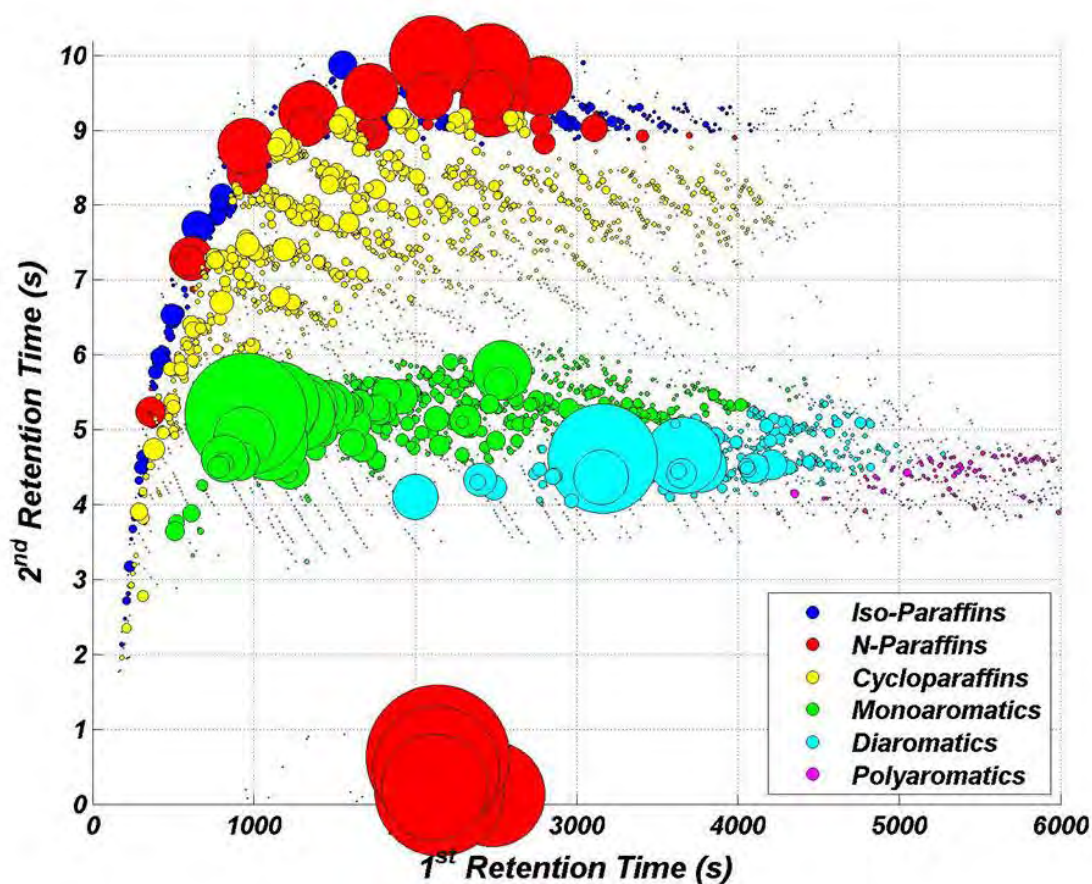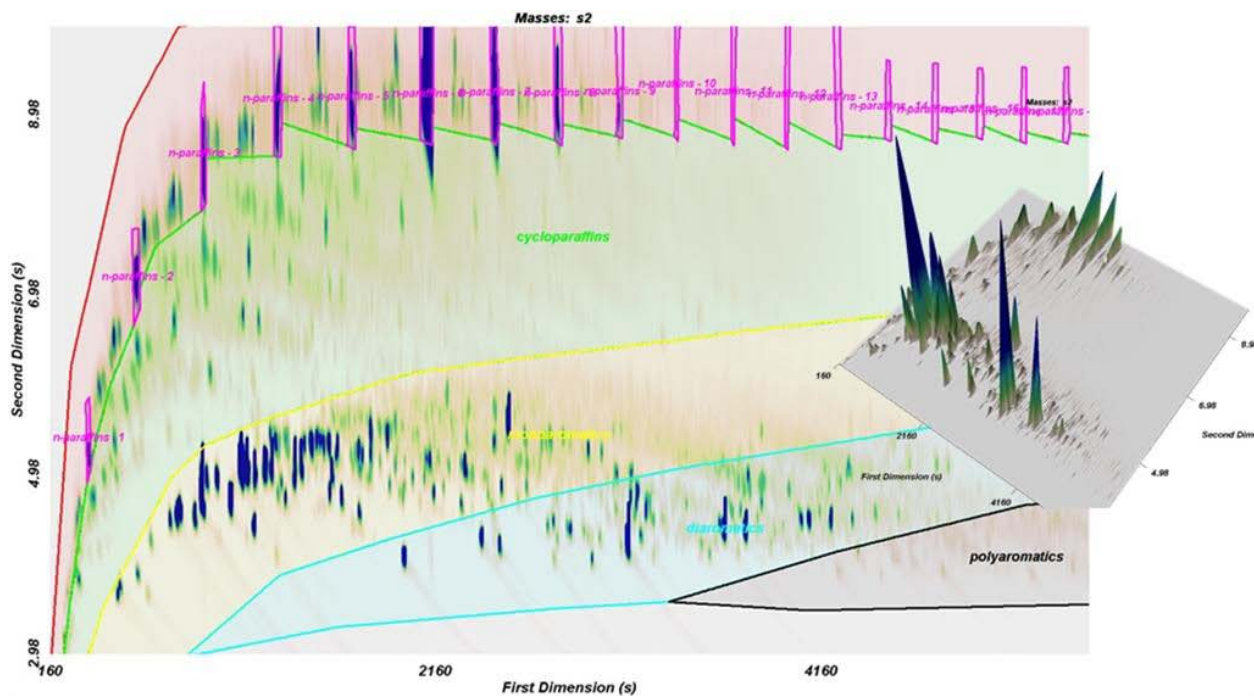
Figure 6.25 Original FD7A. 'Reverse' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a bubble plot (bottom plot).
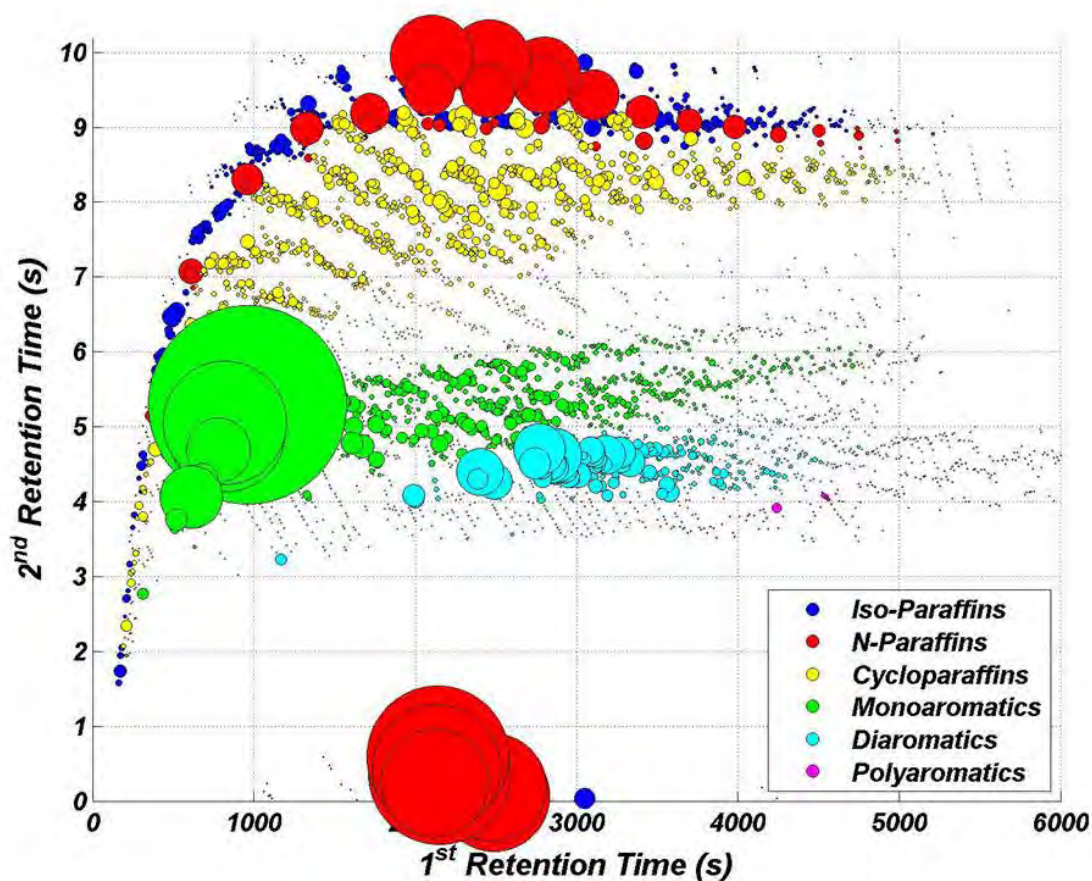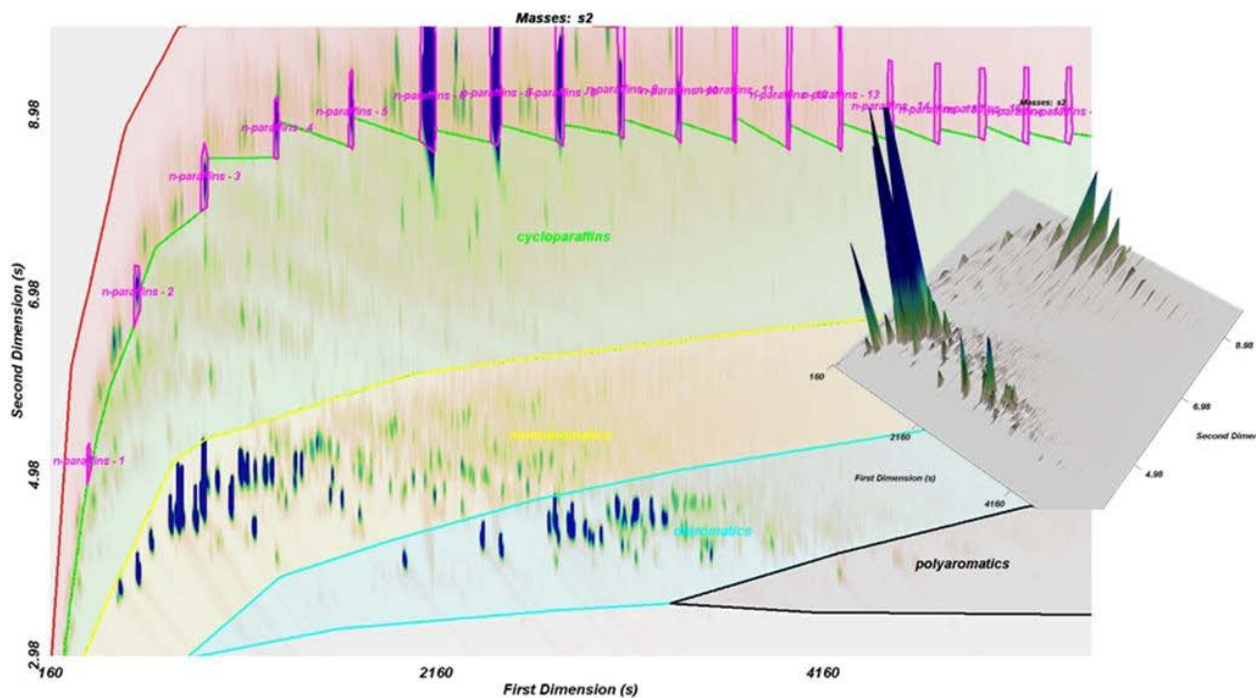
Figure 6.26 Reformulated FD7B. 'Reverse' GCxGC-FID chromatogram with inserted surface map (upper plot) and types of compounds found during 2D GC experiment as a bubble plot (bottom plot).

6.1.5 References

1. Vendeuvre, C., et al., "Characterisation of middle-distillates by comprehensive two-dimensional gas chromatography (GC×GC): A powerful alternative for performing various standard analysis of middle-distillates," *Journal of Chromatography A,* **1086** 21–28 (2005).

2. MATLAB, Release 2008b; The MathWorks, Inc.: Natick, MA, 2008.

6.2   GC-FIMS + PIONA

6.2.1 Introduction

The GC-FIMS method is applicable for fractions that boil above 392°F/200°C as was described in section 5.3. For the diesel components boiling below 392°F/200°C, the sample was injected into a PIONA analyzer with a prefractionator (see PIONA description in section 4.1). In this section the PIONA results are combined with the GC-FIMS data to obtain hydrocarbon composition over the full boiling point range of the analyzed fuel samples (C5-C21).

6.2.2 Results and Discussion

The complete GC-FIMS+PIONA data for all fuels is provided in tabular form in Appendix D. The bar plots in Figures 6.27-6.30 show the different hydrocarbon types found in analyzed samples, with consecutive figures providing a more detailed breakdown. The bar plots in Figure 6.27 capture the breakdown between aromatic and saturate content in the reformulated and original FACE diesel samples (1st level). The bar charts don't sum exactly to 100%, especially for FD2A, because of the apparent detection of other hydrocarbons such as olefins. The results suggest that the aromatics content of the FD2 and FD4 fuels are very close to each other, for both the original and reformulated fuels. This is not consistent with the design of those fuels where the FD2 fuels were designed to have about one half of the aromatics as the FD4 fuels. As discussed in section 4.1. of the PIONA results, this discrepancy is attributed to a problem of properly capturing and analyzing all of the C12 range paraffins for the FD2 fuels. This results in an apparent lower saturates level and higher aromatics level than actually present in those fuels.
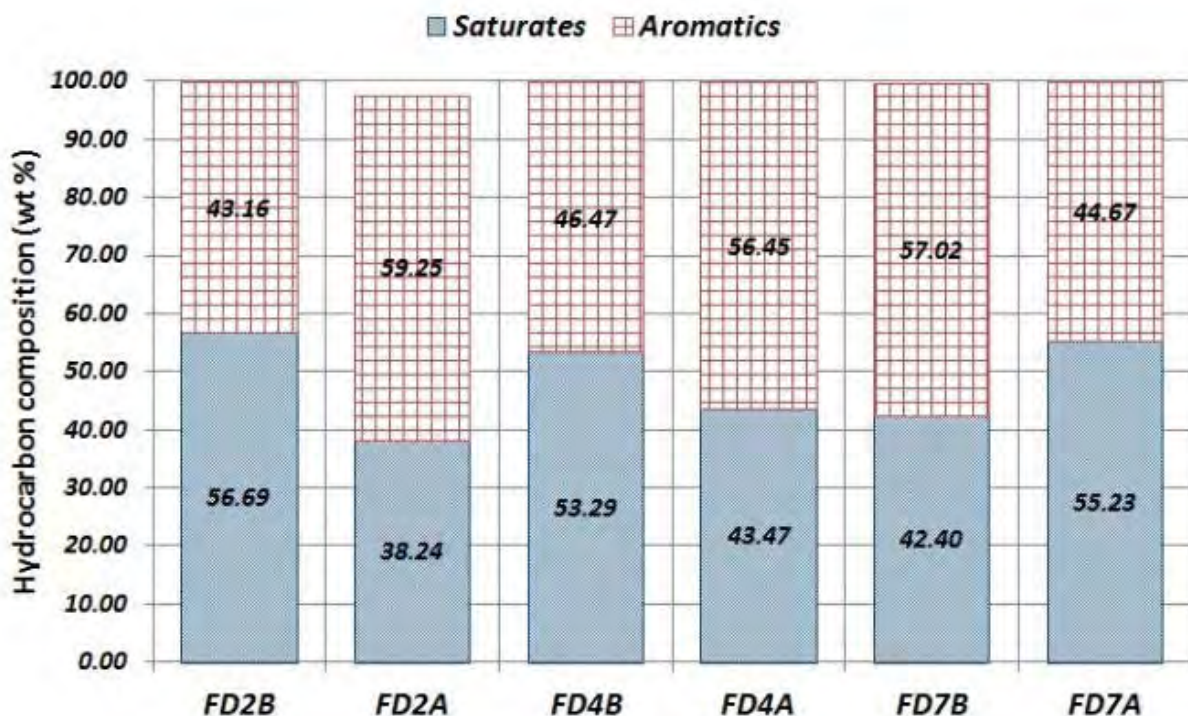
Figure 6.27 Fuel compositions by GC-FIMS+PIONA (1st level – main groups)

In Figure 6.28, saturates were broken down into paraffins and cycloparaffins, and the aromatic group was split into monoaromatics, diaromatics and triaromatics (2nd level).
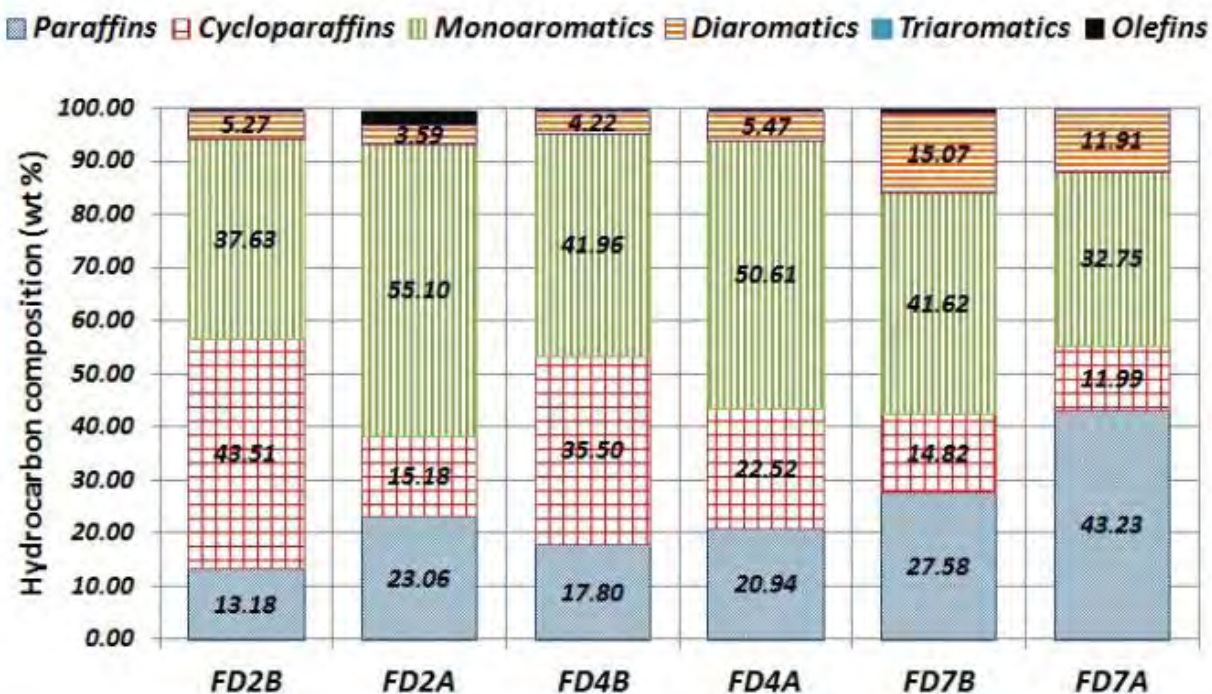
Figure 6.28 Fuel compositions by GC-FIMS+PIONA (2nd level)

A further breakdown (3rd level) of the saturates and aromatics is provided in the bar charts in Figures 6.29 and 6.30, respectively.
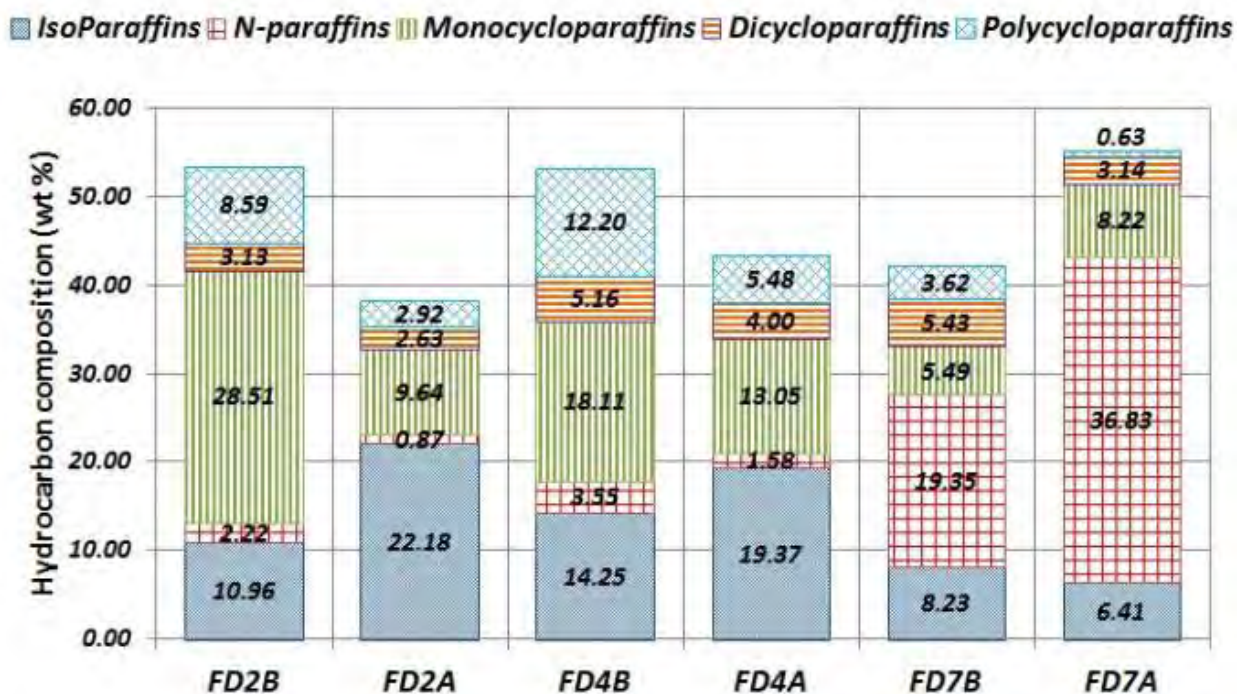
Figure 6.29 GC-FIMS/PIONA data for saturates by GC-FIMS+PIONA (3rd level)
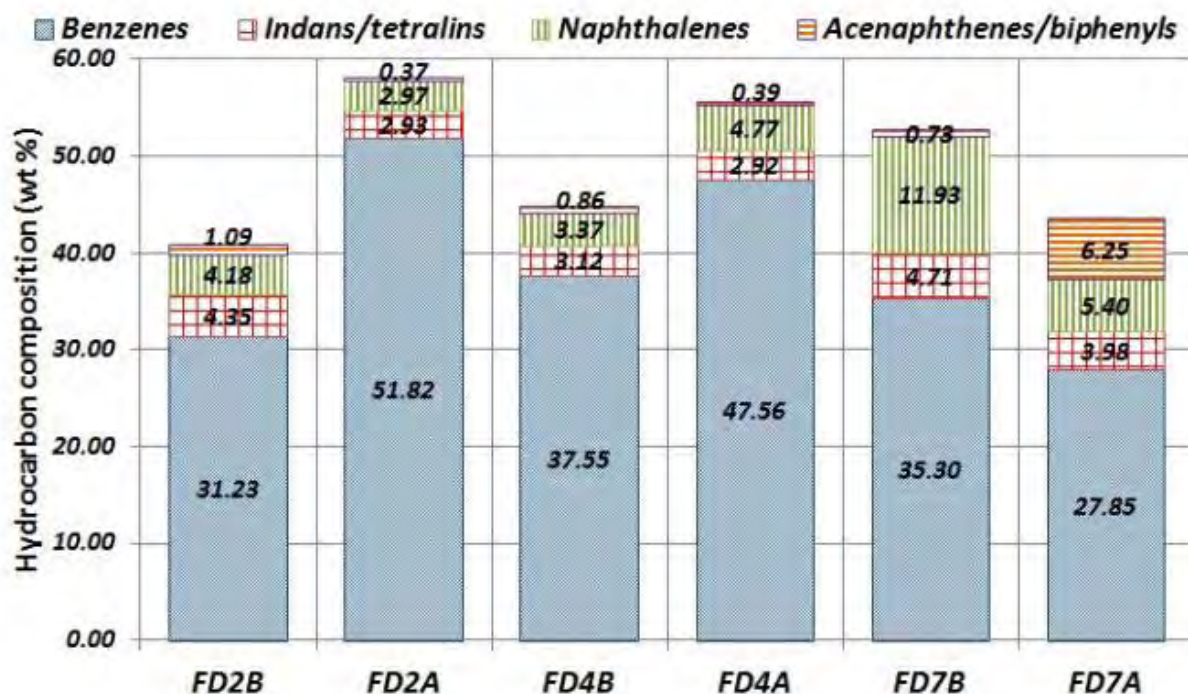
Figure 6.30 GC-FIMS/PIONA data for aromatics by GC-FIMS (3rd level)

Figures 6.31-6.39 use bubble charts to represent the detailed hydrocarbon distributions. Both the color intensity and the size of circles in the charts represent concentration (in wt%) of hydrocarbon classes found in samples. Such visualization allows for detailed comparison of hydrocarbon class distribution by carbon number. We found that the real power of presenting data as bubble plots resides in quick and natural way of looking for differences between samples.

The first three bubble plot sets (Figures 6.31 – 6.33) show side-by-side comparison of 2nd level compositional information for reformulated and original FACE fuels #2, #4 and #7, respectively.

Figure 6.31 GC-FIMS+PIONA hydrocarbon types (2nd level) by carbon number for FACE fuel #2

Figure 6.32 GC-FIMS+PIONA hydrocarbon types (2nd level) by carbon number for FACE fuel #4
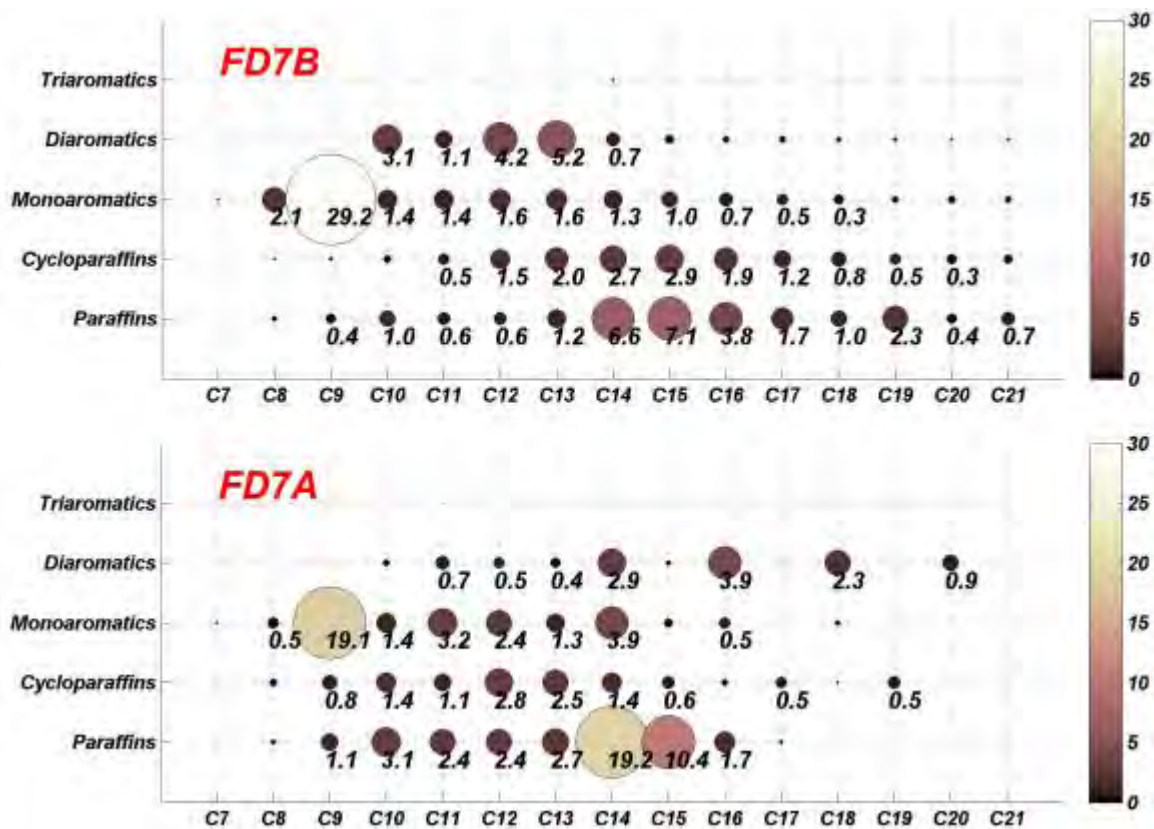
Figure 6.33 GC-FIMS+PIONA hydrocarbon types (2nd level) by carbon number for FACE fuel #7

The next set of bubble plots (Figure 6.34 – 6.39) show side-by-side comparison of the 3ⁿᵈ level compositional information for reformulated and original FACE fuels #2, #4 and #7 respectively.
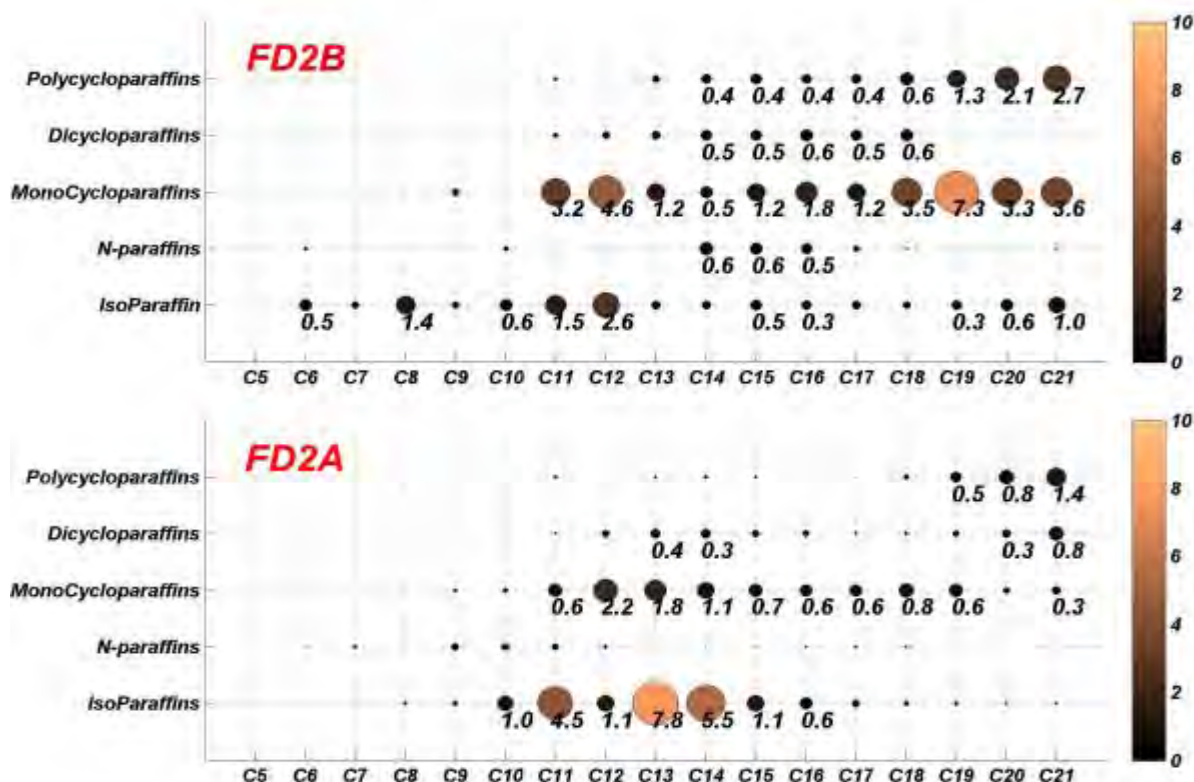
Figure 6.34 GC-FIMS+PIONA results for saturate subtypes (3ʳᵈ level) by carbon number for FACE fuel #2
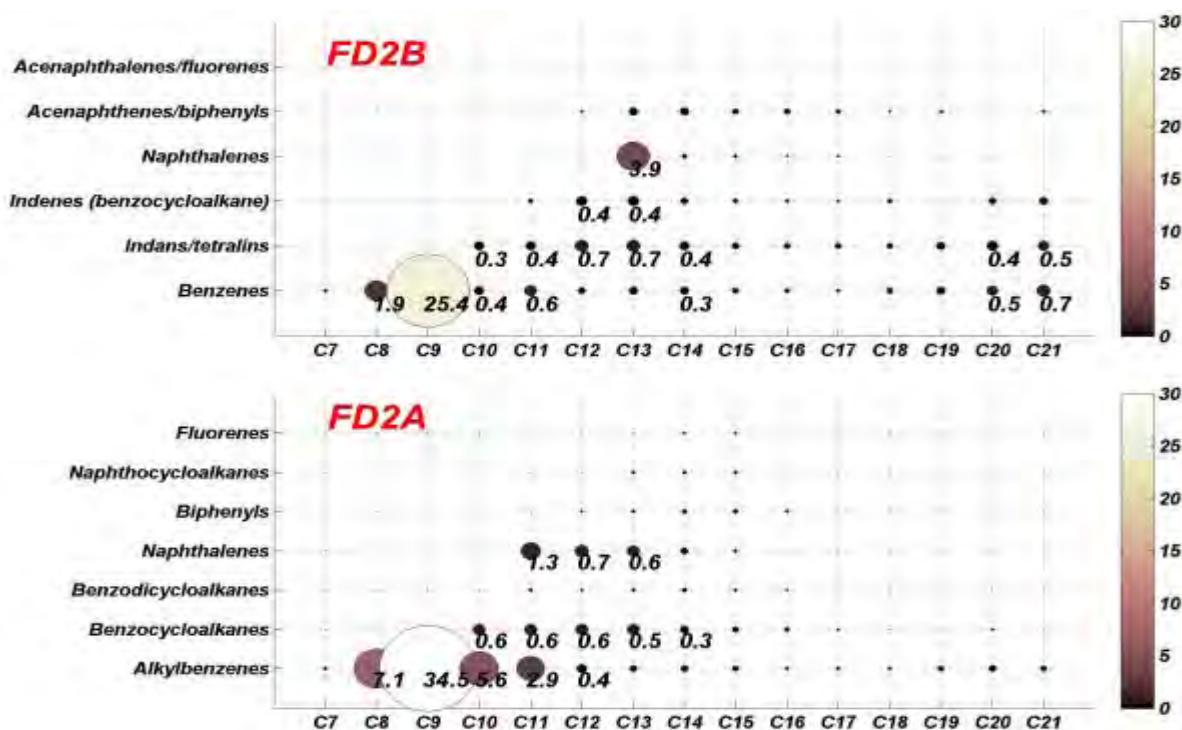
Figure 6.35 GC-FIMS+PIONA results for aromatic subtypes (3ʳᵈ level) by carbon number for FACE fuel #2
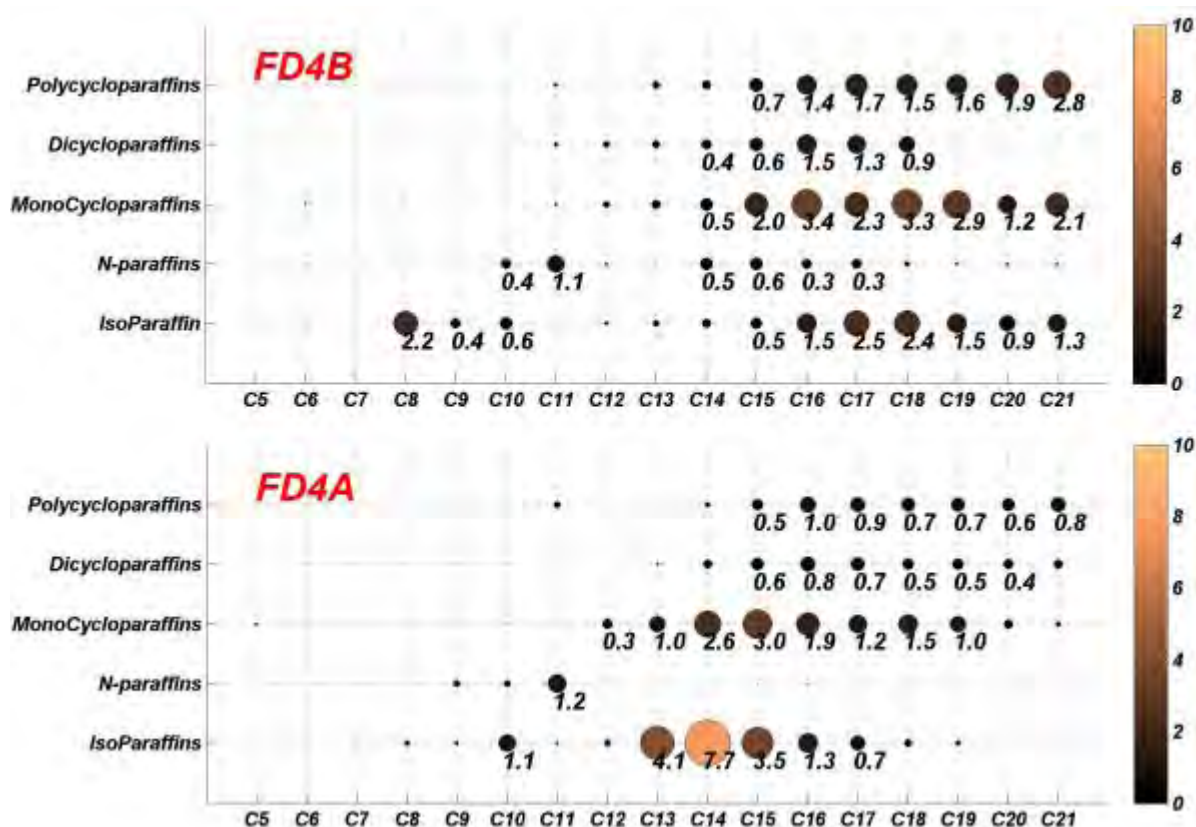
Figure 6.36 GC-FIMS+PIONA results for saturate subtypes (3rd level) by carbon number for FACE fuel #4
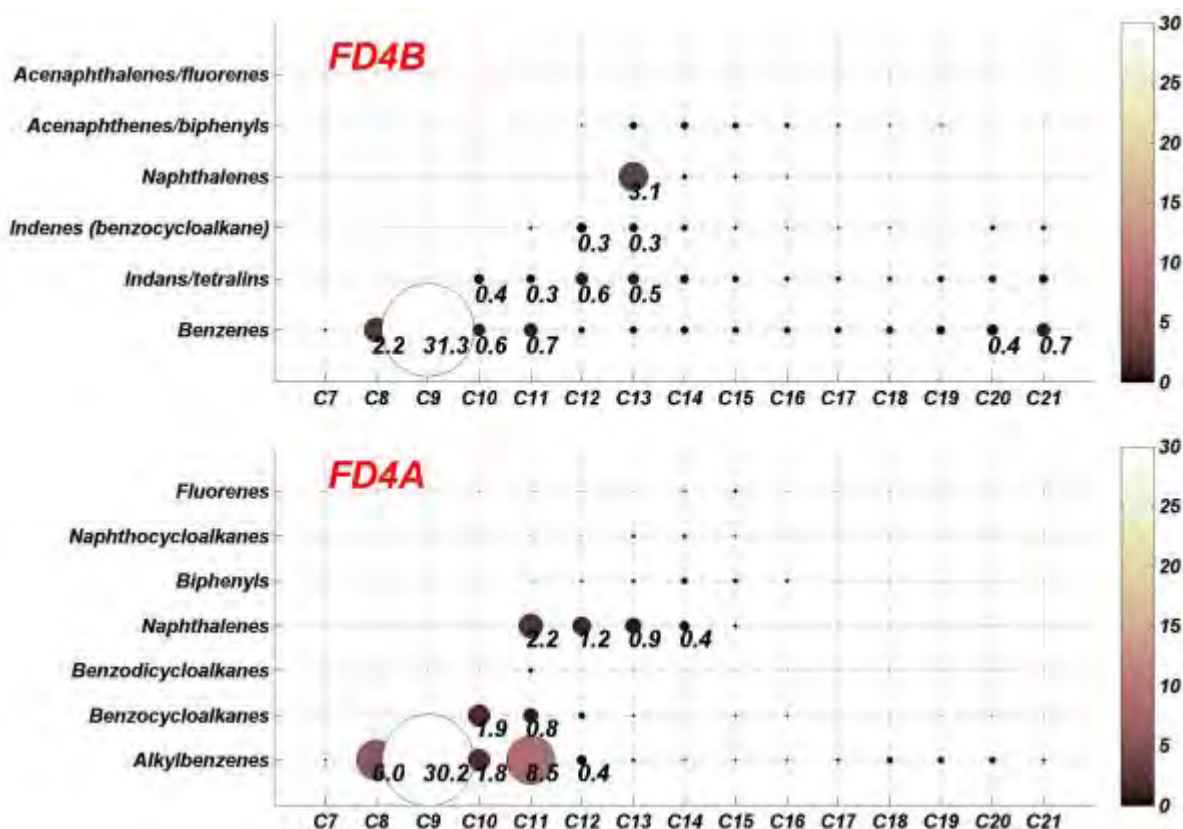
Figure 6.37 GC-FIMS+PIONA results for aromatic subtypes (3rd level) by carbon number for FACE fuel #4

Figure 6.38 GC-FIMS+PIONA results for saturate subtypes (3ʳᵈ level) by carbon number for FACE fuel #7
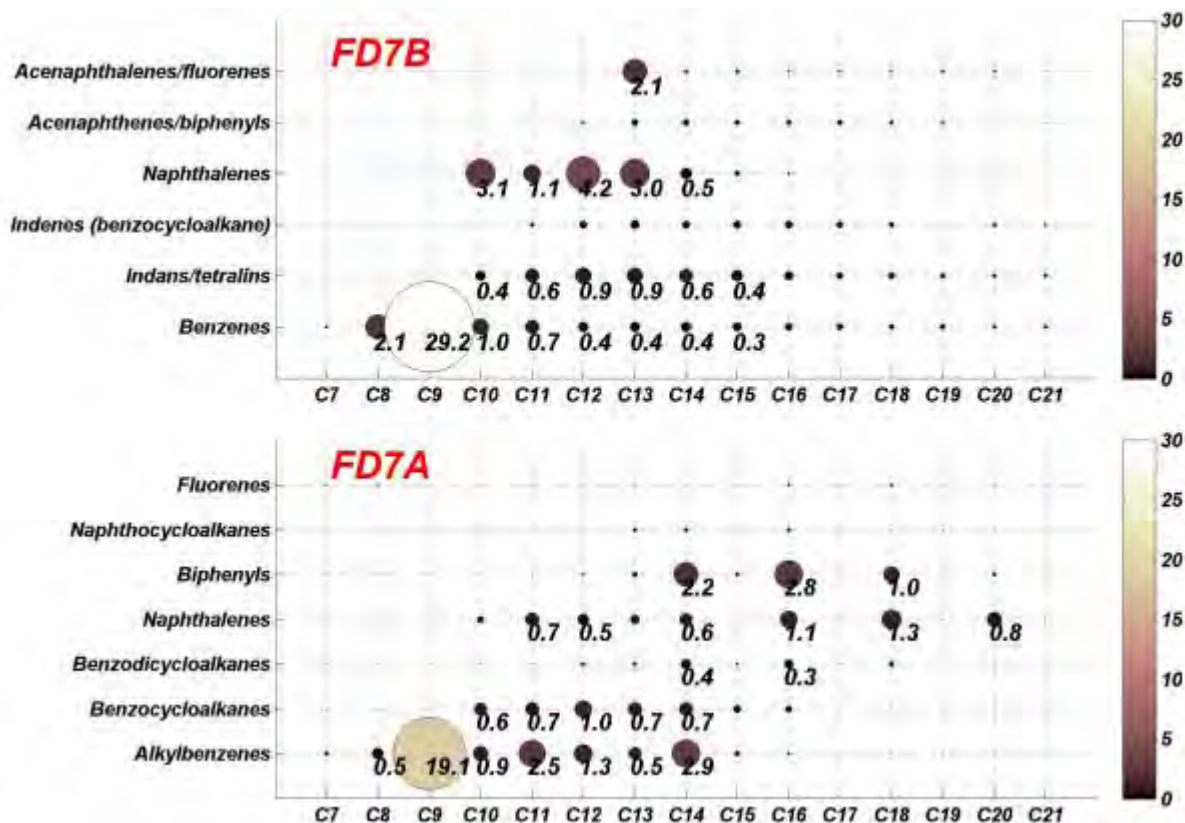
Figure 6.39 GC-FIMS+PIONA results for aromatic subtypes (3ʳᵈ level) by carbon number for FACE fuel #7

6.3   SOLID PHASE EXTRACTION - GAS CHROMATOGRAPHY-MASS SPECTROMETRY/PIONA

6.3.1 Introduction

In this section, the aromatic and saturate GC-MS data are combined with PIONA data to give the total hydrocarbon type contents in full boiling range (IBP-FBP). The scheme of SPE-GC-MS/PIONA is provided in Figure 6.40.
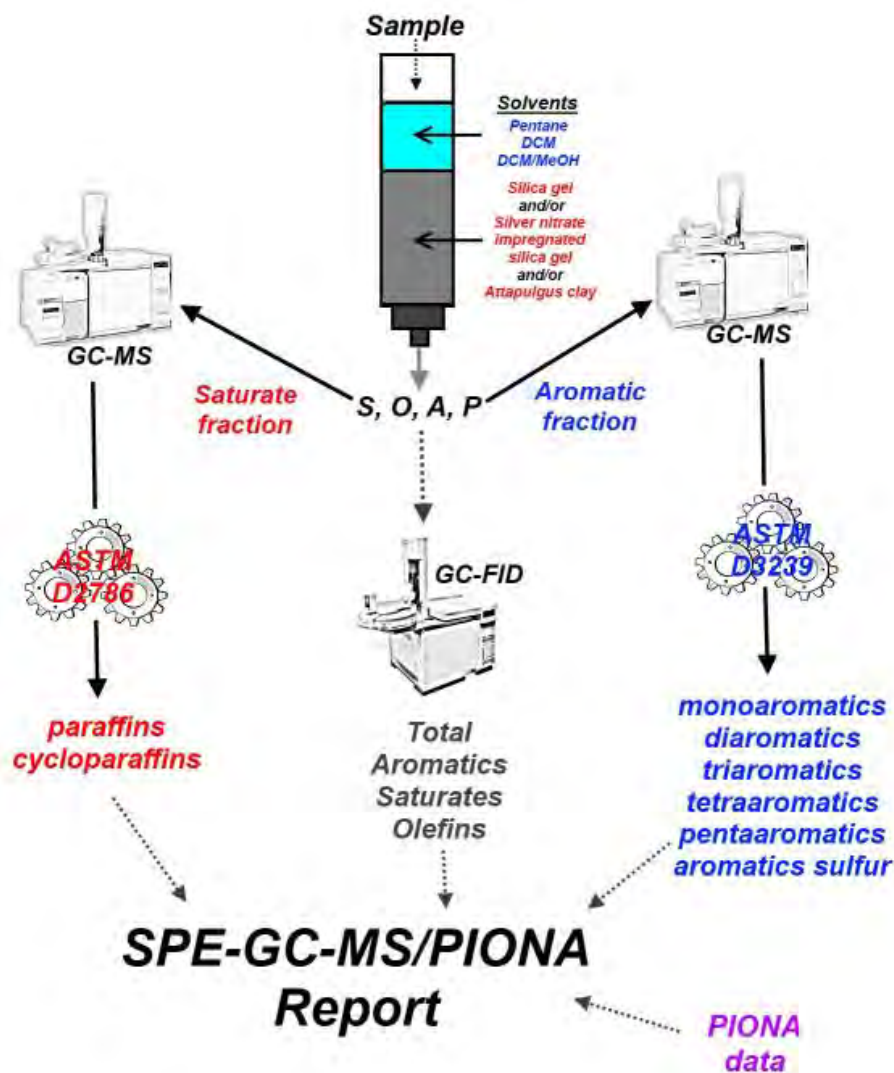
Figure 6.40 Hydrocarbon class separations by combining solid phase extraction, gas chromatography with mass spectrometer and PIONA analysis

6.3.2 Results and Discussion

The SPE-GCMS/PIONA data are provided in tabular form in Appendix C. The total contents for saturates, olefins, aromatics, and polars are given by the earlier SOAP-SPE + PIONA data. Figure 6.41 shows general results of SPE-GCMS/PIONA analysis. In contrast to GC-FIMS this method has no capability to split

74

paraffins into iso- and n-paraffins. Once again the total aromatics level for the FD2 fuels are significantly higher than the design values, which is attributed to the PIONA fractionation issues discussed previously.
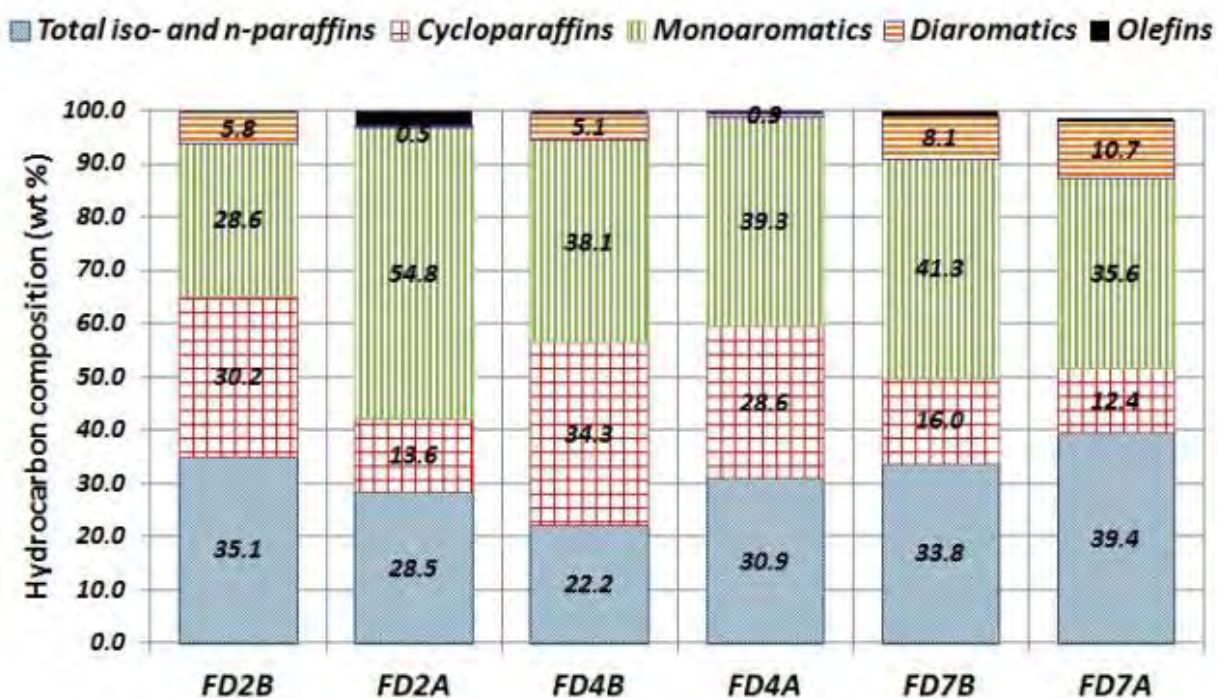
Figure 6.41 SPE-GC-MS + PIONA data for reformulated and original FACE fuels

In Figure 6.42, saturates are broken down into iso- + n-paraffins, monocycloparaffins, dicycloparaffins, tricycloparaffins and 4-Rings cycloparaffins.
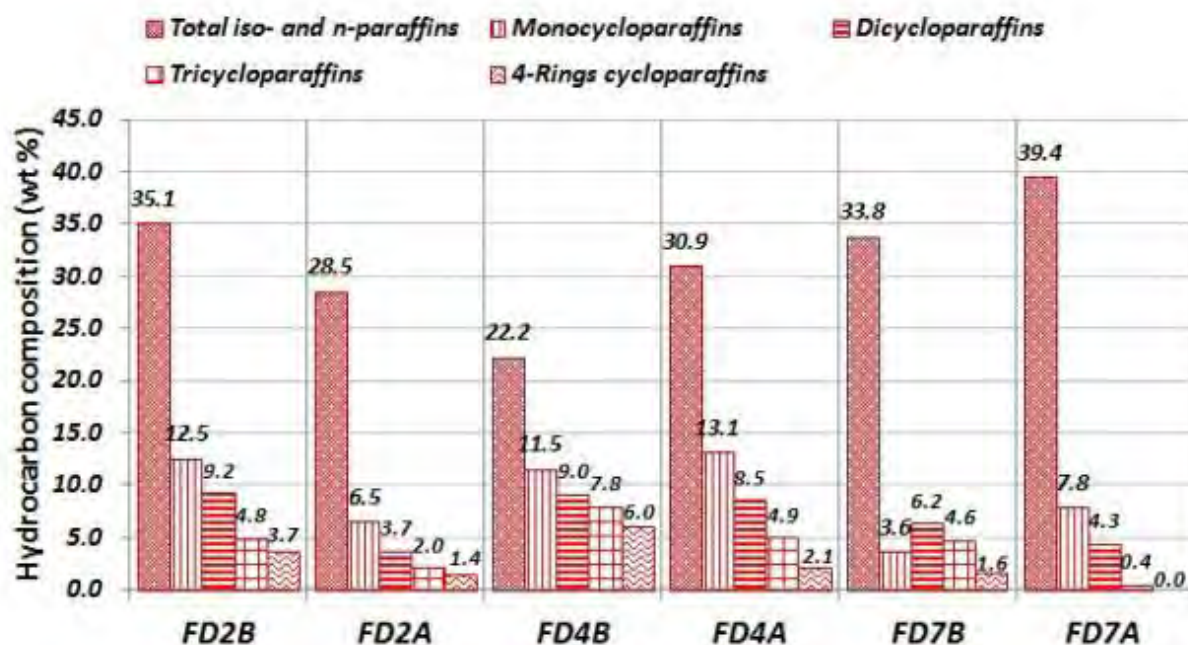
Figure 6.42 SPE-GC-MS + PIONA data for *saturates* in reformulated and original FACE fuels

75

Figure 6.43 shows the detailed hydrocarbon composition of the monoaromatic portion of the samples. In this case, the method allows for the breakdown monoaromatics into alkylbenzenes, benzocycloalakanes and benzodicycloalkanes. It can be observed that in all fuels monoaromatics were composed predominantly of alkylbenzenes.
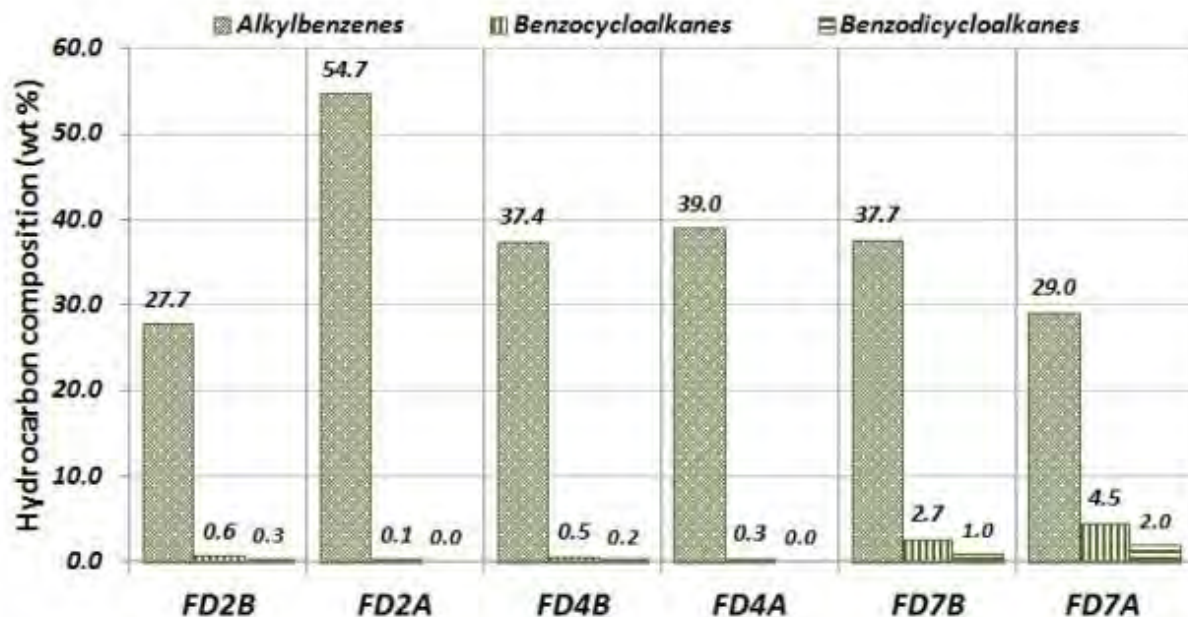
Figure 6.43 SPE-GC-MS + PIONA data for *monoaromatics* in reformulated and original FACE fuels

The diaromatic content given by naphthalene, naphthocycloalkane, and fluorene is shown in Figure 6.44. The diaromatic fraction of original fuel FD7A is mostly composed of naphthocycloalkanes and naphthalene. In the reformulated version of this fuel, the amount of naphthocycloalkanes was diminished. Interestingly, according to the GC-FIMS results presented in a previous chapter, the biphenylalkane class of FD7B was reduced. Are these two results in contradiction? No. It should be noted here that the GC-MS report table provides information about naphthocycloalkanes which are structural isomers of biphenylalkanes (see Figure 6.45).
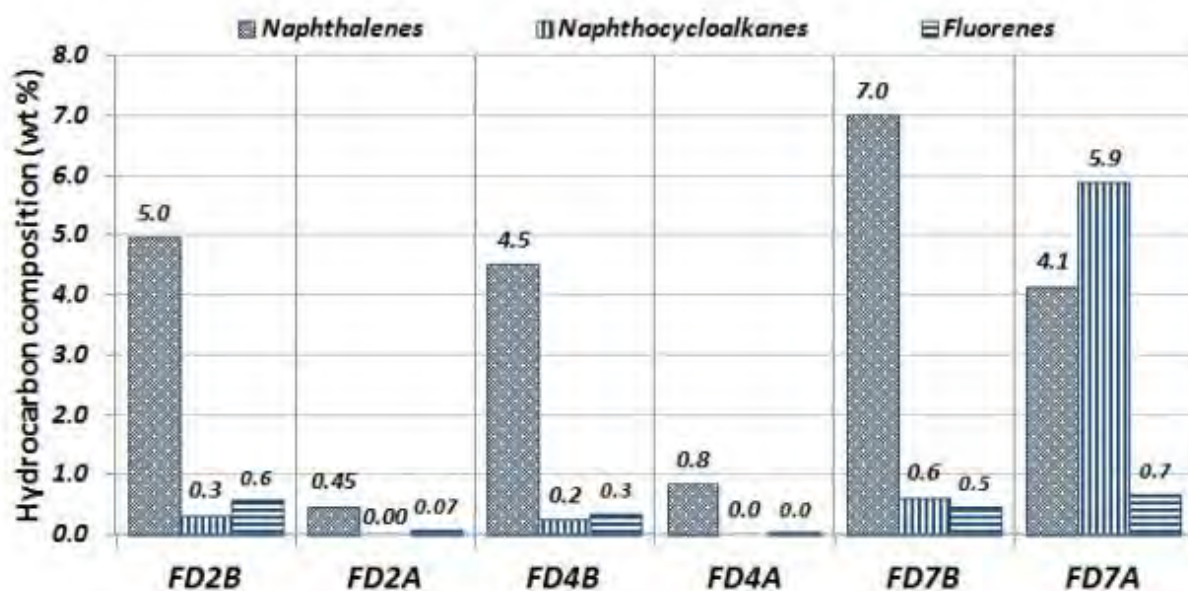
Figure 6.44 SPE-GC-MS + PIONA data for *diaromatics* in reformulated and original FACE fuels
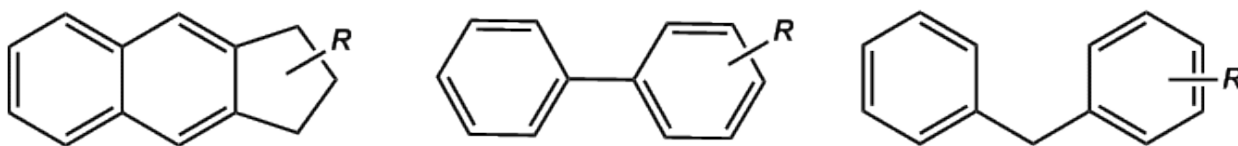
Figure 6.45. Selected structural isomers of naphthocycloalkanes. The common molecular formula for this hydrocarbon group is given as C_nH_{2n-14}

7. METHODS COMPARISON/ADVANCED ANALYSIS SUMMARY

7.1 Methods Comparison for Hydrocarbon Characterization for Fractions Boiling Up to 392°F

The results for hydrocarbon components boiling below 392°F/200°C for the PIONA, DHA, and GCxGC FID methods are presented in Figure 7.1. After converting retention times obtained in the GCxGC FID analyses to boiling point (see section 6.1.3), all components boiling before 392°F/200°C were distributed into two main hydrocarbon classes: saturates and aromatics. Additional assumptions (i.e. SimDis cut point) or using prefractionator during PIONA or DHA analysis sometimes can lead to substantial errors in final hydrocarbon content report.

For the FD4 and FD7 samples there is a good agreement of the compositional values from the 3 different methods. However there is a noticeable discrepancy between the PIONA, DHA and GCxGC-FID results for reformulated and original FACE fuel #2 (an upper row in Figure 7.1). We believe the GCxGC results are more accurate for the FD2 fuels than PIONA and DHA results.
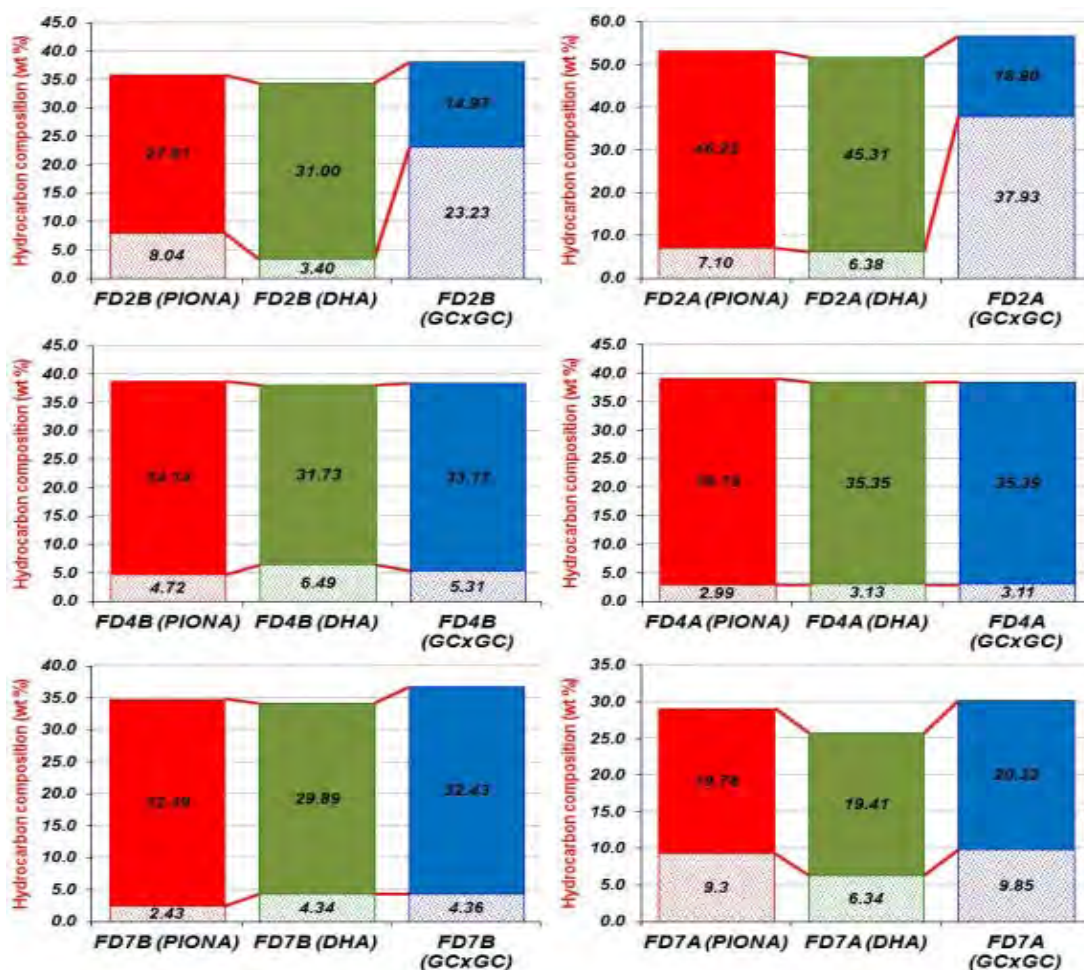
Figure 7.1 Comparison of PIONA, DHA and n-GCxGC-FID results for reformulated and original FACE fuels. Upper part of the bar depicts aromatic content, bottom part saturates content.

A detailed view of PIONA and DHA saturate and aromatic content by carbon number distribution for the reformulated FACE fuels is presented in Figure 7.2 and Figure 7.3. The aromatics distribution trends based on PIONA analysis follow the ones provided from the DHA method for all samples (see Figure 7.3). Unlike aromatics, the saturates distribution by carbon number is characterized by complete disagreement between the two considered methods for all analyzed samples.
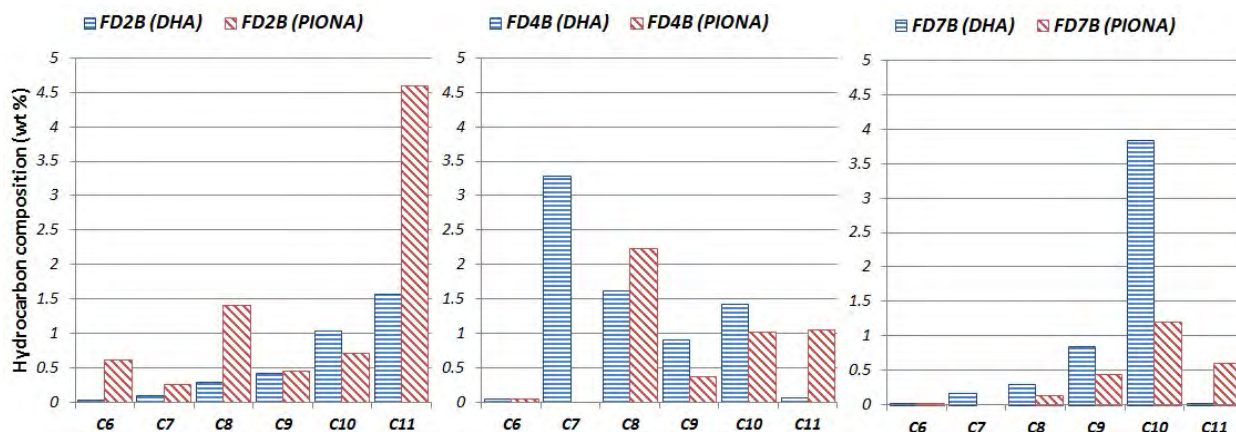
Figure 7.2 Comparison of DHA and PIONA data. Distribution of saturates hydrocarbon type by carbon number.
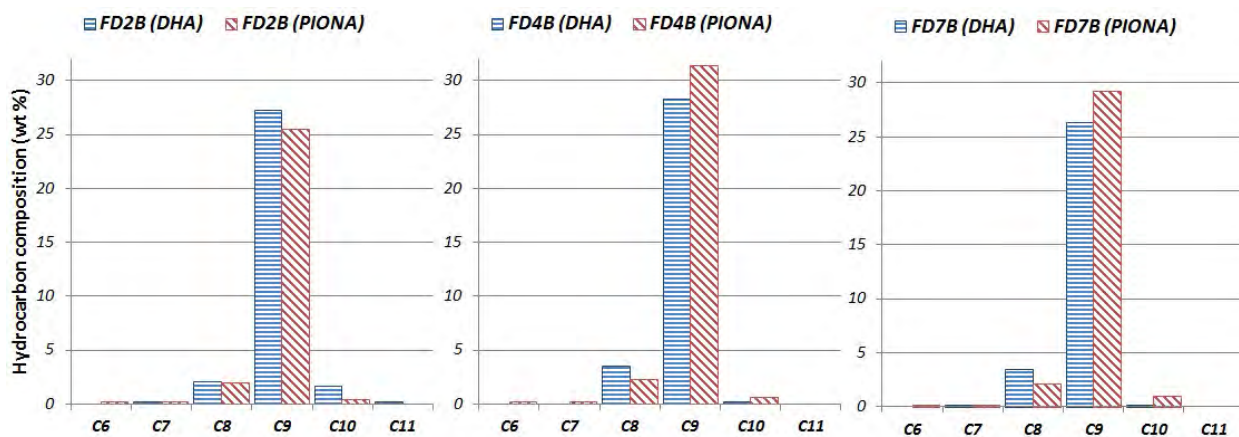
Figure 7.3 Comparison of DHA and PIONA data. Distribution of aromatics type by carbon number.

7.2 Methods Comparison for Hydrocarbon Characterization for Fractions Boiling Above 392°F

This section summarizes the results of methods often used to determine the detailed hydrocarbon composition in the boiling range of 392°F - FBP (200°C - FBP). Figures 7.4 and 7.5 illustrate hydrocarbon comparison of the two main methods used in the aforementioned temperature region: SPE-GCMS and GC-FIMS. The third method, two-dimensional gas chromatography (GCxGC), was included in this comparison as external independent analysis. The GCxGC technique allows for full range comparison so to match temperature restrictions included here are only the hydrocarbon peaks that boil above 392°F/200°C. The two-dimensional gas chromatography performed with 'normal' column setup was used for this comparison, as described in details in section 6.1.3

The results in this section help to identify discrepancies in the 392°F - FBP results before merging with the <392°F results from the PIONA and DHA data. For the reformulated fuels, GC-FIMS gave the highest aromatics and lowest saturates levels, while the GCxGC gave the lowest aromatics and highest saturates values. For these fuels, the GCMS and GCxGC results are very close to each other. These trends apply for the original fuels FD2A and FD4A, but not FD7A, where results from all three methods are very close.

Figure 7.5 further breaks down the saturates and aromatics into paraffins (n- and iso-), cycloparaffins, monoaromatics, and diaromatics. There are no clear cut trends. The results for the three methods for the four hydrocarbon classes are closest for the original fuel FD7A.
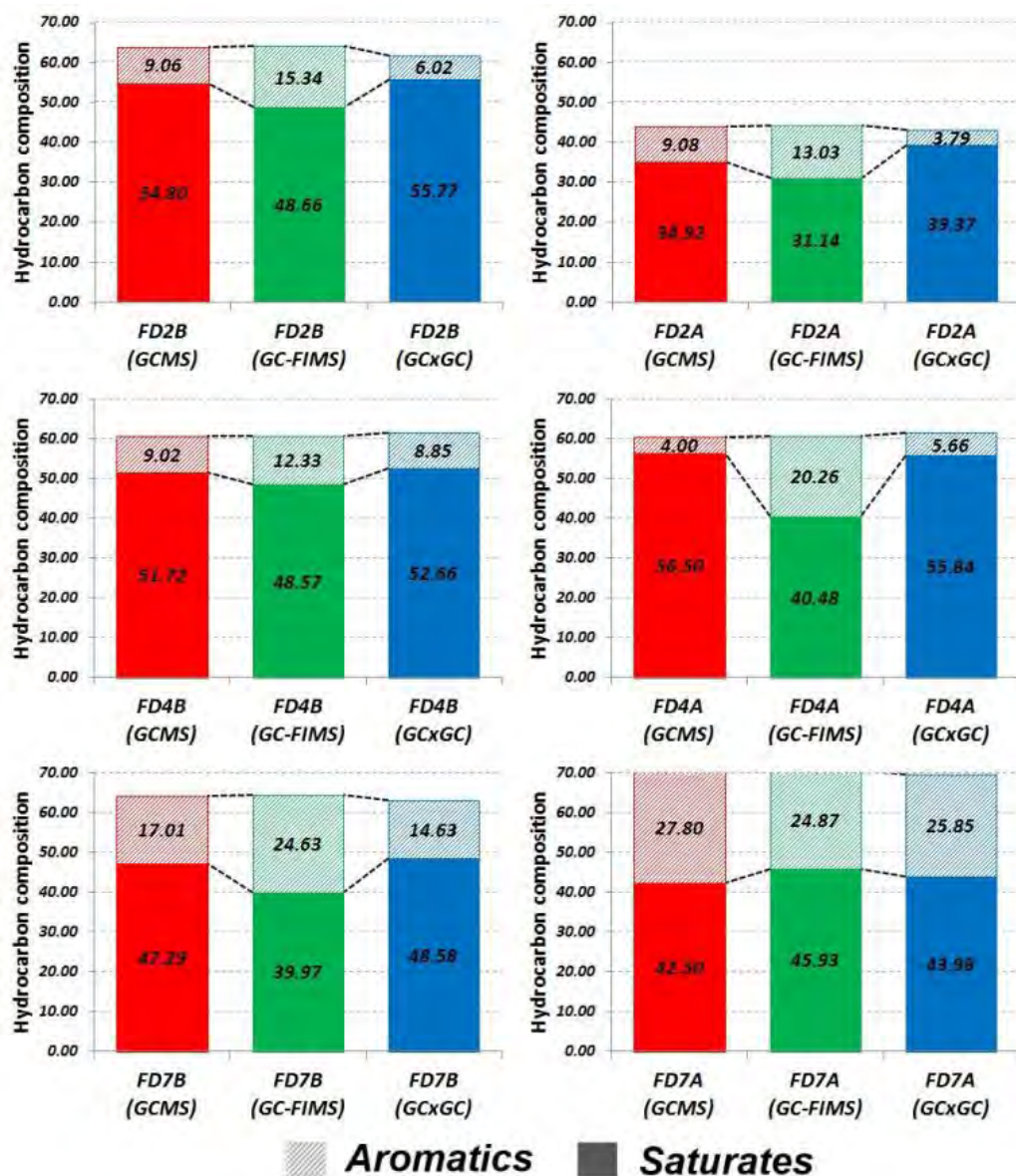
Figure 7.4 Comparison of GC-MS, GC-FIMS and n-GCxGC-FID results for reformulated and original FACE fuels. Upper part of the bar depicts aromatic content, bottom part saturates content.
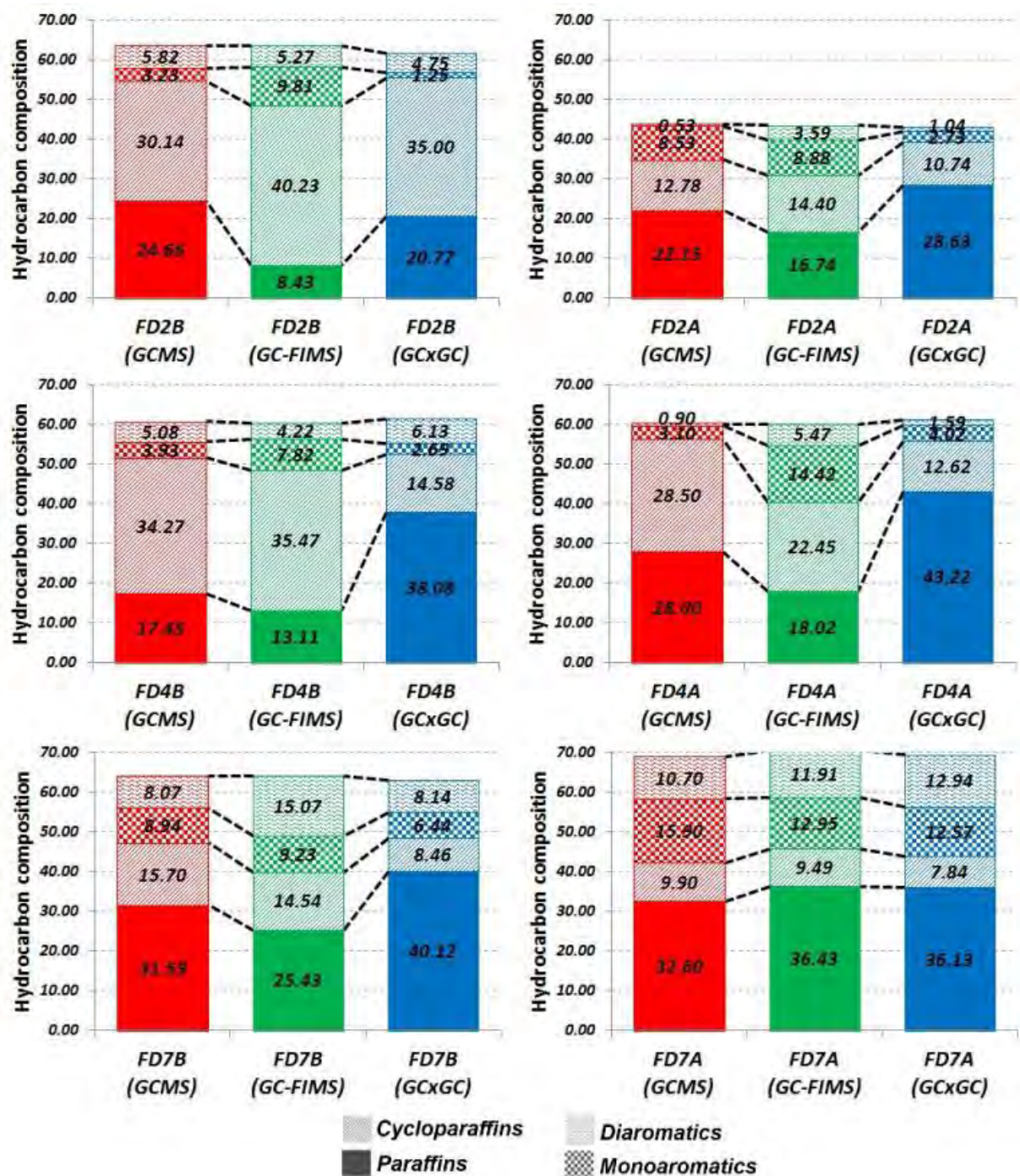
Figure 7.5 Comparison of GC-MS, GC-FIMS and n-GCxGC-FID results for reformulated and original FACE fuels.

7.3 Hydrocarbon Characterization for Fractions Boiling in Full Temperature Range (IBP-FBP)

The purpose of this section is to compare the hydrocarbon composition of reformulated and original FACE fuels determined by a wide range of advanced characterization techniques and the standard ASTM tests.

All the following figures presented in this section include results from
    (a) standard ASTM tests:
        -averaged FIA (ASTM D1319) data reported as volume % (Section 2.3.1. Table 2.9/Figure 2.7). Abbreviation in figures: FIA (avg).
        -averaged SFC (ASTM D5183) data reported as mass % (Section 2.3.2 Table 2.9/Figure 2.8). Abbreviation in figures: SFC (avg).
        -hydrocarbon types by MS (ASTM D2425) data reported as volume % (Section 2.3.3 Table 2.9/Figure 2.9). Abbreviation in figures: D2425.
    (b) advanced characterization methods:
        -'normal' two-dimensional gas chromatography with FID detector reported as mass %. Original FACE fuels (set A) were repeated on recent column combination (Section 6.1.3). Abbreviation in figures: 'n'-GCxGC-FID.
        -'reverse' two-dimensional gas chromatography with FID detector reported as mass %. Both original FACE fuels (set A) and reformulated FACE fuels (set B) were run as a first time on this type of column set combination (Section 6.1.4). Abbreviation in figures: 'r'-GCxGC-FID.
        -'reverse' two dimensional gas chromatography with FID and TOFMS (Time of Flight Mass Spectrometer) detectors reported as mass % (Appendix F, Tables F1 – F6). This analysis was performed only for reformulated FD samples. Analysis for original FACE diesel fuels was performed on normal column combination and was reported (as area %) in previous report. Abbreviation in figures: 'r'-GCxGC-TOFMS/FID.
        -Combination of SPE-GCMS and PIONA data reported as mass % (Section 6.3, Appendix C and F). Abbreviation in figures: PIONA/GC-MS.
        -Combination of GC-FIMS and PIONA data reported as mass % (Section 6.2, Appendix D and F). Abbreviation in figures: PIONA/GC-FIMS.
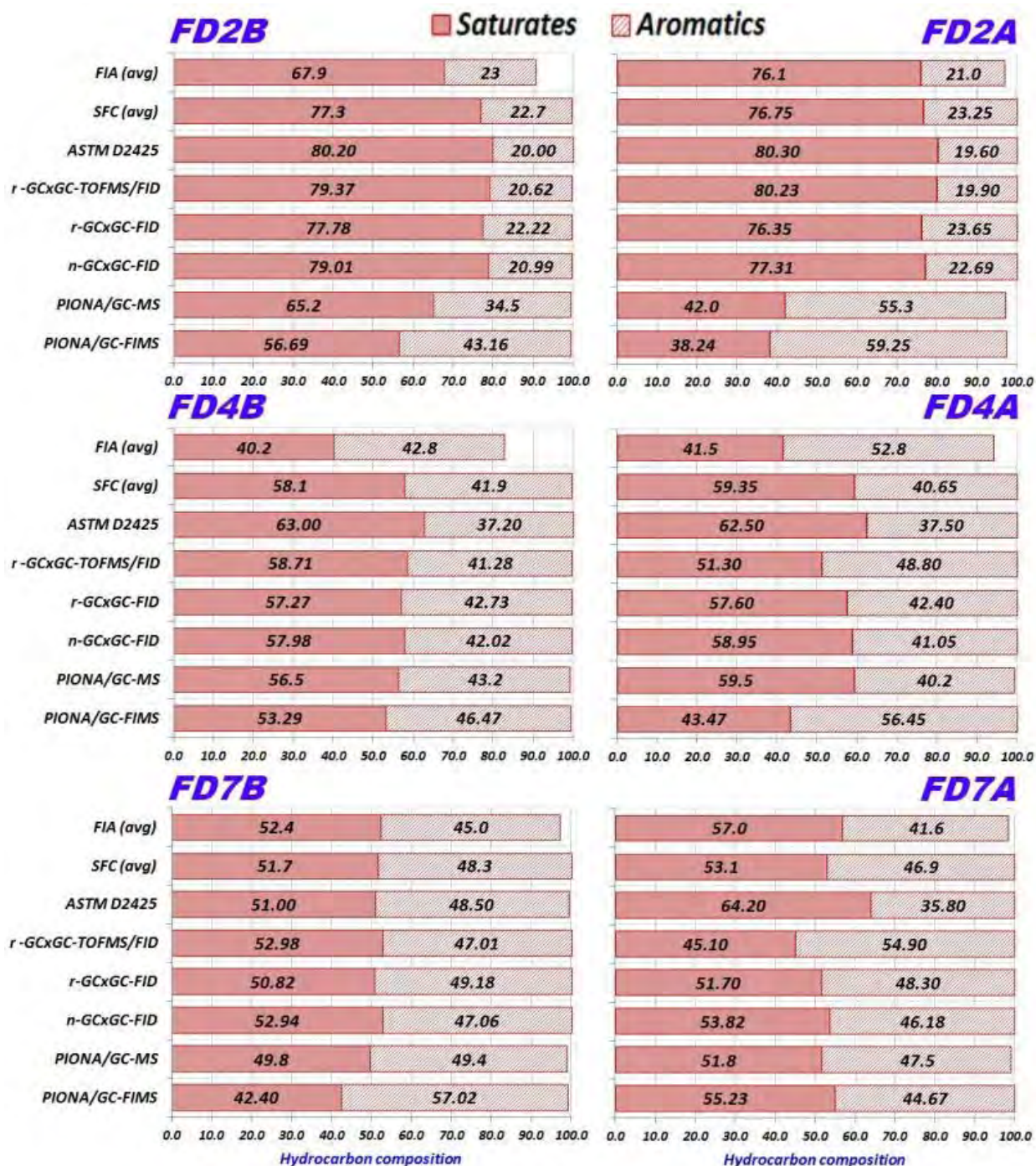
Figure 7.6 Comparison of analytical results for reformulated and original FACE fuels
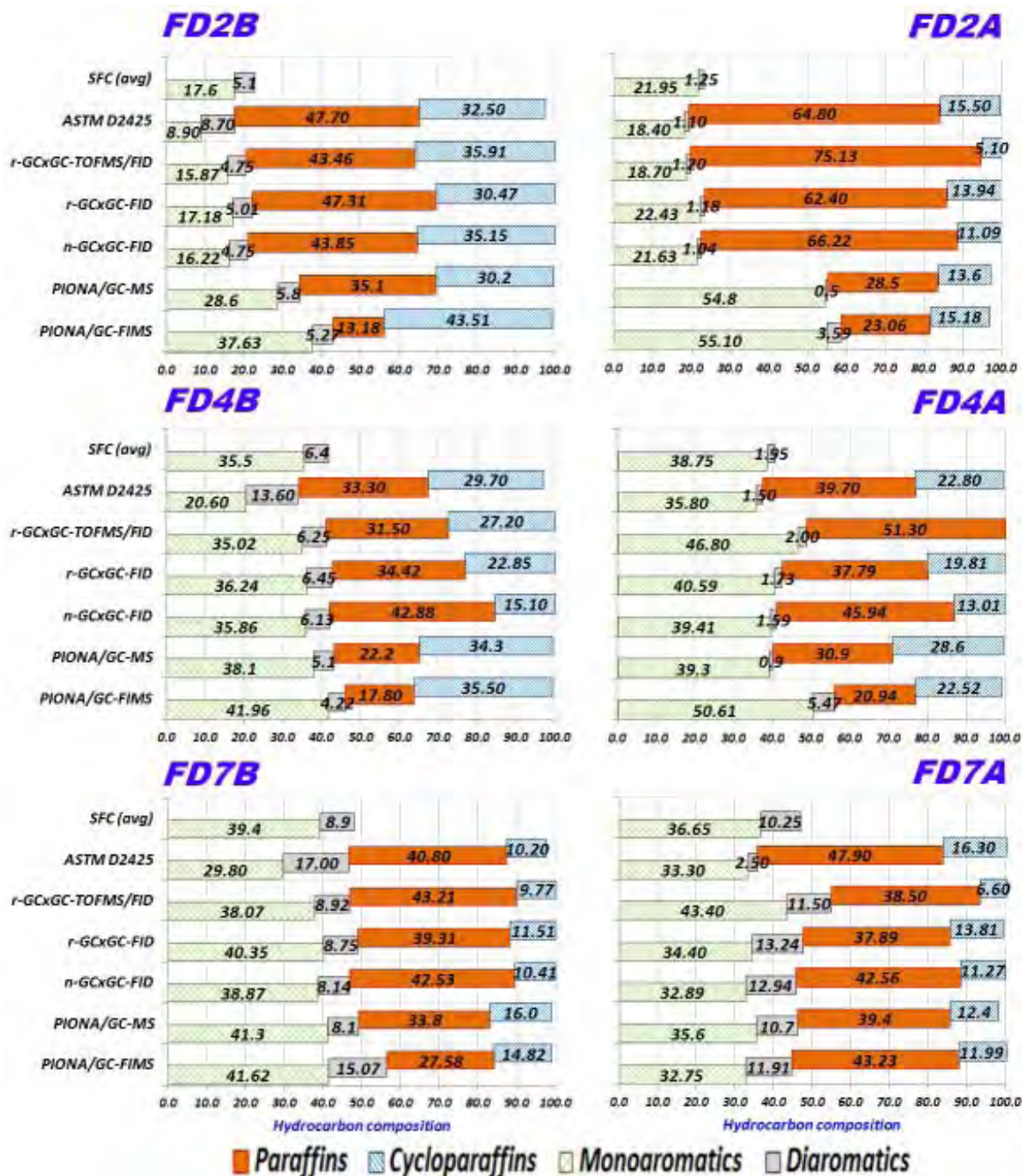
Figure 7.7 Comparison of analytical results based on detailed paraffin and aromatic composition for reformulated and original FACE fuel.
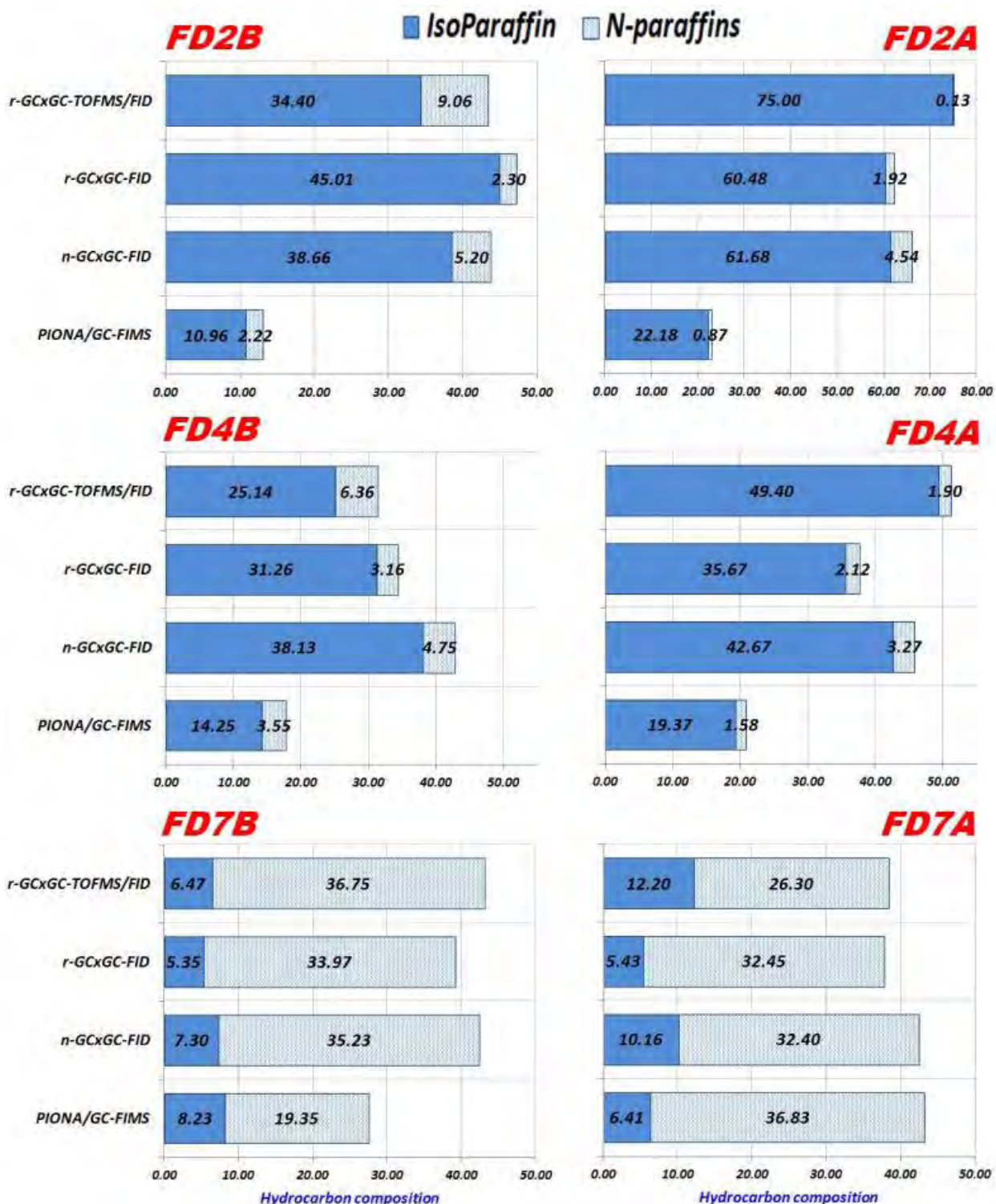
Figure 7.8 Comparison of analytical results based on detailed paraffin composition for reformulated and original FACE fuel

The standard method for hydrocarbon types by MS (ASTM D2425) was included in this comparison as well. The D2425 test method (see section 2.3.3) uses mass spectrometer to determine the hydrocarbon types presented in diesel distillates 400°-650°F (204° to 343°C) boiling range and is normalized to 100%. Precision of this method was determined only for the aforementioned temperature range, so its

accuracy may be questionable if the lower boiling materials are considered. In contrast to other methods found in this section, values from ASTM methods D2425 and D1319 are reported in volume %.

It is worth mentioning that the cycloparaffinic content for reformulated FACE fuel FD2B may be lower than reported in this work, and consequently isoparaffinic concentration would be higher. See Appendix G for discussion of this issue.

Comparing the GC×GC-FID techniques with GC-FIMS/GC-MS, the necessary calibration step in MS to obtain quantitative results becomes a drawback when recent target-design fuel 'men-designed' samples have to be analyzed. Moreover, ASTM D2425 or GC-FIMS is applicable to middle distillates with a limited boiling range. The relative content of heavy hydrocarbons is then underestimated if the content of the heavier (b.p. > 662°F/350°C) boiling point material is non negligible. GC×GC gives the opportunity to extend the carbon range to 842°F/450°C, i.e., to a boiling point equivalent to nC30 (n-triacontane). The boiling points of samples analyzed in this study do not approach such high temperatures. However, lower boiling point limits are easily extended for samples like FD2A where almost 60 vol% boils before 392°F/200°C. For sample like FD2A, a loss of volatile compounds can occur during the evaporation step at the end of the SOAP separation procedures

Both the original and reformulated versions of the FD2 and FD4 are highly isoparaffinic, while the FD7 fuels have proportionally more n-paraffinic hydrocarbons. This is consistent with the fact that the reformulated and original FD7 have higher cetane numbers than the other fuels.

The GCxGC in the reversed mode provides valuable information about hydrocarbon distribution that has not previously been available. The complete two–dimensional separation plane is utilized, and the different compound classes and sub–classes are separated based on both volatility and polarity differences.

There is noticeable good consistency between all GCxGC analyses shown in this report.

 The benefits of hydrocarbon composition analyses by GCxGC relative to other techniques include:

- no need to pre-fractionate into saturate and aromatic fractions,

- no need to pre-fractionate into different boiling fractions,

- valid over full temperature range (IBP-FBP), does not need to combine/add any other analysis to get the final result,

- in addition to hydrocarbon characterization,SimDis curves similar to ASTM D2887 can be obtained. Moreover if the hydrocarbon types are correctly detected, it can provide specific hydrocarbon type SimDis,

two dimensional separations in combination with QSPR (Quantitative Structure-Property Relationship) models can provide an excellent base for future molecular reconstruction of future fuels, as well as offer the possible prediction of important fuel properties such as cetane number, density or viscosity.

8. CARBON-TYPE FROM NMR ANALYSIS

8.1 Introduction

This chapter summarizes the carbon-type analysis from ^{1}H and ^{13}C{^{1}H} nuclear magnetic resonance spectroscopy (NMR) of FACE diesel blends, FD-2B, FD-4B, and FD-7B, and makes comparison of these new blends with the original FACE diesel blends, FD-2A, FD-4A, and FD-7A, as analyzed by Pacific Northwest National Laboratory, Richland, WA, and Natural Resources Canada, CanmetENERGY–Devon, Alberta, Canada.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for quantifying both carbon and hydrogen types in petroleum samples. Much of the motivation for using NMR analyses as a means of characterizing fuel samples may be found in the original FACE report (1). Both CanmetENERGY and PNNL take different approaches to NMR carbon-type analyses, making the results sometimes difficult to compare in some specific measurements, but generally in agreement regarding the overall assessment of the new FACE blends. This is not unusual among laboratories in that differences in NMR integration regions or proprietary algorithms can lead to conclusions that vary among analysts.

At CanmetENERGY, a processing method has been developed using the information from both proton and carbon NMR spectra to quantify all of the carbon types present in the sample. Assignments are based on chemical shifts of model compounds and results from advanced NMR experiments including distortionless enhanced polarization transfer [DEPT] and heteronuclear correlation [HETCOR]). Figures 8.1 and 8.2 illustrate the carbon types quantified. With quantifying "all" carbon species, additional calculations can be performed. For example, in Figure 8.3, the calculation of "average chain segment length" is illustrated. As well, the average ring cluster sizes for aromatic and cycloparaffinic ring clusters can be calculated.

The NMR carbon type analysis method used by CanmetENERGY has previously been used to characterize diesel fuel samples for the Coordinating Research Council (CRC) Advanced Vehicle/Fuel/Lubricants (AVFL) Committee, Project AVFL-18, Surrogate Fuels for Kinetic Modeling. Those results are being used to model the compositional, ignition-quality, volatility, and, eventually, combustion characteristics of diesel fuel surrogates (2).

At PNNL spectral range assignments and interpretation of NMR results are based on ranges and methods presented by Altgelt and Boduszynski (3).
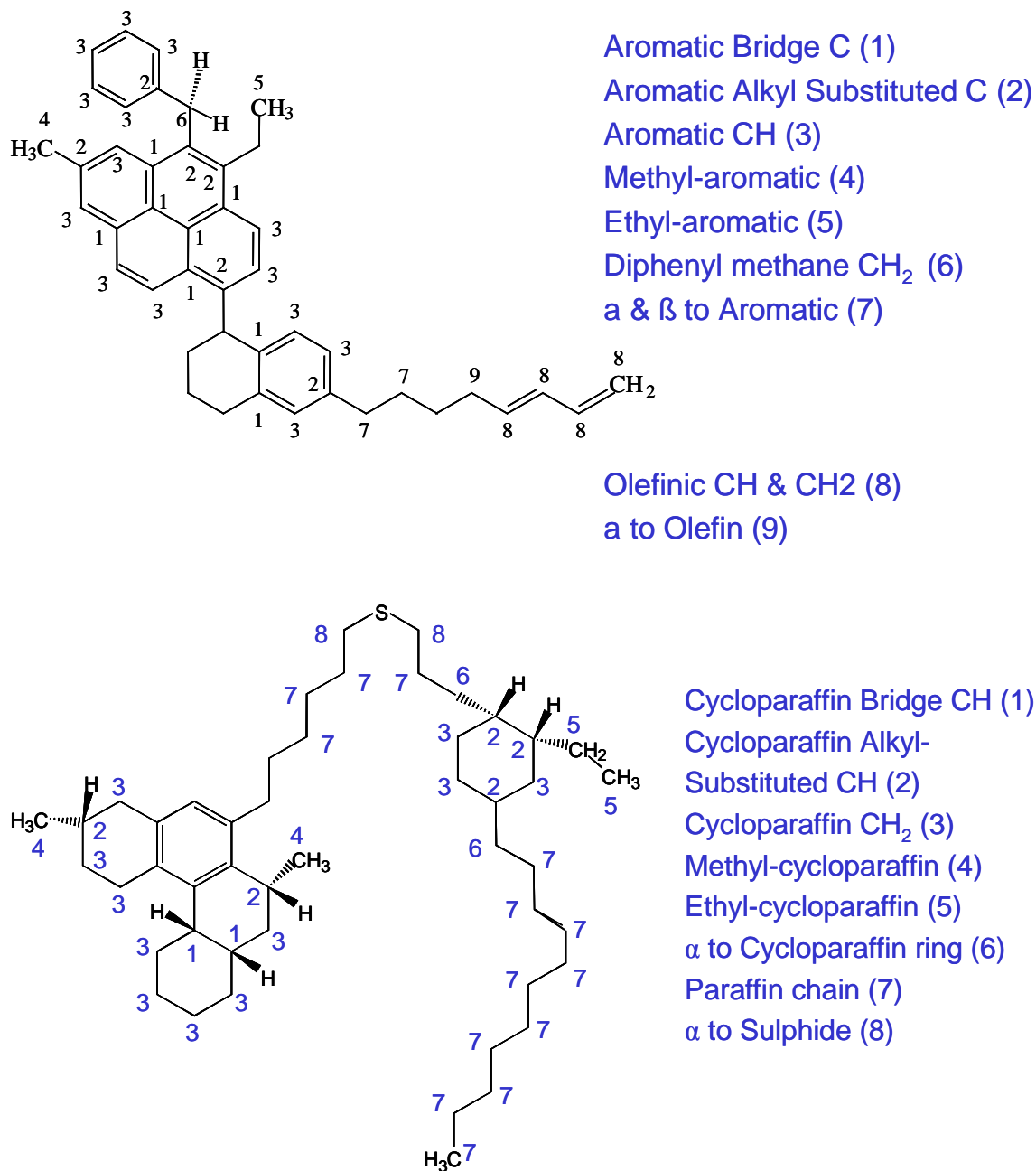
Figure 8.1 Molecular representations of carbon types quantified using NMR data. The upper structure illustrates aromatic and olefinic species while the lower structure illustrates cycloparaffinic and paraffinic species.

Methyl branched chain (1)

Ethyl branched chain (2)

+ Butyl branched chain (3)
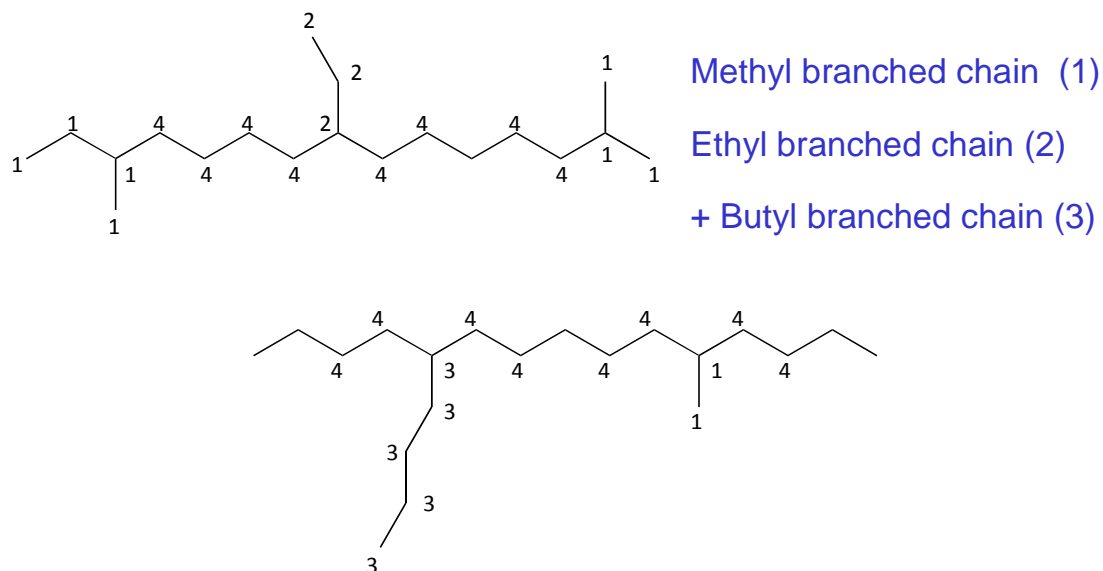
Figure 8.2 Molecular representations of carbon types quantified using NMR data. The structures illustrate branched paraffinic species.

Segment "a" = 6 carbons
Segment "b" = 4 carbons
Segment "c" = 4 carbons

Average length = 14/3 = 4.7 carbon
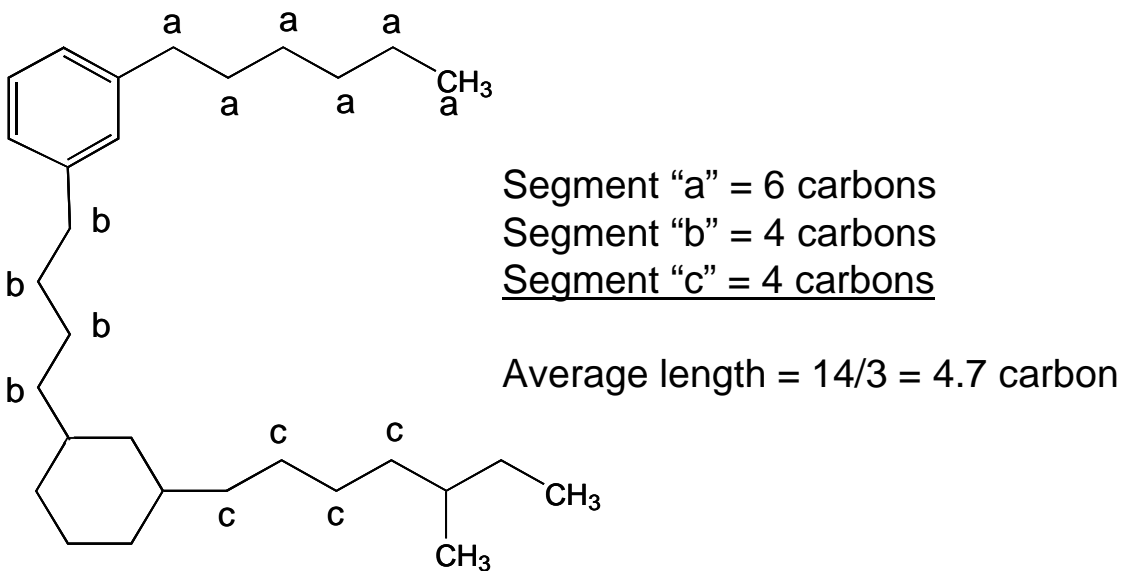
Figure 8.3. Molecular structure that illustrates the calculation of the average "chain segment length."

90

8.2 Results and Discussion

8.2.1 Comparison of FACE Diesel Sets A and B

To provide the best comparison between the previous FACE diesel blends (labeled as A) and the new FACE diesel blends (labeled as B), the data are provided, when possible, in the same format as was previously presented in the 2010 CRC Report (1).   The tables in the following sections summarize the results obtained by CanmetENERGY and PNNL, as indicated, for the current FACE diesel blends, FD-2B, FD-4B, and FD-7B, and make comparison of these new blends with the original FACE diesel blends, FD-2A, FD-4A, and FD-7A. Table 8.1 provides a brief comparison of the data from both institutions for the major carbon types, aromatic, paraffinic, and cycloparaffinic (or naphthenic) carbons. In most cases, there is relatively close agreement regarding the carbon-type values, within a small margin of error, but in the instances highlighted in the table, the values differ to a greater extent. As mentioned previously, these differences arise from the methodology used to analyze the data, whether integration zones or proprietary algorthims, and should not be unexpected. Samples of the original diesel blends were not re-analyzed for this study, but data were taken from the 2010 CRC Report (1), or in some cases data previously obtained were reprocessed, as noted.

Based on ^{1}H and ^{13}C{^{1}H} NMR analysis, appreciable differences in carbon type contents were found comparing the new FACE Diesel blends (FD-2B, -4B, and -7B) and the original FACE Diesel blends (FD-2A, FD-4A, and FD-7A). Table 8.1 shows that the new blends for FD-2 and FD-4 have lower paraffinic (n + iso) content than the previous fuels, and missed results for FD-7, with PNNL reporting roughly consistent paraffin content and CanmetENERGY reporting increased paraffin content. Similarly, cycloparaffins increased from FD-2A to FD-2B, remained roughly consistent between FD-4A and FD-4B, and decreased from FD-7A to FD-7B. The magnitude of the differences in carbon type content are sometimes considerable and reflect significant changes in fuel composition that resulted from reformulation of these three FACE blends. Additionally, aromatic content is shown to have increased from FD-4A to FD-4B and from FD-7A to FD-7B, with mixed results from PNNL and CanmetENERGY for the FD-2 fuels.

Table 8.1   Comparison of PNNL and CanmetENERGY Carbon-Type Analysis - Major Diesel Components

| | Carbon Content (Mole % C) | | | | | | |
| | Aromatic | | | (n- + iso-) Paraffinic | | Cycloparaffinic | |
	CanmetENERGY	PNNL[a]	PNNL[b]	CanmetENERGY	PNNL[a]	CanmetENERGY	PNNL[a]
FD-2A	19.1	13.9	17.0	47.8	56.9	32.9	29.1
FD-2B	16.5	16.4		42.9	43.8	40.6	39.8
FD-4A	26.8	25.2	27.9	45.9	45.2	27.1	29.5
FD-4B	34.0	29.6		36.3	42.5	29.4	27.8
FD-7A	29.4	27.3	30.7	51.5	56.5	18.9	16.2
FD-7B	35.8	33.4		56.5	55.2	7.8	11.2

(a) Tabulated results from PNNL for FD-2A, -4A, and -7A were obtained by re-analyzing NMR data from the original CRC FACE report (1).
(b) Previously reported in the original CRC FACE Report (1).

8.2.2 Detailed Carbon Content Comparison

Tables 8.2 and 8.3 summarize the carbon type information obtained by CanmetENERGY and PNNL, respectively, for each diesel sample. In Table 8.2, the selected carbon type information for both the reformulated and original batches of FACE diesel #2, 4, and 7 are shown. For FD-2B, the reformulated batch has an aromaticity almost 3 mole % lower than the original formulation, FD-2A, and a cycloparaffinic carbon content that is 8 mole% higher. For FD-4B and FD-7B, the reformulated batches have approximately 7 mole % higher aromatic contents, and significantly higher average aromatic ring cluster sizes. Similar conclusions can be drawn from Table 8.3, and although the magnitudes are different, the trends are consistent. Additionally from the breakdown in Table 8.3, the increase of internal or bridgehead carbon atoms implies the presence of more polyaromatic ring structures in the FACE B fuels than in the FACE A fuels.

Table 8.2   Selected Carbon Type Content Information for Both Previous (A) and Current (B) FACE Diesel Fuel Samples

Carbon Type	Carbon Content (mole %)					
	FD2A	FD2B	FD4A	FD4B	FD7A	FD7B
Aromatic	19.1	16.5	26.8	34.0	29.4	35.8
Cycloparaffinic	32.9	40.6	27.1	29.4	18.9	7.8
Branched Paraffinic	14.5	12.7	13.6	8.4	5.2	4.8
Chain Paraffinic (C1+)	33.3	30.2	32.3	27.9	46.3	51.7
Olefinic	0.3	0.0	0.2	0.4	0.3	0.0
C=O*	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0

*C=O was content was not measured

Chain End Type	Content (mole fraction) (±0.1)					
	FD2A	FD2B	FD4A	FD4B	FD7A	FD7B
Aromatic	0.2	0.1	0.2	0.3	0.2	0.1
Olefinic	0.0	0.0	0.0	0.0	0.0	0.0
Cycloparaffinic	0.4	0.5	0.5	0.0	0.3	0.0
Branched Paraffinic	0.2	0.3	0.2	0.5	0.1	0.2
Paraffinic CH3	0.1	0.1	0.1	0.2	0.5	0.8
Sulphidic S	0.0	0.0	0.0	0.0	0.0	0.0
Total*	0.9	1.0	1.0	1.0	1.1	1.1

* Variance from 1.0 due to round-off error

Parameter	FD2A	FD2B	FD4A	FD4B	FD7A	FD7B
Ar Cluster size (#carbons)	6	6	6	10	8	13
Cy Cluster size (#carbons)	7	7	8	6	7	6
Chain segment length	4.5	4.5	3.6	5.2	7.4	10.6
ArC/CyC	0.6	0.4	1.0	1.2	1.6	4.6

Table 8.4, derived from the CanmetENERGY analysis, provides a summary of the FACE diesel blends broken down by carbon classification, as presented in work for the CRC AVFL Committee, Project AVFL-18, Surrogate Diesel Fuels for Kinetic Modeling (2). Carbon classification allows a more standardized method of relating the FACE diesel fuels to the surrogate and target fuels developed under the AVFL-18 project, as well as to any other fuel that has been similarly analyzed.

Table 8.3   Summary of FACE Diesel Fuels Chemical Structure Characteristics from $^{13}C\{^{1}H\}$ NMR Normalized by Percent Carbon Type

	Carbon Content (Mole % C)					
	FD-2A[a]	FD-2B	FD-4A[a]	FD-4B	FD-7A[a]	FD-7B
General Carbon Types						
Aromatic Carbon	13.9	16.4	25.2	29.6	27.3	33.4
Aliphatic Carbon	86.1	83.6	74.8	70.3	72.7	66.4
CH Carbon	8.6	8.0	7.7	7.0	4.4	2.2
CH_2 Carbon	55.3	53.3	46.1	42.6	49.7	45.4
CH_3 Carbon	22.1	22.3	20.9	20.6	18.5	18.7
Aromatic Carbon Breakdown						
Phenolic Carbon	0	0	0	0	0	0
CH_2/CH Substituted Aromatic Carbon	2.4	1.9	4.0	4.4	5.1	4.6
Naphthene Substituted Aromatic Carbon	1.5	1.9	2.7	3.8	1.7	3.9
CH_3 Substituted Aromatic Carbon	1.1	1.7	2.3	2.9	2.2	3.4
Internal (Bridgehead) Aromatic Carbon	0.9	1.3	1.4	2.4	1.4	2.6
Peripheral Unsubstituted Aromatic Carbon	7.8	9.6	14.9	15.9	16.9	18.8
Heteroaromatic Carbon	0	0	0	0	0	0
Total Aromatic Carbon	*13.9*	*16.4*	*25.2*	*29.6*	*27.3*	*33.4*
Paraffinic Breakdown						
Cycloparaffinic CH	4.7	6.4	5.7	5.6	3.3	2.0
Cycloparaffinic CH_2	20.9	28.7	21.2	19.5	10.4	8.1
Cycloparaffinic CH_3	3.6	4.6	2.7	2.7	2.5	1.1
Total Cycloparaffinic Carbon	*29.1*	*39.8*	*29.5*	*27.8*	*16.2*	*11.2*
Total (n + iso) Paraffinic Carbon	*56.9*	*43.8*	*45.2*	*42.5*	*56.5*	*55.2*

(a) Tabulated results from PNNL for FD-2A, -4A, and -7A were obtained by re-analyzing NMR data from the original report (1).

Table 8.4   Complete Carbon Classification for the FACE Diesel Fuels (FD)

Carbon Classification	FD2B	FD4B	FD7B
1. Primary C (CH3)	14.3	16.3	19.8
Terminal chain	6.6	5.4	8.5
Branch	3.6	2.0	1.9
Cycloparaffin	0.3	1.5	2.4
Aromatic	3.8	7.4	7.0
2. Secondary C (CH2)	58.9	45.0	42.2
Chain (α from ends)	15.7	10.3	10.6
Chain (β or greater from ends)	9.5	7.5	24.6
Cycloparaffin	33.6	27.2	7.0
3. Tertiary C (CH)	17.7	19.5	17.9
Branch	3.4	2.2	1.4
Cycloparaffin (Substituted - Alkyl)	5.1	2.1	0.8
Cycloparaffin (Bridge)	1.8	0.0	0.0
Aromatic	7.4	15.2	15.7
4. Quaternary C (C)	9.1	18.8	20.1
Aromatic (Substituted - Alkyl)	9.1	12.1	9.6
Aromatic (Substituted - Cycloparaffin)	0.0	0.0	1.3
Aromatic (Bridge)	0.0	6.7	9.2
5. Other (Olefin + C=O)	0.0	0.4	0.0
Total	100.0	100.0	100.0

8.2.3 ^{1}H NMR Data Comparison

The normalized ^{1}H NMR data shown in Table 8.5 show that there are several significant variations between the FACE A and FACE B fuel sets. As was observed from the ^{13}C data, FD-2A and FD-2B appear to be the most similar in makeup, with more pronounced differences arising in FD-4 and FD-7. The most dramatic differences visible from the 1H NMR data are in the aromatic region, where the monoaromatic components are shown to remain constant for FD-2A and FD-2B, and decrease from FD-4A to FD-4B and from FD-7A to FD-7B. Additionally, the polyaromatic contributions increase from the A Fuels to the B Fuels.

By breaking down the protonated aromatic region of the ^{1}H NMR for the FACE A and B blends, the makeup of the polyaromatic components can be more closely examined. The ability to readily assess fused-ring aromatic content is an advantage of ^{1}H NMR that is more difficult to obtain from ^{13}C{^{1}H} NMR spectra. Presented in Table 8.6 are generally accepted ^{1}H NMR regions associated with fused ring di- and triaromatics; that is, substituted naphthalenes, and anthracenes or phenylanes/phenanthrenes, respectively (3). Fused ring structures greater than three, which have resonances between 8.3 and 10.7 were not observed. With the exception of FD-4A, the FACE A fuels do not show contributions from triatomic components, and the 0.1 mole % of triatomic may not be significant. From Table 8.6, we can see that the polyaromatic components presented in Table 8.5 are predominantly made up of hydrogens associated with diaromatic species (naphthalenes), with an additional fraction of triaromatics, comprising between about 10–15% of the diaromatics.

Table 8.5 ^{1}H NMR Comparison of Original and Reformulated FACE Fuels, <u>Normalized by Hydrogen Type</u>

Label	Structure	Definition	Chemical Shift (ppm)	%H					
				FD-2A[a]	FD-2B	FD-4A[a]	FD-4B	FD-7A[a]	FD-7B
HA1	polyaromatic	H	7.4–10.7	0.2	0.9	0.4	2.4	0.4	3.0
HA2	monoaromatic	H	7.4–6.2	3.6	3.6	7.5	6.7	8.6	7.3
HO1	olefinic	CH	5.1–6.2	0	0	0	0	0	0
HO2	olefinic	CH$_2$	4.8–5.1	0	0	0	0	0	0
HO3	olefinic	CH$_2$	4.3–4.8	0	0	0	0	0	0
HP1	α-to-aromatic	CH$_2$	2.4–4.3	1.8	2.2	2.9	12.2	5.0	13.8
HP2	α-to-aromatic	CH$_3$	2.0–2.4	6.0	5.6	11.9	5.4	8.7	5.6
HP3	aliphatic	CH$_2$	1.09–2.0	33.0	33.4	35.8	40.5	55.2	53.9
HP4	aliphatic	CH$_3$	0.5–1.09	55.2	54.3	41.4	32.8	22.0	16.4

a) Tabulated results from PNNL for FD-2A, -4A, and -7A were obtained by re-analyzing NMR data from the original report (1).

Table 8.6 ^{1}H NMR Aromatic Region, Breakdown of Fused, Protonated Aromatic Ring Hydrogens, Percent <u>Results Normalized by Hydrogen Type</u>

Structure	Chemical Shift	Hydrogen Content (Mole % H)					
		FD-2A[a]	FD-2B	FD-4A[a]	FD-4B	FD-7A[a]	FD-7B
Polyaromatic	8.3-10.7	0	0	0	0	0	0
Triaromatic	7.8-8.3	0	0.2	0.1	0.6	0	0.8
Diaromatic	7.2-7.8	0.4	1.3	0.8	4.1	1.9	4.9
Monoaromatic	6.2-7.2	3.5	3.0	7.1	4.4	7.2	4.7

(a) Tabulated results from PNNL for FD-2A, -4A, and -7A were obtained by re-analyzing NMR data from the original report (1).

Also apparent from the ^{1}H NMR are significant increases in the percent of alkyl protons bound to an aromatic ring for the FD-4 and FD-7 blends. The α-to-aromatic methyl and methylene protons are effectively equivalent for the FD-2A and FD-2B diesels. Table 8.5 shows an increase in protons associated with methylene groups α to an aromatic ring (HP1) for all three fuel blends, and a decrease in protons attached to methyl groups α to an aromatic ring (HP2) for FD-4 and FD-7 diesel blends, implying that more of the aromatic substituent alkyl groups are longer than one carbon in the new fuels.

The absence of olefinic resonances in the ^{1}H NMR spectra is not surprising. Each FACE formulation is produced by blending refined petroleum streams to meet the target parameters. Olefins become saturated during hydrotreating and therefore no longer represent a significant fraction of the resulting fuel.

8.3 Other Advanced Analysis Techniques

Single-bond proton-carbon correlation (HSQC) NMR spectra have also been obtained for the three new FACE diesel fuels (FD-2B, -4B, and -7B). The aromatic region in particular can provide interesting information that can allow us to fingerprint fuels. Figure 8.4 shows the HSQC aromatic region for a series of FACE diesel fuels (FD-2B, -4B, and -7B), and two unrelated diesel fuels: one derived from shale oil and one derived from oil sands. The pattern evident in the FACE diesel fuels, (a)–(c), shows that they have one or more aromatic blend streams in common. Particularly obvious are the three distinct groupings, not present in either the oil shale or oil sands fuels, which are related to the mono-, di-, and triaromatic components of the FACE diesel fuels. When integrated, a quantitative assessment of these fuel components may be obtained. Taken as a whole, each of the fuels presents a different distribution of components, readily obvious in the HSQC data. The shale oil-derived fuel (d) shows monoaromatic components that are similar to the monoaromatic components found in the FACE diesel fuels. This is not the case for the oil sands-derived fuel (e). These clearly observable differences allow us to readily discern different fuel blends or sources, and can later be correlated to physical properties derived from molecular structures within the fuels. Additional information from these and other two-dimensional NMR techniques may be important in determining fuel structure-property relationships and should be explored. These methods are being further developed.

Three clusters related to mono-, di-, and triaromatic components of the FACE Diesel Fuels.
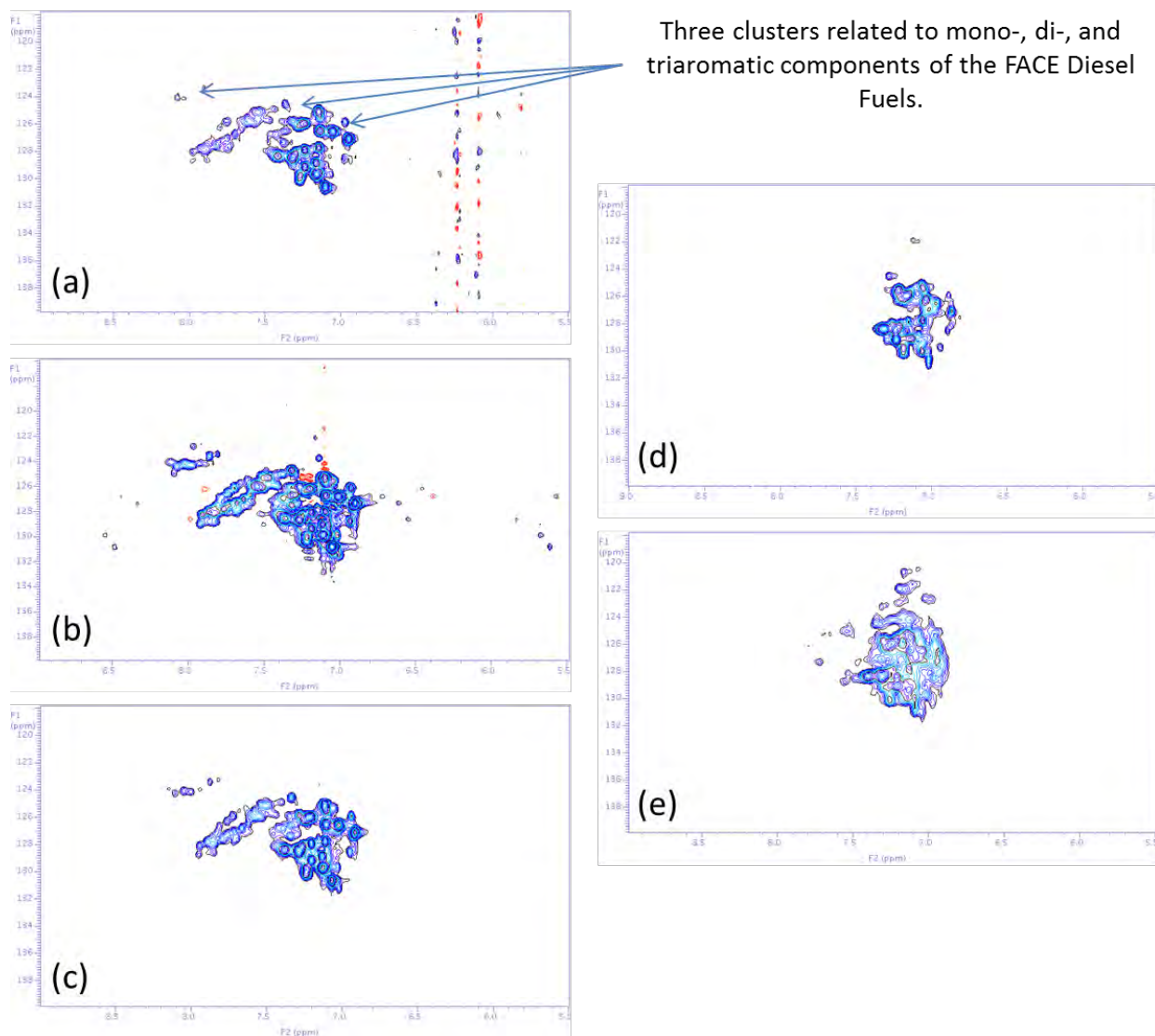
Figure 8.4   Single-bond, Proton-Carbon Correlation (HSQC) NMR Spectra of Fuels: (a) FACE 2B (FD-2B), (b) FACE 4B (FD-4B), (c) FACE 7B (FD-7B), (d) Shale oil-derived Diesel 1, and (e) Oil sands-derived diesel. The vertical axis is a subset of the ^{13}C{^{1}H} NMR spectrum, and the horizontal axis is a subset of the ^{1}H NMR spectrum. Both have units of parts-per-million chemical shift.

8.4 Conclusion

Based on ^{1}H and ^{13}C{^{1}H} NMR analyses, appreciable differences in carbon type contents were found comparing the new FACE diesel blends (FD-2B,FD-4B, and FD-7B) and the previous FACE diesel blends (FD-2A, FD-4A, and FD-7A). As noted above, significant and consistent differences arise in the aromatic region from the introduction of greater quantities of di- and triaromatic compounds to the new FACE diesel blends, as well as greater alkyl-substitution of the aromatic rings. Additionally, Table 8.1 shows that the new blends for FD-2 and FD-4 have lower paraffinic content than the previous fuels, and mixed results for FD-7, with PNNL reporting roughly consistent paraffin content and CanmetENERGY reporting increased paraffin content. Similarly, cycloparaffins increased from FD-2A to FD-2B, remained roughly consistent for FD-4A and FD-4B, and decreased from FD-7A to FD-7B. The magnitude of the differences in carbon type content are sometimes considerable and reflect significant changes in fuel composition that resulted from reformulation of these three FACE blends.

Additionally, differences were noted between the analyses presented by CanmetENERGY and PNNL, which were mostly minor, although more considerable in 6 of 18 measurements (Table 8.1). As mentioned previously, these differences reflect unavoidable variation among analysts as well as differences in methodologies used to identify carbon types. Regardless of these differences, trends were consistent in all but 2 of 18 measurements, and rough magnitudes were consistent in all but 5 of 18 measurements.

8.5 Methods

8.5.1 PNNL Nuclear Magnetic Resonance Method

All quantitative ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were acquired at 499.67 and 125.65 MHz, respectively, on a Varian Inova System. All spectra were recorded at 25.0°C in 5-mm outer diameter NMR tubes, spinning at 20 Hz. Spectra were processed using analysis tools from Varian VNMRJ Version 2.2 Revision D software, or MestReNova Version 6.0.4-5850 software.

Quantitative ^{13}C{^{1}H} spectra were acquired using a 45° observe pulse; acquisition and relaxation delay times of 3 and 5 seconds, respectively, with ^{1}H Waltz decoupling during the acquisition delay period for nuclear Overhauser enhancement (NOE) suppression; and 0.05 M Cr(acac)$_3$ for T$_1$ reduction and quenching of any residual NOE, where acac is CH$_3$C(O)CHC(O)CH$_3$. These conditions lead to an average integral uncertainty of about ±2% (in carbon aromaticity). Carbon-13 spectra are referenced to internal CDCl$_3$ (77.16 ppm)(4), tetramethylsilane (0 ppm), or the α-carbon of linear long chain saturated hydrocarbons (14.16 ppm). Samples consisted of 0.20 mL of fuel diluted to 1.00 mL in CDCl$_3$ with 0.05 M Cr(acac)$_3$. Spectra resulted from 1,500–6,000 scans. Line broadening of 2.5 Hz was used for processing spectra to improve the signal-to-noise ratio. Quantitative results were obtained by integrating each sample spectrum on two or three separate occasions to account for variation in phasing and baseline correction approaches. Results are presented as normalized averages of the integrated area for each spectral region.

Quantitative ^{1}H spectra were acquired using a 30° observe pulse, with acquisition and relaxation delays of 3 and 8 seconds, respectively, for an 11-second recycle time. Samples consisted of about 50 mg of fuel diluted to 1.00 mL in CDCl$_3$. Addition of Cr(acac)$_3$ did not change the integration values for the proton NMR. Measured proton ratios are relatively insensitive to conditions as long as recycle times are kept above about 5 seconds. Chemical shifts are referenced to internal tetramethylsilane (0 ppm) or to internal residual CHCl$_3$ in solvent CDCl$_3$ (7.26 ppm) (4). Spectra resulted from 128 scans. Line broadening was not used. Quantitative results were obtained from single integrations of each spectrum, because unlike the ^{13}C{^{1}H} analyses, ^{1}H seemed to be less susceptible to phasing and baseline correction variations.

^{1}H -^{13}C single-bond proton-carbon correlation (HSQC) spectra were recorded on a 500 MHz Varian Inova spectrometer equipped with a Noralac dual broadband probe. The standard Agilent HSQCAD pulse sequence was used with the standard coupling constant of 146 Hz. Spectral editing was employed to distinguish methine/methyl groups as positive resonances and methylene groups as negative resonances. Acquisition parameters included 32 scans per increment with 400 increments with a spectral width of 5 kHz in the F2 (^{1}H) dimension and 25 kHz in the F1 (^{13}C) dimension. The data were then processed using zero filling to 2048 × 2048 complex data points and a Gaussian window function.

Spectral range assignment and interpretation of NMR results are based on ranges and methods presented by Altgelt and Boduszynski (3).

### 8.5.2 CanmetENERGY Nuclear Magnetic Resonance Method

Nuclear magnetic resonance (NMR) analyses were performed at room temperature (19 ± 1^oC) on a Varian Unity Inova 600 NMR spectrometer, operating at 599.733MHz for proton and 150.817MHz for carbon. For proton samples, 20µL quantities were dissolved in 700µL deutero-chloroform. For carbon, 100µL quantities of diesel samples were dissolved in 600µL of deutero-chloroform. Both proton and carbon spectra were run using a Varian 5mm broadband $^{13}C\{^1H\}$ probe.

The quantitative carbon spectra were acquired using an acquisition time of 1.0s, a sweep width of 36003.6Hz and a flip angle of 26.4° (3.4µs). A relaxation delay of 15s was used. Reverse-gated waltz proton decoupling was used to avoid nuclear Overhauser effect enhancements of the protonated carbon signals. The spectra were the result of 3200 scans. Line broadening of 3Hz was used to improve the signal-to-noise ratio of the spectra. The spectra were referenced to deutero-chloroform at 77ppm.

The quantitative proton spectra were acquired using an acquisition time of 3s, a sweep width of 20000Hz, a pulse flip angle of 30.6^o (3.3µs) and a relaxation delay of 4s. The spectra were the result of 128 scans. Line broadening of 0.30 Hz was used to improve the signal-to-noise ratio of the spectra. The spectra were referenced to deutero-chloroform at 7.24 ppm.

The CanmetENERGY carbon type analysis utilizes integral data from both ^{13}C and ^1H NMR spectra. The integral regions used and the calculations performed were based on the method published previously (5, 6, 7) with enhancements. The aromatic and cycloparaffinic ring cluster size calculations are based upon the method described in Solum *et. al.* (8). Integral values from proton and carbon spectra were used to calculate the mole % of the various carbon types. To check the fit of the data, the mole % carbon was converted to weight % carbon where the total was set to that measured by elemental analysis. The NMR data was then used to calculate the hydrogen content (wt%). The difference between the elemental and NMR-derived hydrogen contents is usually within 1 wt%. The data in this report gives the mole % of carbon types.

8.6 References

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9. SUMMARY AND CONCLUSIONS

Detailed analyses of the physical and chemical properties of the three reformulated FACE Diesel Fuels (FD2B, FD4B, and FD7B) were conducted. The results were compared to those of the corresponding original FACE Diesel Fuels (FD2A, FD4A, and FD7A).

A suite of ASTM tests were run to measure: cetane number [measured by engine and ignition quality tester (IQT) methods]; cetane index; distillation properties; aromatics, saturates, and olefins content; elemental C and H contents; S and N contents; bromine number; specific gravity; net heat of combustion; kinematic viscosity; cloud point; pour point; flash point; and lubricity.

In addition to the ASTM tests, several emerging advanced characterization techniques were conducted by the national labs to obtain more detailed chemical and structural information for the fuels. These techniques included: gas chromatography-field ionization mass spectrometry (GC-FIMS) coupled with paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) analysis and detailed hydrocarbon analysis (DHA); one- and two-dimensional (2-D) gas chromatography-mass spectrometry (GCMS); 2-D gas chromatography using a flame ionization detector (FID); and nuclear magnetic resonance (NMR). Each analysis offers a different perspective on the makeup of the fuels.

All of the reformulated fuels were found to meet the cetane, aromatics level, and T90 design targets at least as well as the original fuels. Compared to the original FACE#2 fuel (FD2A), the reformulated fuel (FD2B) appears to have: significantly less isoparaffins; significantly more cycloparaffins; less monoaromatics; and more diaromatics. Compared to the original FACE#4 fuel (FD4A), the reformulated fuel (FD4B) appears to have: slightly less monoaromatics and slightly more diaromatics. Compared to the original FACE#7 fuel (FD7A), the reformulated fuel (FD7B) appears to have: more monoaromatics and less diaromatics. All of the reformulated fuels appear to have more methyl-substituted naphthalenes and the diphenyl alkanes in the original FD7A fuel appear to have been eliminated. This is good as naphthalenes are more representative of the diaromatics in commercial ULSDs than diphenyl alkanes.

NMR results, which characterize individual carbon atoms rather than whole molecules, indicate that the reformulated fuels have greater quantities of poly-aromatic carbons and greater amounts of alkyl substituents on aromatic rings. The reformulated versions of FD2 and FD4 have lower paraffinic carbon content than the original versions, while cycloparaffinic-type carbons increased for the reformulated FD2 and decreased for the reformulated FD7.

It is hoped that engine and combustion researchers will include the use of the FACE Diesel Fuels in their tests and use the detailed information in this and the previous report to better relate performance and emissions in engines to the physical and chemical properties of fuels.

APPENDIX A. PIONA DATA (Hydrocarbon content reported in wt %)

The PIONA results for FD2A, FD4A and FD7A presented in Tables A.4-A.6 were already reported in:
Alnajjar, M.; Cannella, B.; Dettman, H.; Fairbridge, C.; Franz, J.; Gallant, T.; Gieleciak, R.; Hager, D.; Lay, C.; Lewis, S.; Ratcliff, M.; Sluder, S.; Storey, J.; Yin, H.; Zigler, B.; "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1 (2010).

Table A.1 PIONA Data for FD2B

Carbon Number	Saturated Hydrocarbon Content Paraffins			Unsaturated Hydrocarbon Content Olefins			Monoaromatic Hydrocarbon Content	Totals
	Monocyclo	Iso	Normal	Cyclic	Branched	Straight Chain		
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.03
5	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.03
6	0.01	0.52	0.08	0.00	0.00	0.01	0.03	0.65
7	0.00	0.25	0.00	0.00	0.05	0.00	0.06	0.36
8	0.01	1.39	0.00	0.00	0.00	0.00	1.94	3.34
9	0.22	0.22	0.00	0.00	0.00	0.00	25.39	25.84
10	0.00	0.62	0.09	0.00	0.01	0.01	0.39	1.12
11	3.04	1.52	0.02	0.00	0.02	0.02	0.00	4.62
Totals	3.28	4.56	0.19	0.00	0.11	0.04	27.81	36.00

Table A.2 PIONA Data for FD4B

Carbon Number	Saturated Hydrocarbon Content Paraffins			Unsaturated Hydrocarbon Content Olefins			Monoaromatic Hydrocarbon Content	Totals
	Monocyclo	Iso	Normal	Cyclic	Branched	Straight Chain		
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.02
5	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.03
6	0.02	0.01	0.01	0.00	0.00	0.00	0.02	0.06
7	0.00	0.00	0.00	0.01	0.09	0.00	0.03	0.14
8	0.01	2.22	0.00	0.00	0.00	0.00	2.19	4.42
9	0.00	0.36	0.00	0.00	0.00	0.00	31.31	31.68
10	0.00	0.62	0.39	0.00	0.02	0.02	0.59	1.63
11	0.00	0.00	1.05	0.00	0.04	0.05	0.00	1.14
Totals	0.03	3.23	1.46	0.01	0.18	0.07	34.14	39.12

Table A.3 PIONA Data for FD7B

Carbon Number	Saturated Hydrocarbon Content Paraffins			Unsaturated Hydrocarbon Content Olefins			Monoaromatic Hydrocarbon Content	Totals
	Monocyclo	Iso	Normal	Cyclic	Branched	Straight Chain		
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02
5	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02
6	0.01	0.00	0.01	0.00	0.00	0.01	0.01	0.04
7	0.00	0.00	0.00	0.03	0.02	0.00	0.04	0.09
8	0.02	0.11	0.01	0.00	0.00	0.00	2.10	2.25
9	0.05	0.34	0.05	0.00	0.00	0.00	29.25	29.69
10	0.20	0.32	0.68	0.00	0.02	0.02	0.99	2.22
11	0.00	0.19	0.42	0.03	0.10	0.35	0.00	1.10
Totals	0.28	0.97	1.18	0.07	0.16	0.38	32.39	35.43

Table A.4 PIONA Data for FD2A

Carbon Number	Saturated Hydrocarbon Content Paraffins			Unsaturated Hydrocarbon Content Olefins			Monoaromatic Hydrocarbon Content	Totals
	Monocyclo	Iso	Normal	Cyclic	Branched	Straight Chain		
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
6	0.00	0.00	0.01	0.00	0.00	0.00	0.04	0.06
7	0.00	0.00	0.06	0.01	0.00	0.00	0.06	0.13
8	0.01	0.06	0.01	0.00	0.00	0.00	7.14	7.22
9	0.06	0.09	0.22	0.00	0.00	0.01	34.54	34.91
10	0.10	0.97	0.19	0.00	0.03	0.01	4.45	5.76
11	0.61	4.52	0.17	0.00	2.43	0.00	0.00	7.73
Totals	0.78	5.65	0.67	0.01	2.46	0.03	46.22	55.83

Table A.5 PIONA Data for FD4A

Carbon Number	Saturated Hydrocarbon Content Paraffins			Unsaturated Hydrocarbon Content Olefins			Monoaromatic Hydrocarbon Content	Totals
	Monocyclo	Iso	Normal	Cyclic	Branched	Straight Chain		
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.04
6	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03
7	0.00	0.02	0.01	0.00	0.00	0.00	0.02	0.04
8	0.00	0.10	0.00	0.00	0.00	0.00	5.95	6.05
9	0.01	0.06	0.15	0.00	0.00	0.00	30.16	30.38
10	0.02	1.15	0.15	0.00	0.01	0.00	0.05	1.38
11	0.00	0.04	1.23	0.00	0.06	0.01	0.00	1.34
Totals	0.07	1.37	1.55	0.00	0.07	0.02	36.19	39.26

Table A.6 PIONA Data for FD7A

Carbon Number	Saturated Hydrocarbon Content Paraffins			Unsaturated Hydrocarbon Content Olefins			Monoaromatic Hydrocarbon Content	Totals
	Monocyclo	Iso	Normal	Cyclic	Branched	Straight Chain		
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.01	0.00	0.01	0.00	0.00	0.00	0.03	0.04
7	0.01	0.01	0.01	0.02	0.00	0.00	0.04	0.10
8	0.21	0.07	0.05	0.00	0.00	0.00	0.46	0.80
9	0.79	0.61	0.51	0.00	0.00	0.01	19.15	21.06
10	1.40	1.63	1.50	0.00	0.00	0.02	0.08	4.62
11	0.11	0.39	1.99	0.00	0.04	0.00	0.00	2.53
Totals	2.53	2.71	4.06	0.02	0.05	0.03	19.76	29.15

APPENDIX B. DETAILED HYDROCARBON ANALYSIS DATA BY CARBON NUMBER AND BOILING POINT (Hydrocarbon content reported in wt %)

The DHA results for FD2A, FD4A and FD7A presented in Tables B.7-B.12 were already reported in: Alnajjar, M.; Cannella, B.; Dettman, H.; Fairbridge, C.; Franz, J.; Gallant, T.; Gieleciak, R.; Hager, D.; Lay, C.; Lewis, S.; Ratcliff, M.; Sluder, S.; Storey, J.; Yin, H.; Zigler, B.; "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1 (2010).

Table B.1 DHA by carbon number for FD2B

Report in wt% for Simdis≤ 392°F/200°C	36.00						
Carbon Number	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Totals
3	0.00	0.00	0.00	0.00	0.00		0.00
4	0.00	0.00	0.00	0.00	0.00		0.00
5	0.00	0.02	0.00	0.00	0.00		0.02
6	0.00	0.00	0.00	0.02	0.00		0.02
7	0.00	0.08	1.18	0.01	0.19		1.46
8	0.00	0.13	0.24	0.15	1.98		2.50
9	0.00	0.25	0.10	0.16	27.22		27.73
10	0.18	0.81	0.07	0.04	1.59		2.69
11	0.00	1.56	0.00	0.00	0.01		1.57
Totals	0.18	2.85	1.59	0.37	31.00	0.01	36.00

Table B.2 DHA by carbon number for FD4B

Report in wt% for Simdis≤ 392°F/200°C	39.12						
Carbon Number	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Totals
3	0.00	0.00	0.00	0.00	0.00		0.00
4	0.00	0.00	0.00	0.00	0.00		0.00
5	0.00	0.00	0.00	0.00	0.00		0.00
6	0.00	0.00	0.00	0.04	0.00		0.04
7	0.00	3.27	0.00	0.00	0.00		3.27
8	0.00	1.29	0.00	0.32	3.41		5.02
9	0.00	0.54	0.00	0.36	28.23		29.13
10	0.00	1.32	0.00	0.09	0.10		1.51
11	0.00	0.06	0.00	0.00	0.00		0.06
Totals	0.00	6.49	0.00	0.81	31.73	0.08	39.12

Table B.3 DHA by carbon number for FD7B

Report in wt% for Simdis≤ 392°F/200°C	35.43						
Carbon Number	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Totals
3	0.00	0.00	0.00	0.00	0.00		0.00
4	0.00	0.00	0.00	0.00	0.00		0.00
5	0.00	0.00	0.00	0.00	0.00		0.00
6	0.00	0.01	0.01	0.01	0.00		0.03
7	0.01	0.08	0.00	0.07	0.07		0.22
8	0.02	0.08	0.01	0.20	3.45		3.75
9	0.13	0.28	0.13	0.43	26.31		27.29
10	0.21	3.51	0.08	0.12	0.06		3.97
11	0.00	0.02	0.00	0.00	0.00		0.02
Totals	0.36	3.98	0.22	0.83	29.89	0.15	35.43

Table B.4 DHA by boiling point for FD2B

Start BP (°C)	-	-	106	120	130	140	150	160	170	180	190	Sum of By Bp	Total by CNo
End BP (°C)	-	106	120	130	140	150	160	170	180	190	200		
Simdis %off		0.50	0.18	0.13	0.13	0.37	0.68	7.26	6.08	8.81	11.86		
n-Paraffins		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.09	0.18
Isoparaffins		0.04	0.04	0.01	0.09	0.02	0.13	0.28	0.21	4.35	2.72	7.88	2.85
Olefins		0.45	0.07	0.00	0.00	0.02	0.01	0.03	0.00	0.00	0.00	0.59	1.59
Naphthenes		0.01	0.00	0.12	0.01	0.00	0.13	0.00	0.00	0.14	0.00	0.41	0.37
Aromatics		0.00	0.06	0.00	0.03	0.33	0.42	6.95	5.78	4.33	8.60	26.49	31.00
Unknown		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.53	0.53	0.01
Totals		**0.50**	**0.18**	**0.13**	**0.13**	**0.37**	**0.68**	**7.26**	**6.08**	**8.81**	**11.86**	**36.00**	**36.00**

Table B.5 DHA by boiling point for FD4B

Start BP (°C)	-	93.8	110	120	130	140	150	160	170	180	190	Sum of By Bp	Total by CNo
End BP (°C)	93.8	110	120	130	140	150	160	170	180	190	200		
Simdis %off	0.50	1.11	0.38	0.39	0.39	1.43	0.74	15.31	14.27	3.27	1.33		
n-Paraffins	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isoparaffins	0.42	1.10	0.38	0.00	0.39	0.10	0.22	0.73	0.33	0.00	0.00	3.67	6.49
Olefins	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Naphthenes	0.08	0.00	0.00	0.39	0.00	0.09	0.07	0.00	0.16	0.00	0.00	0.79	0.81
Aromatics	0.00	0.00	0.00	0.00	0.00	1.24	0.44	14.58	13.71	0.00	0.00	29.98	31.73
Unknown	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.09	0.08
Totals	**0.50**	**1.11**	**0.38**	**0.39**	**0.39**	**1.43**	**0.74**	**15.31**	**14.27**	**0.00**	**0.00**	**34.52**	**39.12**

Table B.6 DHA by boiling point for FD7B

Start BP (°C)	-	-	-	-	-	-	141	160	170	180	190	Sum of By Bp	Total by CNo
End BP (°C)	-	-	-	-	-	141	160	170	180	190	200		
Simdis %off						0.50	2.42	13.65	13.36	3.31	2.20		
n-Paraffins						0.02	0.06	0.00	0.31	0.00	0.00	0.39	0.36
Isoparaffins						0.15	0.19	2.15	0.19	0.28	0.00	2.95	3.98
Olefins						0.03	0.05	0.03	0.04	0.00	0.00	0.15	0.22
Naphthenes						0.22	0.15	0.05	0.14	0.66	0.00	1.21	0.83
Aromatics						0.08	1.97	11.38	12.57	2.12	0.00	28.12	29.89
Unknown						0.00	0.01	0.03	0.11	0.26	0.00	0.41	0.15
Totals						**0.50**	**2.42**	**13.65**	**13.36**	**3.31**	**0.00**	**33.24**	**35.43**

Table B.7 DHA by carbon number for FD2A

Report in wt% for Simdis≤ 392°F/200°C	55.83						
Carbon Number	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Totals
3	0.00	0.00	0.00	0.00	0.00		0.00
4	0.00	0.00	0.00	0.00	0.00		0.00
5	0.00	0.01	0.00	0.00	0.00		0.01
6	0.01	0.02	0.05	0.02	0.00		0.09
7	0.07	0.06	0.04	0.01	0.00		0.18
8	0.03	0.14	0.08	0.17	6.93		7.35
9	0.25	0.19	0.10	0.21	29.83		30.59
10	0.50	1.56	0.02	0.12	8.38		10.59
11	0.02	3.52	0.00	0.00	0.17		3.71
Totals	0.88	5.50	0.29	0.53	45.31	3.32	55.83

Table B.8 DHA by carbon number for FD4A

Report in wt% for Simdis≤ 392°F/200°C	39.26						
Carbon Number	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Totals
3	0.00	0.00	0.00	0.00	0.00		0.00
4	0.00	0.00	0.00	0.00	0.00		0.00
5	0.00	0.00	0.00	0.04	0.00		0.05
6	0.00	0.01	0.00	0.00	0.00		0.01
7	0.01	0.02	0.00	0.00	0.00		0.04
8	0.00	0.15	0.04	0.03	7.27		7.49
9	0.19	0.36	0.14	0.20	26.89		27.78
10	0.32	1.39	0.01	0.02	1.18		2.92
11	0.00	0.67	0.00	0.00	0.00		0.68
Totals	0.53	2.60	0.19	0.29	35.35	0.31	39.26

Table B.9 DHA by carbon number for FD7A

Report in wt% for Simdis≤ 392°F/200°C	29.15						
Carbon Number	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Totals
3	0.00	0.00	0.00	0.00	0.00		0.00
4	0.00	0.00	0.00	0.00	0.00		0.00
5	0.00	0.00	0.00	0.00	0.00		0.00
6	0.01	0.00	0.03	0.01	0.00		0.05
7	0.01	0.03	0.02	0.05	0.05		0.17
8	0.07	0.11	0.16	0.41	0.54		1.29
9	0.58	0.69	0.41	0.88	13.03		15.59
10	1.63	1.89	0.19	0.38	5.75		9.85
11	0.06	1.24	0.00	0.00	0.03		1.33
Totals	2.37	3.97	0.80	1.73	19.41	0.88	29.15

Table B.10 DHA by boiling point for FD2A

												Sum of By Bp	Total by CNo
Start BP (°C)	-	-	-	-	-	-	140.4	160	170	180	190	Sum of By Bp	Total by CNo
End BP (°C)	-	-	-	-	-	140.4	160	170	180	190	200		
Simdis %off						0.5	3.1	6.9	6.5	16.7	22.2		
n-Paraffins						0.03	0.10	0.00	0.23	0.00	0.26	0.62	0.88
Isoparaffins						0.10	0.09	0.39	0.48	3.69	2.97	7.71	5.50
Olefins						0.07	0.02	0.00	0.00	0.00	0.00	0.10	0.29
Naphthenes						0.07	0.05	0.00	0.05	0.07	0.00	0.25	0.53
Aromatics						0.16	2.80	6.51	5.61	9.50	15.48	40.06	45.31
Unknown						0.07	0.03	0.01	0.13	3.40	3.46	7.10	3.32
Totals						0.50	3.08	6.92	6.50	16.67	22.17	55.83	55.83

Table B.11 DHA by boiling point for FD4A

												Sum of By Bp	Total by CNo
Start BP (°C)	-	-	-	-	-	-	139.6	150	160	170	180	190	Sum of By Bp	Total by CNo
End BP (°C)	-	-	-	-	139.6	150	160	170	180	190	200		
Simdis %off					0.5	4.7	1.3	13.4	9.7	6.3	3.4		
n-Paraffins					0.01	0.00	0.16	0.00	0.30	0.00	0.00	0.47	0.53
Isoparaffins					0.12	0.14	0.23	0.80	0.69	0.40	0.00	2.38	2.60
Olefins					0.03	0.06	0.02	0.00	0.00	0.00	0.00	0.12	0.19
Naphthenes					0.04	0.01	0.14	0.01	0.01	0.02	0.00	0.24	0.29
Aromatics					0.28	4.47	0.67	12.54	8.55	5.76	2.96	35.22	35.35
Unknown					0.02	0.00	0.10	0.00	0.12	0.15	0.45	0.83	0.31
Totals					0.50	4.69	1.31	13.36	9.67	6.33	3.41	39.26	39.26

Table B.12 DHA by boiling point for FD7A

												Sum of By Bp	Total by CNo
Start BP (°C)	-	-	-	-	-	-	140.4	160	170	180	190	Sum of By Bp	Total by CNo
End BP (°C)	-	-	-	-	-	140.4	160	170	180	190	200		
Simdis %off						0.5	1.4	2.9	8.4	9.4	6.5		
n-Paraffins						0.03	0.31	0.00	1.06	0.00	0.58	1.97	2.37
Isoparaffins						0.08	0.46	0.70	0.54	1.06	1.06	3.90	3.97
Olefins						0.09	0.20	0.05	0.00	0.00	0.00	0.34	0.80
Naphthenes						0.18	0.25	0.13	0.03	0.51	0.00	1.10	1.73
Aromatics						0.07	0.22	2.01	6.62	7.34	4.34	20.59	19.41
Unknown						0.05	0.01	0.06	0.15	0.47	0.51	1.25	0.88
Totals						0.50	1.44	2.95	8.40	9.38	6.49	29.15	29.15

APPENDIX C. SPE GC-MS + PIONA DATA (Hydrocarbon content reported in wt %)

The SPE GC-MS + PIONA results for FD2A, FD4A and FD7A presented in Table C.3 were already reported in: Alnajjar, M.; Cannella, B.; Dettman, H.; Fairbridge, C.; Franz, J.; Gallant, T.; Gieleciak, R.; Hager, D.; Lay, C.; Lewis, S.; Ratcliff, M.; Sluder, S.; Storey, J.; Yin, H.; Zigler, B.; "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1 (2010).

Table C.1 SPE GC-MS + PIONA data for FACE diesel fuels FD2B, FD4B and FD7B

	FD2B			FD4B			FD7B		
Method	PIONA	SPE GC-MS	Total	PIONA	SPE GC-MS	Total	PIONA	SPE GC-MS	Total
Boiling range	IBP-200°C	200°C-FBP	IBP-FBP	IBP-200°C	200°C-FBP	IBP-FBP	IBP-200°C	200°C-FBP	IBP-FBP
Saturates	**8.0**	**54.8**	**65.2**	**4.7**	**51.7**	**56.5**	**2.5**	**47.3**	**49.8**
Total paraffins	**4.8**	**24.7**	**35.1**	**4.7**	**17.4**	**22.2**	**2.2**	**31.6**	**33.8**
Isoparaffins	4.6			3.2			1.0		
n-Paraffins	0.2			1.5			1.2		
Cycloparaffins	**3.3**	**30.1**	**30.2**	**0.0**	**34.3**	**34.3**	**0.3**	**15.7**	**16.0**
Monocycloparaffins	3.3	12.5	12.5	0.0	11.4	11.5	0.3	3.3	3.6
Dicycloparaffins		9.2	9.2		9.0	9.0		6.2	6.2
Tricycloparaffins		4.8	4.8		7.8	7.8		4.6	4.6
4-Rings cycloparaffins		3.7	3.7		6.0	6.0		1.6	1.6
5-Rings cycloparaffins		0.0	0.0		0.0	0.0		0.0	0.0
6-Rings cycloparaffins		0.0	0.0		0.0	0.0		0.0	0.0
AROMATICS	**27.8**	**9.1**	**34.5**	**34.1**	**9.0**	**43.2**	**32.4**	**17.0**	**49.4**
Monoaromatics	**27.8**	**3.2**	**28.6**	**34.1**	**3.9**	**38.1**	**32.4**	**8.9**	**41.3**
Alkylbenzenes	27.8	2.3	27.7	34.1	3.3	37.4	32.4	5.3	37.7
Benzocycloalkanes		0.6	0.6		0.5	0.5		2.7	2.7
Benzodicycloalkanes		0.3	0.3		0.2	0.2		1.0	1.0
Diaromatics		**5.8**	**5.8**		**5.1**	**5.1**		**8.1**	**8.1**
Naphthalenes		5.0	5.0		4.5	4.5		7.0	7.0
Naphthocycloalkanes		0.3	0.3		0.2	0.2		0.6	0.6
Fluorenes		0.6	0.6		0.3	0.3		0.5	0.5
Triaromatics		**0.0**	**0.0**		**0.0**	**0.0**		**0.0**	**0.0**
Phenanthrenes		0.0	0.0		0.0	0.0		0.0	0.0
Phenanthrocycloalkanes		0.0	0.0		0.0	0.0		0.0	0.0
Tetraaromatics		**0.0**	**0.0**		**0.0**	**0.0**		**0.0**	**0.0**
Pyrenes/Benzofluorenes		0.0	0.0		0.0	0.0		0.0	0.0
Chrysenes		0.0	0.0		0.0	0.0		0.0	0.0
Pentaaromatics		**0.0**	**0.0**		**0.0**	**0.0**		**0.0**	**0.0**
Aromatic Sulfur		**0.0**	**0.0**		**0.0**	**0.0**		**0.0**	**0.0**
Benzothiophenes		0.0	0.0		0.0	0.0		0.0	0.0
Dibenzothiophenes		0.0	0.0		0.0	0.0		0.0	0.0
Benzonaphthothiophenes		0.0	0.0		0.0	0.0		0.0	0.0
OLEFINS	**0.2**	**0.2**	**0.3**	**0.3**	**0.2**	**0.4**	**0.6**	**0.3**	**0.9**
TOTAL	**36.0**	**64.0**	**100.0**	**39.1**	**60.9**	**100.0**	**35.4**	**64.6**	**100.0**

Table C.2 SPE GC-MS + PIONA data for FACE diesel fuels FD2A, FD4A and FD7A

	FD2A			FD4A			FD7A		
Method	PIONA	SPE GC-MS	Total	PIONA	SPE GC-MS	Total	PIONA	SPE GC-MS	Total
Boiling range	IBP-200°C	200°C-FBP	IBP-FBP	IBP-200°C	200°C-FBP	IBP-FBP	IBP-200°C	200°C-FBP	IBP-FBP
Saturates	**7.1**	**34.9**	**42.0**	**3.0**	**56.5**	**59.5**	**9.3**	**42.5**	**51.8**
Total paraffins	**6.3**	**22.1**	**28.5**	**2.9**	**28.0**	**30.9**	**6.8**	**32.6**	**39.4**
Isoparaffins	5.7			1.4			2.7		
n-Paraffins	0.7			1.6			4.1		
Cycloparaffins	**0.8**	**12.8**	**13.6**	**0.1**	**28.5**	**28.6**	**2.5**	**9.9**	**12.4**
Monocycloparaffins	0.8	5.7	6.5	0.1	13.0	13.1	2.5	5.2	7.8
Dicycloparaffins		3.7	3.7		8.5	8.5		4.3	4.3
Tricycloparaffins		2.0	2.0		4.9	4.9		0.4	0.4
4-Rings cycloparaffins		1.4	1.4		2.1	2.1		0.0	0.0
5-Rings cycloparaffins		0.1	0.1		0.0	0.0		0.0	0.0
6-Rings cycloparaffins		0.0	0.0		0.0	0.0		0.0	0.0
AROMATICS	**46.2**	**9.1**	**55.3**	**36.2**	**4.0**	**40.2**	**19.8**	**27.8**	**47.5**
Monoaromatics	**46.2**	**8.5**	**54.8**	**36.2**	**3.1**	**39.3**	**19.8**	**15.9**	**35.6**
Alkylbenzenes	46.2	8.4	54.7	36.2	2.8	39.0	19.8	9.3	29.0
Benzocycloalkanes		0.1	0.1		0.3	0.3		4.5	4.5
Benzodicycloalkanes		0.0	0.0		0.0	0.0		2.0	2.0
Diaromatics		**0.5**	**0.5**		**0.9**	**0.9**		**10.7**	**10.7**
Naphthalenes		0.5	0.5		0.8	0.8		4.1	4.1
Naphthocycloalkanes		0.0	0.0		0.0	0.0		5.9	5.9
Fluorenes		0.1	0.1		0.0	0.0		0.7	0.7
Triaromatics		**0.0**	**0.0**		**0.0**	**0.0**		**0.3**	**0.3**
Phenanthrenes		0.0	0.0		0.0	0.0		0.3	0.3
Phenanthrocycloalkanes		0.0	0.0		0.0	0.0		0.0	0.0
Tetraaromatics		**0.0**	**0.0**		**0.0**	**0.0**		**0.0**	**0.0**
Pyrenes/Benzofluorenes		0.0	0.0		0.0	0.0		0.0	0.0
Chrysenes		0.0	0.0		0.0	0.0		0.0	0.0
Pentaaromatics		**0.0**	**0.0**		**0.0**	**0.0**		**0.0**	**0.0**
Aromatic Sulfur		**0.0**	**0.0**		**0.0**	**0.0**		**1.0**	**1.0**
Benzothiophenes		0.0	0.0		0.0	0.0		0.9	0.9
Dibenzothiophenes		0.0	0.0		0.0	0.0		0.1	0.1
Benzonaphthothiophenes		0.0	0.0		0.0	0.0		0.0	0.0
OLEFINS	**2.5**	**0.2**	**2.7**	**0.1**	**0.3**	**0.4**	**0.1**	**0.6**	**0.7**
TOTAL	**55.8**	**44.2**	**100.0**	**39.3**	**60.7**	**100.0**	**29.2**	**70.8**	**100.0**

APPENDIX D. GC-FIMS + PIONA DATA (Hydrocarbon content reported in wt %)

The GC-FIMS + PIONA results for FD2A, FD4A and FD7A presented in Tables D.4-D.6 were already reported in:
Alnajjar, M.; Cannella, B.; Dettman, H.; Fairbridge, C.; Franz, J.; Gallant, T.; Gieleciak, R.; Hager, D.; Lay, C.; Lewis, S.; Ratcliff, M.; Sluder, S.; Storey, J.; Yin, H.; Zigler, B.; "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1 (2010).

Table D.1 GC-FIMS + PIONA data for FACE diesel fuels FD2B

HC Type / #C	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Sum	Piona IBP-200C	FIMS 200-FBP	TOTAL IBP-FBP
Saturates	**0.00**	**0.31**	**7.50**	**2.03**	**2.26**	**3.23**	**3.51**	**2.49**	**4.92**	**8.97**	**6.00**	**7.44**	**48.66**	**8.03**	**48.66**	**56.69**
Paraffins	**0.00**	**0.00**	**2.65**	**0.29**	**0.90**	**1.11**	**0.82**	**0.43**	**0.22**	**0.36**	**0.58**	**1.07**	**8.43**	**4.75**	**8.43**	**13.18**
IsoParaffin	0.00	0.00	2.63	0.29	0.26	0.50	0.33	0.26	0.19	0.34	0.57	1.04	6.40	4.56	**6.40**	10.96
N-paraffins	0.00	0.00	0.02	0.01	0.65	0.61	0.48	0.16	0.03	0.02	0.01	0.03	2.03	0.19	**2.03**	2.22
Cycloparaffins	**0.00**	**0.31**	**4.85**	**1.73**	**1.35**	**2.12**	**2.69**	**2.06**	**4.70**	**8.61**	**5.42**	**6.37**	**40.23**	**3.28**	**40.23**	**43.51**
MonoCycloparaffins	0.00	0.15	4.61	1.23	0.54	1.20	1.77	1.23	3.50	7.33	3.33	3.63	28.51	3.28	**28.51**	31.79
Dicycloparaffins	0.00	0.09	0.24	0.26	0.45	0.50	0.55	0.46	0.57	0.00	0.00	0.00	3.13		**3.13**	3.13
Polycycloparaffins	0.00	0.06	0.00	0.24	0.36	0.42	0.37	0.38	0.63	1.28	2.09	2.74	8.59		**8.59**	8.59
Aromatics	**0.35**	**1.08**	**1.40**	**5.58**	**1.34**	**0.78**	**0.54**	**0.40**	**0.45**	**0.66**	**1.20**	**1.57**	**15.34**	**27.82**	**15.34**	**43.16**
Monoaromatics	**0.33**	**1.07**	**1.37**	**1.39**	**0.90**	**0.50**	**0.33**	**0.26**	**0.40**	**0.58**	**1.17**	**1.50**	**9.81**	**27.82**	**9.81**	**37.63**
Benzenes	0.00	0.62	0.21	0.27	0.30	0.19	0.11	0.08	0.13	0.29	0.50	0.73	3.41	27.82	**3.41**	31.23
Indans/tetralins	0.33	0.36	0.73	0.68	0.37	0.21	0.16	0.13	0.18	0.29	0.43	0.48	4.35		**4.35**	4.35
Indenes (benzocycloalkane)	0.00	0.10	0.43	0.44	0.23	0.10	0.06	0.04	0.09	0.00	0.25	0.30	2.04		**2.04**	2.04
Diaromatics	**0.00**	**0.00**	**0.03**	**4.16**	**0.38**	**0.23**	**0.17**	**0.11**	**0.05**	**0.06**	**0.01**	**0.06**	**5.27**		**5.27**	**5.27**
Naphthalenes	0.00	0.00	0.00	3.90	0.11	0.07	0.04	0.03	0.01	0.01	0.01	0.01	4.18		**4.18**	4.18
Acenaphthenes/biphenyls	0.00	0.00	0.03	0.26	0.27	0.16	0.14	0.08	0.03	0.06	0.00	0.05	1.09		**1.09**	1.09
Acenaphthalenes/fluorenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Triaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.04**	**0.02**	**0.01**	**0.01**	**0.00**	**0.01**	**0.01**	**0.01**	**0.11**		**0.11**	**0.11**
Phenanthrenes/anthracenes	0.00	0.00	0.00	0.00	0.04	0.02	0.01	0.00	0.00	0.01	0.01	0.01	0.11		**0.11**	0.11
Cyclopentanophenanthrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Tetraaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**		**0.01**	**0.01**
Pyrenes/fluoranthenes	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01		**0.01**	0.01
Chrysenes/benzoanthracenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Aromatic Sulfur	**0.01**	**0.01**	**0.00**	**0.03**	**0.02**	**0.03**	**0.02**	**0.02**	**0.00**	**0.00**	**0.00**	**0.00**	**0.13**		**0.13**	**0.13**
Benzothiophenes	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04		**0.04**	0.04
Dibenzothiophenes	0.00	0.00	0.00	0.02	0.02	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.09		**0.09**	0.09
Naphthobenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Olefin	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.15**		**0.15**
Total	**0.35**	**1.39**	**8.91**	**7.60**	**3.59**	**4.01**	**4.06**	**2.89**	**5.37**	**9.63**	**7.20**	**9.01**	**64.00**	**36.00**	**64.00**	**100.00**

Table D.2 GC-FIMS + PIONA data for FACE diesel fuels FD4B

HC Type / #C	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Sum	Piona IBP-200C	FIMS 200-FBP	TOTAL IBP-FBP
Saturates	**0.00**	**0.13**	**0.42**	**0.88**	**2.02**	**4.42**	**8.05**	**8.11**	**8.28**	**6.01**	**4.09**	**6.14**	**48.56**	**4.72**	**48.57**	**53.29**
Paraffins	**0.00**	**0.00**	**0.10**	**0.19**	**0.80**	**1.10**	**1.82**	**2.82**	**2.54**	**1.49**	**0.92**	**1.32**	**13.10**	**4.69**	**13.11**	**17.80**
IsoParaffin	0.00	0.00	0.08	0.17	0.26	0.48	1.48	2.48	2.43	1.47	0.89	1.29	11.02	3.23	**11.02**	14.25
N-paraffins	0.00	0.00	0.02	0.02	0.54	0.62	0.34	0.34	0.11	0.02	0.03	0.04	2.09	1.46	**2.09**	3.55
Cycloparaffins	**0.00**	**0.13**	**0.32**	**0.69**	**1.22**	**3.32**	**6.23**	**5.29**	**5.74**	**4.52**	**3.17**	**4.81**	**35.45**	**0.03**	**35.47**	**35.50**
MonoCycloparaffins	0.00	0.03	0.18	0.27	0.52	1.95	3.37	2.26	3.29	2.95	1.23	2.06	18.10	0.03	**18.11**	18.14
Dicycloparaffins	0.00	0.05	0.15	0.21	0.40	0.65	1.46	1.32	0.92	0.00	0.00	0.00	5.16		**5.16**	5.16
Polycycloparaffins	0.00	0.05	0.00	0.21	0.30	0.72	1.40	1.71	1.53	1.58	1.94	2.76	12.19		**12.20**	12.20
Aromatics	**0.36**	**1.11**	**1.11**	**4.40**	**1.07**	**0.64**	**0.48**	**0.40**	**0.37**	**0.50**	**0.75**	**1.12**	**12.32**	**34.14**	**12.33**	**46.47**
Monoaromatics	**0.36**	**1.10**	**1.08**	**1.04**	**0.68**	**0.38**	**0.30**	**0.30**	**0.33**	**0.42**	**0.74**	**1.08**	**7.82**	**34.14**	**7.82**	**41.96**
Benzenes	0.00	0.69	0.18	0.22	0.24	0.15	0.15	0.18	0.21	0.28	0.43	0.69	3.41	34.14	**3.41**	37.55
Indans/tetralins	0.36	0.33	0.57	0.50	0.27	0.16	0.11	0.08	0.09	0.14	0.22	0.28	3.11		**3.12**	3.12
Indenes (benzocycloalkane)	0.00	0.08	0.34	0.32	0.17	0.07	0.04	0.03	0.03	0.00	0.09	0.11	1.29		**1.29**	1.29
Diaromatics	**0.00**	**0.00**	**0.03**	**3.33**	**0.32**	**0.20**	**0.14**	**0.08**	**0.04**	**0.05**	**0.01**	**0.03**	**4.22**		**4.22**	**4.22**
Naphthalenes	0.00	0.00	0.00	3.12	0.10	0.07	0.03	0.02	0.01	0.01	0.01	0.01	3.37		**3.37**	3.37
Acenaphthenes/biphenyls	0.00	0.00	0.03	0.21	0.23	0.13	0.10	0.06	0.03	0.04	0.00	0.02	0.85		**0.86**	0.86
Acenaphthalenes/fluorenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Triaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.04**	**0.02**	**0.01**	**0.01**	**0.00**	**0.02**	**0.01**	**0.01**	**0.12**		**0.12**	**0.12**
Phenanthrenes/anthracenes	0.00	0.00	0.00	0.00	0.04	0.02	0.01	0.00	0.00	0.02	0.01	0.01	0.12		**0.12**	0.12
Cyclopentanophenanthrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Tetraaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**		**0.01**	**0.01**
Pyrenes/fluoranthenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01		**0.01**	0.01
Chrysenes/benzoanthracenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Aromatic Sulfur	**0.01**	**0.00**	**0.00**	**0.02**	**0.03**	**0.04**	**0.03**	**0.02**	**0.00**	**0.00**	**0.00**	**0.00**	**0.16**		**0.16**	**0.16**
Benzothiophenes	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03		**0.03**	0.03
Dibenzothiophenes	0.00	0.00	0.00	0.02	0.02	0.04	0.03	0.02	0.00	0.00	0.00	0.00	0.12		**0.12**	0.12
Naphthobenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Olefin	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.26**		**0.26**
Total	**0.36**	**1.23**	**1.54**	**5.28**	**3.09**	**5.06**	**8.53**	**8.52**	**8.65**	**6.51**	**4.84**	**7.26**	**60.88**	**39.12**	**60.90**	**100.02**

Table D.3 GC-FIMS + PIONA data for FACE diesel fuels FD7B

HC Type / #C	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Sum	Piona IBP-200C	FIMS 200-FBP	TOTAL IBP-FBP
Saturates	**0.00**	**0.31**	**7.50**	**2.03**	**2.26**	**3.23**	**3.51**	**2.49**	**4.92**	**8.97**	**6.00**	**7.44**	**48.66**	**2.43**	**39.97**	**42.40**
Paraffins	**0.00**	**0.00**	**2.65**	**0.29**	**0.90**	**1.11**	**0.82**	**0.43**	**0.22**	**0.36**	**0.58**	**1.07**	**8.43**	**2.15**	**25.43**	**27.58**
IsoParaffin	0.00	0.00	2.63	0.29	0.26	0.50	0.33	0.26	0.19	0.34	0.57	1.04	6.40	0.97	**7.26**	8.23
N-paraffins	0.00	0.00	0.02	0.01	0.65	0.61	0.48	0.16	0.03	0.02	0.01	0.03	2.03	1.18	**18.17**	19.35
Cycloparaffins	**0.00**	**0.31**	**4.85**	**1.73**	**1.35**	**2.12**	**2.69**	**2.06**	**4.70**	**8.61**	**5.42**	**6.37**	**40.23**	**0.28**	**14.54**	**14.82**
MonoCycloparaffins	0.00	0.15	4.61	1.23	0.54	1.20	1.77	1.23	3.50	7.33	3.33	3.63	28.51	0.28	**5.49**	5.77
Dicycloparaffins	0.00	0.09	0.24	0.26	0.45	0.50	0.55	0.46	0.57	0.00	0.00	0.00	3.13		**5.43**	5.43
Polycycloparaffins	0.00	0.06	0.00	0.24	0.36	0.42	0.37	0.38	0.63	1.28	2.09	2.74	8.59		**3.62**	3.62
Aromatics	**0.35**	**1.08**	**1.40**	**5.58**	**1.34**	**0.78**	**0.54**	**0.40**	**0.45**	**0.66**	**1.20**	**1.57**	**15.34**	**32.39**	**24.63**	**57.02**
Monoaromatics	**0.33**	**1.07**	**1.37**	**1.39**	**0.90**	**0.50**	**0.33**	**0.26**	**0.40**	**0.58**	**1.17**	**1.50**	**9.81**	**32.39**	**9.23**	**41.62**
Benzenes	0.00	0.62	0.21	0.27	0.30	0.19	0.11	0.08	0.13	0.29	0.50	0.73	3.41	32.39	**2.91**	35.30
Indans/tetralins	0.33	0.36	0.73	0.68	0.37	0.21	0.16	0.13	0.18	0.29	0.43	0.48	4.35		**4.71**	4.71
Indenes (benzocycloalkane)	0.00	0.10	0.43	0.44	0.23	0.10	0.06	0.04	0.09	0.00	0.25	0.30	2.04		**1.60**	1.60
Diaromatics	**0.00**	**0.00**	**0.03**	**4.16**	**0.38**	**0.23**	**0.17**	**0.11**	**0.05**	**0.06**	**0.01**	**0.06**	**5.27**		**15.07**	**15.07**
Naphthalenes	0.00	0.00	0.00	3.90	0.11	0.07	0.04	0.03	0.01	0.01	0.01	0.01	4.18		**11.93**	11.93
Acenaphthenes/biphenyls	0.00	0.00	0.03	0.26	0.27	0.16	0.14	0.08	0.03	0.06	0.00	0.05	1.09		**0.73**	0.73
Acenaphthalenes/fluorenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**2.41**	2.41
Triaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.04**	**0.02**	**0.01**	**0.01**	**0.00**	**0.01**	**0.01**	**0.01**	**0.11**		**0.11**	**0.11**
Phenanthrenes/anthracenes	0.00	0.00	0.00	0.00	0.04	0.02	0.01	0.00	0.00	0.01	0.01	0.01	0.11		**0.10**	0.10
Cyclopentanophenanthrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.01**	0.01
Tetraaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**		**0.01**	**0.01**
Pyrenes/fluoranthenes	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01		**0.01**	0.01
Chrysenes/benzoanthracenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Aromatic Sulfur	**0.01**	**0.01**	**0.00**	**0.03**	**0.02**	**0.03**	**0.02**	**0.02**	**0.00**	**0.00**	**0.00**	**0.00**	**0.13**		**0.21**	**0.21**
Benzothiophenes	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04		**0.03**	0.03
Dibenzothiophenes	0.00	0.00	0.00	0.02	0.02	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.09		**0.18**	0.18
Naphthobenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		**0.00**	0.00
Olefin	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.61**		**0.61**
Total	**0.35**	**1.39**	**8.91**	**7.60**	**3.59**	**4.01**	**4.06**	**2.89**	**5.37**	**9.63**	**7.20**	**9.01**	**64.00**	**35.43**	**64.60**	**100.03**

122

Table D.4 GC-FIMS + PIONA data for FACE diesel fuels FD2A

HC Type / #C	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Sum	Piona IBP-200C	FIMS 200-FBP	TOTAL IBP-FBP
Saturates	**0.00**	**0.00**	**0.24**	**8.20**	**22.46**	**15.79**	**4.71**	**3.02**	**2.11**	**2.44**	**3.07**	**2.86**	**5.61**	**70.50**	**31.14**	**7.1**	**38.24**
Paraffins	**0.00**	**0.00**	**0.00**	**2.76**	**17.61**	**12.44**	**2.61**	**1.35**	**0.59**	**0.28**	**0.16**	**0.05**	**0.05**	**37.89**	**16.74**	**6.3**	**23.06**
IsoParaffin	0.00	0.00	0.00	2.59	17.61	12.40	2.59	1.26	0.53	0.20	0.16	0.05	0.05	37.43	16.53	5.7	22.18
N-paraffins	0.00	0.00	0.00	0.17	0.00	0.04	0.02	0.08	0.06	0.09	0.00	0.00	0.00	0.46	0.20	0.7	0.87
Cycloparaffins	**0.00**	**0.00**	**0.24**	**5.44**	**4.85**	**3.34**	**2.10**	**1.68**	**1.51**	**2.16**	**2.91**	**2.81**	**5.56**	**32.60**	**14.40**	**0.8**	**15.18**
MonoCycloparaffins	0.00	0.00	0.04	5.01	3.96	2.40	1.50	1.35	1.39	1.83	1.47	0.40	0.72	20.05	8.86	0.8	9.64
Dicycloparaffins	0.00	0.00	0.05	0.43	0.83	0.79	0.52	0.30	0.10	0.12	0.40	0.71	1.70	5.95	2.63		2.63
Polycycloparaffins	0.00	0.00	0.15	0.00	0.06	0.16	0.08	0.02	0.03	0.21	1.04	1.71	3.15	6.60	2.92		2.92
Aromatics	**0.12**	**3.81**	**10.88**	**4.11**	**3.46**	**2.47**	**1.46**	**0.76**	**0.33**	**0.38**	**0.69**	**0.57**	**0.44**	**29.50**	**13.03**	**46.2**	**59.25**
Monoaromatics	**0.00**	**3.80**	**7.85**	**2.26**	**1.88**	**1.44**	**0.88**	**0.46**	**0.19**	**0.15**	**0.33**	**0.46**	**0.41**	**20.11**	**8.88**	**46.2**	**55.10**
Alkylbenzenes	0.00	2.54	6.48	0.81	0.55	0.50	0.31	0.18	0.11	0.13	0.30	0.41	0.38	12.67	5.60	46.2	51.82
Benzocycloalkanes	0.00	1.26	1.26	1.40	1.19	0.72	0.40	0.20	0.07	0.01	0.03	0.06	0.04	6.63	2.93		2.93
Benzodicycloalkanes	0.00	0.00	0.11	0.05	0.14	0.22	0.17	0.08	0.02	0.01	0.00	0.00	0.00	0.80	0.35		0.35
Diaromatics	**0.00**	**0.00**	**3.03**	**1.73**	**1.56**	**1.02**	**0.57**	**0.20**	**0.02**	**0.00**	**0.00**	**0.00**	**0.01**	**8.14**	**3.59**		**3.59**
Naphthalenes	0.00	0.00	3.03	1.66	1.29	0.55	0.16	0.02	0.00	0.00	0.00	0.00	0.00	6.71	2.97		2.97
Biphenyls	0.00	0.00	0.00	0.05	0.14	0.26	0.22	0.14	0.01	0.00	0.00	0.00	0.00	0.83	0.37		0.37
Naphthocycloalkanes	0.00	0.00	0.00	0.02	0.12	0.16	0.13	0.03	0.01	0.00	0.00	0.00	0.00	0.46	0.20		0.20
Fluorenes	0.00	0.00	0.00	0.00	0.01	0.05	0.06	0.02	0.00	0.00	0.00	0.00	0.01	0.13	0.06		0.06
Polyaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Triaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.03**	**0.03**	**0.01**		**0.01**
Phenanthrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01		0.01
Phenanthrocycloalkanes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01		0.01
Tetraaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**
Pyrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Chrysenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Aromatic Sulfur	**0.12**	**0.01**	**0.00**	**0.13**	**0.03**	**0.01**	**0.02**	**0.10**	**0.12**	**0.23**	**0.36**	**0.10**	**0.00**	**1.23**	**0.54**		**0.54**
Benzothiophenes	0.12	0.01	0.00	0.00	0.00	0.00	0.02	0.10	0.12	0.23	0.36	0.10	0.00	1.06	0.47		0.47
Dibenzothiophenes	0.00	0.00	0.00	0.13	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.07		0.07
Naphthobenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Olefins														**0.00**	**0.00**	**2.50**	**2.50**
Polar														**0.00**	**0.00**	**0.00**	**0.00**
Total														**100.00**	**44.17**	**55.8**	**100.00**

Table D.5 GC-FIMS + PIONA data for FACE diesel fuels FD4A

HC Type / #C	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Sum	Piona IBP-200C	FIMS 200-FBP	TOTAL IBP-FBP
Saturates	**0.00**	**0.00**	**0.29**	**0.84**	**8.47**	**17.74**	**12.62**	**8.26**	**5.84**	**4.82**	**3.77**	**2.03**	**1.95**	**66.64**	**40.48**	**3.0**	**43.47**
Paraffins	**0.00**	**0.00**	**0.00**	**0.28**	**6.82**	**12.76**	**5.84**	**2.24**	**1.23**	**0.35**	**0.15**	**0.00**	**0.00**	**29.67**	**18.02**	**2.9**	**20.94**
IsoParaffin	0.00	0.00	0.00	0.28	6.82	12.76	5.82	2.22	1.23	0.35	0.15	0.00	0.00	29.63	18.00	1.4	19.37
N-paraffins	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.04	0.03	1.6	1.58
Cycloparaffins	**0.00**	**0.00**	**0.29**	**0.56**	**1.65**	**4.98**	**6.78**	**6.02**	**4.61**	**4.47**	**3.63**	**2.03**	**1.95**	**36.97**	**22.45**	**0.1**	**22.52**
MonoCycloparaffins	0.00	0.00	0.01	0.56	1.61	4.35	5.00	3.13	2.05	2.41	1.62	0.47	0.17	21.37	12.98	0.1	13.05
Dicycloparaffins	0.00	0.00	0.00	0.00	0.04	0.44	0.97	1.31	1.15	0.85	0.78	0.58	0.46	6.59	4.00		4.00
Polycycloparaffins	0.00	0.00	0.28	0.00	0.00	0.19	0.81	1.58	1.42	1.21	1.22	0.98	1.32	9.01	5.48		5.48
Aromatics	**0.14**	**5.99**	**19.15**	**3.04**	**1.91**	**1.06**	**0.55**	**0.24**	**0.20**	**0.29**	**0.37**	**0.25**	**0.14**	**33.36**	**20.26**	**36.2**	**56.45**
Monoaromatics	**0.00**	**5.98**	**15.45**	**0.93**	**0.17**	**0.07**	**0.09**	**0.08**	**0.13**	**0.23**	**0.24**	**0.24**	**0.13**	**23.74**	**14.42**	**36.2**	**50.61**
Alkylbenzenes	0.00	2.93	13.95	0.67	0.12	0.05	0.04	0.04	0.13	0.22	0.22	0.22	0.12	18.71	11.37	36.2	47.56
Benzocycloalkanes	0.00	3.05	1.31	0.23	0.05	0.02	0.05	0.04	0.01	0.01	0.02	0.02	0.01	4.81	2.92		2.92
Benzodicycloalkanes	0.00	0.00	0.18	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.13		0.13
Diaromatics	**0.00**	**0.00**	**3.70**	**2.02**	**1.72**	**0.99**	**0.43**	**0.12**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**9.00**	**5.47**		**5.47**
Naphthalenes	0.00	0.00	3.70	1.97	1.48	0.60	0.10	0.00	0.00	0.00	0.00	0.00	0.00	7.85	4.77		4.77
Biphenyls	0.00	0.00	0.00	0.04	0.12	0.22	0.18	0.08	0.01	0.00	0.00	0.00	0.00	0.65	0.39		0.39
Naphthocycloalkanes	0.00	0.00	0.00	0.01	0.11	0.12	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.30	0.19		0.19
Fluorenes	0.00	0.00	0.00	0.00	0.01	0.06	0.09	0.03	0.00	0.00	0.00	0.00	0.00	0.20	0.12		0.12
Polyaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Triaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.02**	**0.01**		**0.01**
Phenanthrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01		0.01
Phenanthrocycloalkanes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Tetraaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**
Pyrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Chrysenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Aromatic Sulfur	**0.14**	**0.01**	**0.00**	**0.09**	**0.02**	**0.00**	**0.03**	**0.04**	**0.06**	**0.07**	**0.13**	**0.01**	**0.00**	**0.61**	**0.37**		**0.37**
Benzothiophenes	0.14	0.01	0.00	0.00	0.00	0.00	0.03	0.04	0.06	0.07	0.13	0.01	0.00	0.49	0.30		0.30
Dibenzothiophenes	0.00	0.00	0.00	0.09	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.07		0.07
Naphthobenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Olefins														**0.00**	**0.00**	**0.09**	**0.09**
Polar														**0.00**	**0.00**	**0.00**	**0.00**
Total														**100.00**	**60.74**	**39.3**	**100.00**

Table D.6 GC-FIMS + PIONA data for FACE diesel fuels FD7A

HC Type / #C	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Sum	Piona IBP-200C	FIMS 200-FBP	TOTAL IBP-FBP
Saturates	**0.00**	**0.04**	**1.33**	**7.40**	**7.30**	**29.17**	**15.51**	**2.56**	**0.79**	**0.03**	**0.74**	**0.00**	**0.00**	**64.87**	**45.93**	**9.30**	**55.23**
Paraffins	**0.00**	**0.00**	**0.00**	**3.42**	**3.77**	**27.15**	**14.67**	**2.34**	**0.11**	**0.00**	**0.00**	**0.00**	**0.00**	**51.46**	**36.43**	**6.80**	**43.23**
IsoParaffin	0.00	0.00	0.00	1.06	2.04	1.43	0.41	0.29	0.00	0.00	0.00	0.00	0.00	5.24	3.71	2.70	6.41
N-paraffins	0.00	0.00	0.00	2.36	1.73	25.72	14.25	2.06	0.11	0.00	0.00	0.00	0.00	46.22	32.73	4.10	36.83
Cycloparaffins	**0.00**	**0.04**	**1.33**	**3.98**	**3.53**	**2.01**	**0.85**	**0.22**	**0.68**	**0.03**	**0.74**	**0.00**	**0.00**	**13.41**	**9.49**	**2.50**	**11.99**
MonoCycloparaffins	0.00	0.00	0.37	2.28	2.41	1.40	0.29	0.00	0.59	0.00	0.74	0.00	0.00	8.08	5.72	2.50	8.22
Dicycloparaffins	0.00	0.00	0.87	1.61	1.03	0.33	0.44	0.10	0.03	0.01	0.00	0.00	0.00	4.43	3.14		3.14
Polycycloparaffins	0.00	0.04	0.09	0.09	0.10	0.28	0.11	0.11	0.06	0.02	0.00	0.00	0.00	0.90	0.63		0.63
Aromatics	**0.00**	**2.07**	**5.53**	**4.01**	**2.39**	**9.60**	**0.56**	**6.24**	**0.03**	**3.45**	**0.01**	**1.24**	**0.00**	**35.13**	**24.87**	**19.80**	**44.67**
Monoaromatics	**0.00**	**1.87**	**4.55**	**3.32**	**1.80**	**5.51**	**0.42**	**0.67**	**0.00**	**0.14**	**0.01**	**0.00**	**0.00**	**18.29**	**12.95**	**19.80**	**32.75**
Alkylbenzenes	0.00	1.09	3.54	1.77	0.75	4.03	0.12	0.04	0.00	0.00	0.01	0.00	0.00	11.37	8.05	19.80	27.85
Benzocycloalkanes	0.00	0.79	0.99	1.46	0.96	0.97	0.27	0.18	0.00	0.00	0.00	0.00	0.00	5.62	3.98		3.98
Benzodicycloalkanes	0.00	0.00	0.02	0.08	0.08	0.50	0.03	0.45	0.00	0.14	0.00	0.00	0.00	1.31	0.93		0.93
Diaromatics	**0.00**	**0.19**	**0.97**	**0.69**	**0.59**	**4.09**	**0.15**	**5.57**	**0.02**	**3.30**	**0.00**	**1.24**	**0.00**	**16.83**	**11.91**		**11.91**
Naphthalenes	0.00	0.19	0.97	0.64	0.40	0.84	0.01	1.50	0.00	1.88	0.00	1.18	0.00	7.63	5.40		5.40
Biphenyls	0.00	0.00	0.00	0.04	0.13	3.16	0.10	3.94	0.02	1.38	0.00	0.06	0.00	8.82	6.25		6.25
Naphthocycloalkanes	0.00	0.00	0.00	0.01	0.06	0.09	0.02	0.08	0.00	0.01	0.00	0.00	0.00	0.28	0.20		0.20
Fluorenes	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.00	0.04	0.00	0.00	0.00	0.10	0.07		0.07
Polyaromatics	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.02**	**0.01**		**0.01**
Triaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**
Phenanthrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Phenanthrocycloalkanes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Tetraaromatics	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**
Pyrenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Chrysenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Aromatic Sulfur	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.02**	**0.01**		**0.01**
Benzothiophenes	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01		0.01
Dibenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Naphthobenzothiophenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Olefins														**0.00**	**0.00**	**0.10**	**0.10**
Polar														**0.00**	**0.00**	**0.00**	**0.00**
Total														**100.00**	**70.80**	**29.20**	**100.00**

APPENDIX E. 'Normal'- GCxGC-FID DATA (Hydrocarbon content reported in wt %)

Table E.1 'normal' - GCxGC-FID hydrocarbon speciation and concentration (wt %) for reformulated and original FACE diesel fuels

Hydrocarbon Type	FD2B Reformulated	FD2A Original	FD4B Reformulated	FD4A Original	FD7B Reformulated	FD7A Original
N-Paraffins						
n-C5	0.01	0.00	0.02	0.00	0.01	0.00
n-C6	0.04	0.01	0.07	0.04	0.05	0.00
n-C7	0.00	0.02	0.00	0.01	0.01	0.01
n-C8	0.02	0.01	0.02	0.00	0.04	0.06
n-C9	0.03	0.09	0.08	0.19	0.07	0.40
n-C10	0.06	0.13	0.01	0.11	0.30	0.76
n-C11	1.67	2.44	0.05	0.04	0.30	1.21
n-C12	0.48	0.51	0.11	0.39	0.32	0.92
n-C13	0.04	0.07	0.38	0.26	0.51	1.16
n-C14	0.28	0.08	0.42	0.26	20.74	19.82
n-C15	0.28	0.14	0.38	0.21	8.92	6.58
n-C16	0.57	0.11	0.73	0.41	2.36	1.19
n-C17	0.40	0.24	0.77	0.12	0.60	0.18
n-C18	0.14	0.13	0.58	0.19	0.35	0.06
n-C19	0.00	0.08	0.38	0.23	0.22	0.02
n-C20	0.27	0.07	0.00	0.15	0.17	0.02
n-C21	0.28	0.12	0.11	0.11	0.11	0.00
n-C22	0.00	0.15	0.35	0.48	0.06	0.00
n-C23	0.00	0.09	0.00	0.00	0.04	0.00
n-C24	0.41	0.00	0.10	0.03	0.02	0.00
n-C25	0.08	0.03	0.10	0.02	0.01	0.00
n-C26	0.11	0.01	0.05	0.01	0.00	0.00
n-C27	0.01	0.00	0.01	0.00	0.00	0.00
n-C28	0.01	0.00	0.00	0.00	0.00	0.00
n-C29	0.01	0.00	0.00	0.00	0.00	0.00
n-C30	0.01	0.00	0.00	0.00	0.00	0.00
n-C31	0.01	0.00	0.00	0.00	0.00	0.00
n-C32	0.00	0.00	0.00	0.00	0.00	0.00
n-C33	0.00	0.00	0.00	0.00	0.00	0.00
n-C34	0.00	0.00	0.00	0.00	0.00	0.00
n-C35	0.00	0.00	0.00	0.00	0.00	0.00
n-C36	0.00	0.00	0.00	0.00	0.00	0.00
Total	**5.22**	**4.53**	**4.72**	**3.26**	**35.21**	**32.39**
Iso-Paraffins						
iP-C7	0.47	0.02	1.45	0.04	0.03	0.01
iP-C8	0.26	0.02	0.77	0.05	0.09	0.07
iP-C9	0.12	0.06	0.37	0.22	0.29	0.56
iP-C10	0.62	1.14	1.32	1.46	0.56	1.19
iP-C11	16.49	31.63	0.57	0.43	0.57	1.83
iP-C12	14.19	19.18	0.97	2.27	0.56	1.63
iP-C13	1.55	2.74	1.36	11.07	0.57	1.85
iP-C14	1.05	0.21	2.97	7.58	0.85	1.11
iP-C15	1.87	0.51	5.78	4.30	0.88	0.66
iP-C16	2.03	0.55	6.15	3.41	0.61	0.45
iP-C17	0.00	0.34	4.18	2.72	0.66	0.44
iP-C18	0.00	0.26	2.26	1.96	0.70	0.19
iP-C19	0.00	0.39	2.12	1.68	0.35	0.07
iP-C20	0.00	0.36	2.63	1.43	0.21	0.05
iP-C21	0.00	0.78	1.35	0.91	0.14	0.02
iP-C22	0.00	1.45	1.49	1.44	0.10	0.01
iP-C23	0.00	1.22	0.78	0.90	0.05	0.01

iP-C24	0.00	0.63	1.04	0.53	0.04	0.00
iP-C25	0.00	0.14	0.33	0.17	0.02	0.00
iP-C26	0.00	0.03	0.14	0.05	0.01	0.00
iP-C27	0.00	0.01	0.05	0.02	0.00	0.00
iP-C28	0.00	0.01	0.03	0.01	0.00	0.00
iP-C29	0.00	0.00	0.01	0.00	0.00	0.00
iP-C30	0.00	0.00	0.00	0.00	0.00	0.00
iP-C31	0.00	0.00	0.00	0.00	0.00	0.00
iP-C32	0.00	0.00	0.00	0.00	0.00	0.00
iP-C33	0.00	0.00	0.00	0.00	0.00	0.00
iP-C34	0.00	0.00	0.00	0.00	0.00	0.00
iP-C35	0.00	0.00	0.00	0.00	0.00	0.00
Total	38.65	61.68	38.12	42.65	7.29	10.15

Cycloparaffins

Cyc-C9	0.11	0.28	0.31	0.31	0.35	0.58
Cyc-C10	0.04	0.07	0.19	0.07	0.70	0.92
Cyc-C11	0.00	0.00	0.02	0.01	0.62	1.02
Cyc-C12	0.09	0.03	0.01	0.00	0.79	1.79
Cyc-C13	0.08	0.14	0.01	0.01	1.23	2.56
Cyc-C14	0.01	0.05	0.01	0.01	1.21	1.69
Cyc-C15	0.28	0.11	0.94	0.89	1.09	1.00
Cyc-C16	0.80	0.14	1.99	0.91	1.11	0.59
Cyc-C17	5.64	0.42	2.22	1.67	1.34	0.47
Cyc-C18	5.49	0.19	1.08	0.58	0.54	0.21
Cyc-C19	5.19	0.04	0.01	0.07	0.43	0.18
Cyc-C20	4.20	0.60	0.03	0.47	0.34	0.17
Cyc-C21	3.67	2.10	1.16	2.21	0.25	0.07
Cyc-C22	2.50	3.11	2.44	2.61	0.21	0.01
Cyc-C23	4.45	2.45	2.35	2.00	0.12	0.00
Cyc-C24	1.21	1.02	1.36	0.93	0.06	0.00
Cyc-C25	0.76	0.26	0.63	0.20	0.02	0.00
Cyc-C26	0.35	0.07	0.25	0.05	0.01	0.00
Cyc-C27	0.09	0.01	0.07	0.01	0.00	0.00
Cyc-C28	0.08	0.00	0.02	0.00	0.00	0.00
Cyc-C29	0.04	0.00	0.01	0.00	0.00	0.00
Cyc-C30	0.03	0.00	0.01	0.00	0.00	0.00
Cyc-C31	0.01	0.00	0.00	0.00	0.00	0.00
Cyc-C32	0.01	0.00	0.00	0.00	0.00	0.00
Cyc-C33	0.00	0.00	0.00	0.00	0.00	0.00
Cyc-C34	0.00	0.00	0.00	0.00	0.00	0.00
Cyc-C35	0.00	0.00	0.00	0.00	0.00	0.00
Cyc-C36	0.00	0.00	0.00	0.00	0.00	0.00
Cyc-C37	0.00	0.00	0.00	0.00	0.00	0.00
Cyc-C38	0.00	0.00	0.00	0.00	0.00	0.00
Total	35.15	11.09	15.10	13.01	10.41	11.27

Monoaromatics

a6-C0	0.00	0.00	0.00	0.00	0.00	0.00
a6-C1	0.01	0.01	0.01	0.00	0.03	0.03
a6-C2	0.93	2.85	2.04	5.34	2.02	0.33
a6-C3	12.19	11.19	27.14	21.15	26.16	8.44
a6-C4	2.03	5.18	4.31	9.83	4.63	12.09
a6-C5	0.18	0.96	0.37	1.55	0.69	2.81
a6-C6	0.05	0.06	0.06	0.06	0.24	1.33
a6-C7	0.05	0.05	0.08	0.02	0.45	1.82
a6-C8	0.06	0.04	0.08	0.02	0.31	0.59
a6-C9	0.04	0.04	0.06	0.06	0.43	0.33
a6-C10	0.02	0.03	0.04	0.04	0.39	0.07
a6-C11	0.00	0.04	0.18	0.24	0.25	0.09

a6-C12	0.00	0.05	0.11	0.09	0.23	0.03
a6-C13	0.01	0.10	0.14	0.12	0.13	0.01
a6-C14	0.01	0.19	0.13	0.08	0.07	0.01
a6-C15	0.00	0.02	0.02	0.00	0.01	0.00
a6-C16	0.00	0.00	0.05	0.00	0.00	0.00
Total	**15.56**	**20.82**	**34.81**	**38.60**	**36.04**	**27.98**
Indans/tetralins						
a6A5/a6A6-1	0.02	0.03	0.03	0.04	0.03	0.02
a6A5/a6A6-2	0.09	0.28	0.18	0.42	0.37	0.55
a6A5/a6A6-3	0.06	0.08	0.07	0.06	0.34	0.88
a6A5/a6A6-4	0.24	0.20	0.31	0.20	0.79	1.33
a6A5/a6A6-5	0.15	0.08	0.21	0.01	0.46	0.61
a6A5/a6A6-6	0.05	0.05	0.07	0.00	0.32	0.92
a6A5/a6A6-7	0.02	0.03	0.02	0.00	0.15	0.37
a6A5/a6A6-8	0.00	0.02	0.03	0.01	0.13	0.16
a6A5/a6A6-9	0.03	0.04	0.12	0.07	0.25	0.07
Total	**0.66**	**0.81**	**1.05**	**0.82**	**2.83**	**4.92**
Naphthalenes						
a6a6-C0	0.10	0.35	0.19	0.67	0.20	0.53
a6a6-C1	0.64	0.29	0.85	0.47	1.10	0.56
a6a6-C2	2.07	0.12	2.62	0.16	3.44	2.31
a6a6-C3	1.27	0.10	1.63	0.11	2.13	2.69
a6a6-C4	0.33	0.06	0.40	0.06	0.53	2.83
a6a6-C5-C14	0.12	0.07	0.15	0.06	0.29	3.50
a6a6-C15+	0.00	0.00	0.00	0.00	0.00	0.00
Total	**4.53**	**0.99**	**5.84**	**1.53**	**7.69**	**12.42**
Acenaphthalenes/fluorenes						
a6A5a6-1	0.00	0.00	0.00	0.00	0.00	0.00
a6A5a6-2	0.00	0.00	0.00	0.00	0.00	0.00
a6A5a6-3	0.12	0.01	0.15	0.01	0.21	0.03
a6A5a6-4	0.07	0.02	0.09	0.01	0.12	0.05
a6A5a6-5	0.03	0.02	0.05	0.02	0.08	0.09
a6A5a6-6	0.01	0.01	0.01	0.01	0.05	0.26
a6A5a6-7	0.00	0.00	0.00	0.00	0.00	0.07
Total	**0.23**	**0.06**	**0.3**	**0.05**	**0.46**	**0.5**
Phenanthrenes						
a6a6a6-1	0.01	0.00	0.02	0.00	0.02	0.01
a6a6a6-2	0.01	0.01	0.01	0.01	0.02	0.02
a6a6a6-3	0.00	0.01	0.00	0.01	0.00	0.03
a6a6a6-4	0.00	0.00	0.00	0.01	0.00	0.02
a6a6a6-5	0.00	0.00	0.00	0.00	0.00	0.21
Total	**0.02**	**0.02**	**0.03**	**0.03**	**0.04**	**0.29**
Phenanthronaphthenes						
a6a6a6a5-1	0.00	0.00	0.00	0.00	0.00	0.00
a6a6a6a5-3	0.00	0.00	0.00	0.00	0.00	0.01
a6a6a6a5-4	0.00	0.00	0.00	0.00	0.00	0.01
a6a6a6a5-5	0.00	0.00	0.00	0.00	0.00	0.02
a6a6a6a5-6	0.00	0.00	0.00	0.00	0.00	0.01
a6a6a6a5-7	0.00	0.00	0.00	0.00	0.00	0.01
a6a6a6a5-8	0.00	0.00	0.00	0.00	0.00	0.01
Total	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.07**

APPENDIX F. SUMMARY OF ADVANCED HYDROCARBON ANALYSIS

Table F.1 Summary of results from advanced hydrocarbon analysis for FD2B

Class	PIONA/GC-FIMS Conc (% wt)	PIONA/GC-MS Conc (% wt)	n-GCxGC-FID Conc (% wt)	r-GCxGC-FID Conc (% wt)	r'-GCxGC-TOFMS/FID Conc (% wt)	ASTM D2425 Conc (% vol)	SFC (avg) Conc (% wt)	FIA (avg) Conc (% vol)
Saturates	56.69	65.2	79.01	77.78	79.37	80.20	77.3	67.9
Paraffins	13.18	35.1	43.85	47.31	43.46	47.70		
IsoParaffin	10.96		38.66	45.01	34.40			
N-paraffins	2.22		5.20	2.30	9.06			
Cycloparaffins	43.51	30.2	35.15	30.47	35.91	32.50		
Aromatics	43.16	34.5	20.99	22.22	20.62	20.00	22.7	23
Monoaromatics	37.63	28.6	16.22	17.18	15.87	8.90	17.6	
Benzenes	31.23	27.7	15.56		15.11			
Indans/tetralins	4.35	0.6	0.66		0.76			
Indenes (benzocycloalkane)	2.04	0.3						
Diaromatics	5.27	5.8	4.75	5.01	4.75	8.70	5.1	
Naphthalenes	4.18	5.0	4.52		4.75			
Acenaphthenes/biphenyls	1.09							
Acenaphthalenes/fluorenes	0.00	0.6	0.23		0.00			
Polyaromatics	0.12	0.0	0.02	0.03	0.01	2.40		
Aromatic Sulfur	0.13	0.0						
Olefins	0.15	0.3						9

Table F.2 Summary of results from advanced hydrocarbon analysis for FD2A

Class	PIONA/GC-FIMS Conc (% wt)	PIONA/GC-MS Conc (% wt)	n-GCxGC-FID Conc (% wt)	r-GCxGC-FID Conc (% wt)	n-GCxGC-TOFMS Conc (% area)	ASTM D2425 Conc (% vol)	SFC (avg) Conc (% wt)	FIA (avg) Conc (% vol)
Saturates	38.24	42.0	77.31	76.35	80.23	80.30	76.75	76.1
Paraffins	23.06	28.5	66.22	62.40	75.13	64.80		
IsoParaffin	22.18		61.68	60.48	75.00			
N-paraffins	0.87		4.54	1.92	0.13			
Cycloparaffins	15.18	13.6	11.09	13.94	5.10	15.50		
Aromatics	59.25	55.3	22.69	23.65	19.90	19.60	23.25	21.0
Monoaromatics	55.10	54.8	21.63	22.43	18.70	18.40	21.95	
Benzenes	51.82	54.7	20.82					
Indans/tetralins	2.93	0.1	0.81					
Indenes (benzocycloalkane)	0.35							
Diaromatics	3.59	0.5	1.04	1.18	1.20	1.10	1.25	
Naphthalenes	2.97	0.5	0.98					
Acenaphthenes/biphenyls	0.37							
Acenaphthalenes/fluorenes	0.26	0.1	0.06					
Polyaromatics	0.01	0.0	0.02	0.04		0.10		
Aromatic Sulfur	0.54	0.0						
Olefins	2.50	2.7						3.2

Table F.3 Summary of results from advanced hydrocarbon analysis for FD4B

Class	PIONA/GC-FIMS Conc (% wt)	PIONA/GC-MS Conc (% wt)	n-GCxGC-FID Conc (% wt)	r-GCxGC-FID Conc (% wt)	r-GCxGC-TOFMS/FID Conc (% wt)	ASTM D2425 Conc (% vol)	SFC (avg) Conc (% wt)	FIA (avg) Conc (% vol)
Saturates	53.29	56.5	57.98	57.27	58.71	63.00	58.1	40.2
Paraffins	17.80	22.2	42.88	34.42	31.50	33.30		
IsoParaffin	14.25		38.13	31.26	25.14			
N-paraffins	3.55		4.75	3.16	6.36			
Cycloparaffins	35.50	34.3	15.10	22.85	27.20	29.70		
Aromatics	46.47	43.2	42.02	42.73	41.28	37.20	41.9	42.8
Monoaromatics	41.96	38.1	35.86	36.24	35.02	20.60	35.5	
Benzenes	37.55	37.4	34.81		33.71			
Indans/tetralins	3.12	0.5	1.05		1.31			
Indenes (benzocycloalkane)	1.29	0.2						
Diaromatics	4.22	5.1	6.13	6.45	6.25	13.60	6.4	
Naphthalenes	3.37	4.5	5.84		6.25			
Acenaphthenes/biphenyls	0.86							
Acenaphthalenes/fluorenes	0.00	0.3	0.29		0.00			
Polyaromatics	0.13	0.0	0.03	0.04	0.01	3.00		
Aromatic Sulfur	0.16	0.0						
Olefins	0.26	0.4						13.4

Table F.4 Summary of results from advanced hydrocarbon analysis for FD4A

Class	PIONA/GC-FIMS Conc (% wt)	PIONA/GC-MS Conc (% wt)	n-GCxGC-FID Conc (% wt)	r-GCxGC-FID Conc (% wt)	n-GCxGC-TOFMS Conc (% area)	ASTM D2425 Conc (% vol)	SFC (avg) Conc (% wt)	FIA (avg) Conc (% vol)
Saturates	43.47	59.5	58.95	57.60	51.30	62.50	59.35	41.5
Paraffins	20.94	30.9	45.94	37.79	51.30	39.70		
IsoParaffin	19.37		42.67	35.67	49.40			
N-paraffins	1.58		3.27	2.12	1.90			
Cycloparaffins	22.52	28.6	13.01	19.81	0.00	22.80		
Aromatics	56.45	40.2	41.05	42.40	48.80	37.50	40.65	52.8
Monoaromatics	50.61	39.3	39.41	40.59	46.80	35.80	38.75	
Benzenes	47.56	39.0	38.60					
Indans/tetralins	2.92	0.3	0.82					
Indenes (benzocycloalkane)	0.13							
Diaromatics	5.47	0.9	1.59	1.73	2.00	1.50	1.95	
Naphthalenes	4.77	0.8	1.53					
Acenaphthenes/biphenyls	0.39							
Acenaphthalenes/fluorenes	0.31	0.0	0.06					
Polyaromatics	0.01	0.0	0.05	0.07		0.20		
Aromatic Sulfur	0.37	0.0						
Olefins	0.09	0.4						5.8

Table F.5 Summary of results from advanced hydrocarbon analysis for FD7B

Class	PIONA/GC-FIMS	PIONA/GC-MS	n-GCxGC-FID	r-GCxGC-FID	r-GCxGC-TOFMS/FID	ASTM D2425	SFC (avg)	FIA (avg)
	Conc (% wt)	Conc (% wt)	Conc (% wt)	Conc (% wt)	Conc (% wt)	Conc (% vol)	Conc (% wt)	Conc (% vol)
Saturates	42.40	49.8	52.94	50.82	52.98	51.00	51.7	52.4
Paraffins	27.58	33.8	42.53	39.31	43.21	40.80		
IsoParaffin	8.23		7.30	5.35	6.47			
N-paraffins	19.35		35.23	33.97	36.75			
Cycloparaffins	14.82	16.0	10.41	11.51	9.77	10.20		
Aromatics	57.02	49.4	47.06	49.18	47.01	48.50	48.3	45.0
Monoaromatics	41.62	41.3	38.87	40.35	38.07	29.80	39.4	
Benzenes	35.30	37.7	36.04		34.28			
Indans/tetralins	4.71	2.7	2.83		3.79			
Indenes (benzocycloalkane)	1.60							
Diaromatics	15.07	8.1	8.14	8.75	8.92	17.00	8.9	
Naphthalenes	11.93	7.0	7.68		8.91			
Acenaphthenes/biphenyls	0.73							
Acenaphthalenes/fluorenes	2.41	0.5	0.46		0.01			
Polyaromatics	0.12	0.0	0.05	0.08	0.01	1.70		
Aromatic Sulfur	0.21	0.0						
Olefins	0.61	0.9						2.2

Table F.6 Summary of results from advanced hydrocarbon analysis for FD7A

Class	PIONA/GC-FIMS	PIONA/GC-MS	n-GCxGC-FID	r-GCxGC-FID	n-GCxGC-TOFMS	ASTM D2425	SFC (avg)	FIA (avg)
	Conc (% wt)	Conc (% wt)	Conc (% wt)	Conc (% wt)	Conc (% area)	Conc (% vol)	Conc (% wt)	Conc (% vol)
Saturates	55.23	51.8	53.82	51.70	45.10	64.20	53.1	57
Paraffins	43.23	39.4	42.56	37.89	38.50	47.90		
IsoParaffin	6.41		10.16	5.43	12.20			
N-paraffins	36.83		32.40	32.45	26.30			
Cycloparaffins	11.99	12.4	11.27	13.81	6.60	16.30		
Aromatics	44.67	47.5	46.18	48.30	54.90	35.80	46.9	41.6
Monoaromatics	32.75	35.6	32.89	34.40	43.40	33.30	36.65	
Benzenes	27.85	29.0	27.98					
Indans/tetralins	3.98	4.5	4.92					
Indenes (benzocycloalkane)	0.93							
Diaromatics	11.91	10.7	12.94	13.24	11.50	2.50	10.25	
Naphthalenes	5.40	4.1	12.43					
Acenaphthenes/biphenyls	6.25							
Acenaphthalenes/fluorenes	0.27	0.7	0.50					
Polyaromatics	0.00	0.3	0.35	0.66		0.00		
Aromatic Sulfur	0.01	1.0						
Olefins	0.10	0.7						2.5