CRC Report No. FACE-1

CHEMICAL AND PHYSICAL PROPERTIES OF THE FUELS FOR ADVANCED COMBUSTION ENGINES (FACE) RESEARCH DIESEL FUELS

July 2010

COORDINATING RESEARCH COUNCIL, INC.
3650 MANSELL ROAD·SUITE 140·ALPHARETTA, GA 30022

The Coordinating Research Council, Inc. (CRC) is a non-profit corporation supported by the petroleum and automotive equipment industries. CRC operates through the committees made up of technical experts from industry and government who voluntarily participate. The four main areas of research within CRC are : air pollution (atmospheric and engineering studies); aviation fuels, lubricants, and equipment performance, heavy-duty vehicle fuels, lubricants, and equipment performance (e.g., diesel trucks); and light-duty vehicle fuels, lubricants, and equipment performance (e.g., passenger cars). CRC's function is to provide the mechanism for joint research conducted by the two industries that will help in determining the optimum combination of petroleum products and automotive equipment. CRC's work is limited to research that is mutually beneficial to the two industries involved, and all information is available to the public.

CRC makes no warranty expressed or implied on the application of information contained in this report. In formulating and approving reports, the appropriate committee of the Coordinating Research Council, Inc. has not investigated or considered patents which may apply to the subject matter. Prospective users of the report are responsible for protecting themselves against liability for infringement of patents.

Coordinating Research Council

CHEMICAL AND PHYSICAL PROPERTIES OF THE FUELS FOR ADVANCED COMBUSTION ENGINES (FACE) RESEARCH DIESEL FUELS

Mikhail Alnajjar,* Bill Cannella,[†] Heather Dettman,[‡] Craig Fairbridge,[‡] James Franz,*
Tom Gallant,* Rafal Gieleciak,[‡] Darcy Hager,[‡] Cecile Lay,[‡] Sam Lewis,[§]
Matthew Ratcliff,** Scott Sluder,[§] John Storey,[§] Haiyan Yin,[‡] Brad Zigler**

*Pacific Northwest National Laboratory
[†]Chevron
[‡]Natural Resources Canada, CanmetENERGY
[§]Oak Ridge National Laboratory
**National Renewable Energy Laboratory

Date Published: July 2010

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
managed by
UT-BATTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

Page

FIGURES

TABLES

ACRONYMS

1-D	one-dimensional
2-D	two-dimensional
ASTM International	Formerly the American Society for Testing and Materials
CA	certificate of analysis
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
EGR	exhaust gas recirculation
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 FD1A)
FIA	fluorescent indicator adsorption
FID	flame ionization detector
FIMS	field ionization mass spectrometry
GC	gas chromatography/chromatographic
HCCI	homogeneous charge compression ignition
IBP	initial boiling point
ID	ignition delay
IQT	ignition quality tester
LC	liquid chromatography
MS	mass spectrometry/spectrometric
n-	normal (as in normal paraffins)
NCUT	National Centre for Upgrading Technology
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser enhancement
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
QSPR	quantitative structure-property relationships
RT	retention time
SFC	supercritical fluid chromatography
SOAP	saturates, olefins, aromatics, and polars
SPE	solid phase extraction
SwRI	Southwest Research Institute
TOF	time-of-flight
WSD	wear scar diameter

ACKNOWLEDGMENTS

The work in this report was conducted and coordinated by a fuels characterization subgroup of CRC's AVFL Committee FACE Working Group. CRC FACE WG members of the subgroup included: Bill Cannella, Craig Fairbridge, Jim Franz, Tom Gallant, Matt Ratcliff, Scott Sluder, and Brad Zigler. These FACE WG members also enlisted the efforts of others in their organizations, who are also listed as co-authors of the report. The NREL co-authors also wish to acknowledge the contributions of former NREL colleagues Dr. Joshua Taylor and Dr. Colleen Stroud Alexander, who performed initial experiments and analysis related to the IQT work.

The authors acknowledge the extensive efforts of ORNL's editorial staff, particularly Vj Ewing, related to editing and consistent formatting of the various sections of the report.

The time and testing expenses of the authors were largely funded by their respective organizations. Members of the U.S. Department of Energy National Laboratories (NREL, ORNL, and PNNL) used funding from their budgets provided by U.S. DOE Vehicle Technologies Program. Members of National Resources Canada and the National Centre for Upgrading Technology used funding from their budgets provided by the Government of Canada's interdepartmental Program of Energy Research and Development, the Alberta Research Council, and the Alberta Energy Research Institute.

EXECUTIVE SUMMARY

This report provides detailed results from a variety of standard ASTM International-type analyses and advanced characterization techniques conducted to measure the chemical and physical properties of a matrix of diesel test fuels known as the Fuels for Advanced Combustion Engines (FACE) diesel fuels. The work was coordinated by a fuels characterization subgroup of the Coordinating Research Council's (CRC's) Advanced Vehicle / Fuel / Lubricants Committee's FACE Working Group.

The FACE diesel fuels matrix consists of nine fuels designed around three properties of primary importance to the performance of advanced combustion engines: ignition quality (represented by cetane number); fuel chemistry (represented by aromatics volume fraction); and volatility (represented by distillation T90). A 2 × 2 × 2 matrix of eight diesel fuels with target cetane numbers of 30 and 55, aromatics volumetric contents of 20 and 45%, and T90s of 270 and 340°C was built around a center-point fuel with target cetane number of 42.5, aromatics content of 32.5%, and T90 of 305°C to represent an average marketplace diesel fuel. The CRC FACE Working Group designed this matrix of research fuels and made arrangements for manufacture and sale by a commercial fuels blender to enable advanced combustion researchers to compare results across different laboratories and test platforms using the same set of fuels for consistency.

The goal of the current project was to characterize as fully as possible the chemical and physical properties of the FACE diesel fuels and to make that information available to the advanced combustion research and development (R&D) community to enable selection of standardized test fuels for their programs and correlation of test results to fuel composition and properties.

In support of this project, standard ASTM tests were conducted at several different laboratories to measure the following properties: cetane number [measured by engine and ignition quality tester (IQT) methods] and 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. Tables showing the results of the ASTM tests are included in the report and posted on the CRC Web site. Results of those ASTM analyses indicate the following.

- For most of the FACE diesel fuels, the fuels blender was able to meet the targeted cetane number, aromatics content, and T90 value.
- As expected, the greatest deviation between target and actual values occurred for the two high cetane, high aromatic fuels (FD7A and FD8A) as aromatic compounds typically have lower cetane numbers.
- The shape of the distillation curves was reasonable for most of the fuels, but the curve for fuel FD2A was much flatter over most of the distillation range coupled with a steeper rise toward the end to meet the T90 target.
- Although derived cetane numbers measured by the IQT instrument agreed well with the engine measured values for the fuels having mid-to-high cetane numbers (43–55), the IQT values were up to 6.6 points higher for the fuels having a low nominal cetane number of 30 (FD1A–FD4A). A plausible explanation is that the established ASTM equations for correlating the engine and IQT test results were developed primarily for marketplace-type fuels having cetane numbers in the 40–60 range.
- Repeatability and reproducibility of some of the other ASTM test results were a bit poorer than typically obtained with commercial fuels. These findings are not surprising given that the target

design properties of some of the FACE diesel fuels (and hence their formulations) fall outside the envelope of commercial fuel properties for which the ASTM tests were developed.

In addition to the standard ASTM tests, several emerging advanced characterization techniques were used to obtain more detailed chemical and structural composition information for the fuels. This project was able to leverage from and piggyback on an existing collaboration between the U.S. Department of Energy (Oak Ridge National Laboratory, Pacific Northwest National Laboratory, and the National Renewable Energy Laboratory) and National Resources Canada National Centre for Upgrading Technology formed to characterize complex fuels such as those derived from oil sands and oil shales. The techniques included gas chromatography-field ionization mass spectrometry coupled with paraffins, isoparaffins, olefins, naphthenes, and aromatics analysis and detailed hydrocarbon analysis; one- and two-dimensional (2-D) gas chromatography-mass spectrometry; 2-D gas chromatography using a flame ionization detector; and nuclear magnetic resonance (NMR). The extensive classification that was done for each of the FACE diesel fuels should provide very useful information to help advanced combustion researchers select fuels for testing and to correlate combustion results to chemical and structural composition. In addition to tables and bar charts of the detailed results, the report contains bubble plots that visually show the distribution of compounds of the various hydrocarbon classes versus carbon number and boiling point. An additional use of the NMR information was presented in which sets of five model compounds were constructed as surrogate-type representations of three of the FACE diesel fuels (FD3A, FD8A, FD9A).

Key findings from the advanced characterization analyses include the following.

- The fuels predominantly contain n-paraffins, isoparaffins, cycloparaffins, and aromatics, with little-to-no olefins. This is consistent with commercial diesel fuels. Many, but not all, of the fuels have a normal distribution of n-paraffins peaking at about C14–C15, similar to commercial diesel fuels. Fuels FD2A and FD4A show the greatest deviation from this.
- The low cetane number fuels (FD1A–FD4A) contain a relatively large amount (>20%) of light (C8–C10) monoaromatics, which is not typical of commercial diesel fuels.
- Some of the fuels (most notably FD7A and FD8A) contain diphenylalkanes, which are not typically found in commercial diesel fuels but have been used previously in some diesel test fuels.
- The compositional differences between some of the fuels in this matrix of R&D fuels versus commercial diesel fuels are not surprising given the trade-offs that are required to formulate fuels having target properties beyond the normal range for commercial fuels.
- The advanced characterization techniques show great promise for speciating distillate fuels into individual components; however, identification and quantification (in terms of volume or weight percent) of each component requires extensive calibration with known standards.
- The ^{13}C and ^{1}H NMR analyses complement the detailed hydrocarbon speciation results of the other techniques by providing information about the amounts of the various types of carbon-carbon and carbon-hydrogen bonds. This type of information may be more relevant than compositional information for some aspects of combustion, such as soot formation.

We recommend that advanced combustion researchers use these well-characterized FACE diesel fuels in their test programs to enable comparison of results across different laboratories and test platforms. In addition, we recommend that researchers characterize as fully as possible the chemical and physical properties of other fuels that they test, using the standard ASTM-type analyses and advanced characterization methods used in this project.

1. BACKGROUND

This is an account of the results of standard ASTM International-type analyses and advanced characterization techniques conducted to measure the chemical and physical properties of a matrix of diesel test fuels known as the Fuels for Advanced Combustion Engines (FACE) diesel fuels. It also provides information about the capabilities and state of implementation of the advanced characterization techniques.

The FACE diesel fuels were blended based on target values established by the Coordinating Research Council (CRC) Advanced Vehicle / Fuel / Lubricants Committee's FACE Working Group. The mission of the FACE Working Group is to recommend sets of test fuels well-suited for research so that researchers evaluating advanced combustion systems can compare results from different laboratories using the same sets of fuels for consistency. The group determined that three fuel properties were of primary importance to the performance of advanced combustion engines. These were a measure of ignition quality [cetane number (CN)], a measure of chemistry (volume fraction of aromatics), and a measure of volatility (T_{90}). Target levels for these three variables were selected. To keep the total number of fuels within reason, two levels of each of the design variables were targeted to form the corners of a cubic design space. The target levels selected were CN of 30 and 55; T_{90} of 270 and 340°C; and aromatics content of 20 and 45%. A fuel was also targeted near the center of the design space to represent average marketplace values of the design variables in the fuel matrix. Target properties for this fuel were: CN of 42.5, T_{90} of 305°C, and aromatics content of 32.5%. This resulted in a matrix containing nine target fuels. A graphical representation of these fuels is shown in Figure 1.1. Two other constraints were imposed on all of the fuels: sulfur content was capped at 15 parts per million (ppm) by weight and olefin content was capped at 4% by volume. While the working group recognized the importance of other design variables (notably other aspects of fuel chemistry) this matrix neglected those variables in the interest of keeping the number of fuels to a manageable size.

l

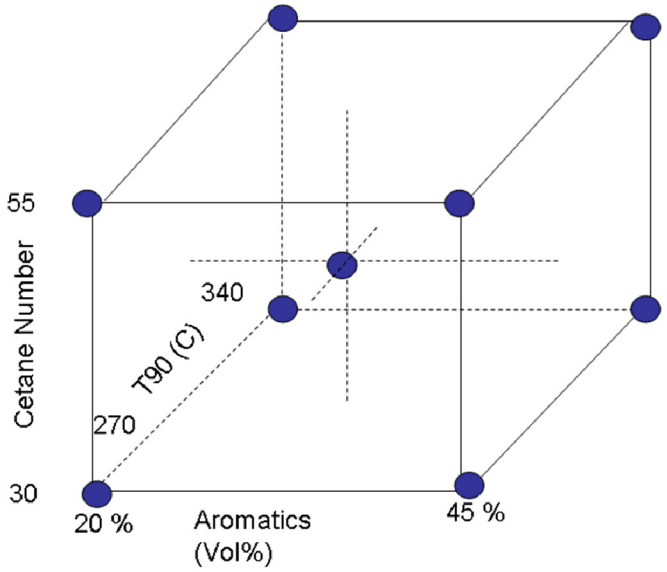

Figure 1.1. Graphical representation of the FACE diesel fuel design space.

The fuels were manufactured and are being sold by Chevron Phillips Chemical Company (CPChem). In general, the fuels were successfully formulated to match the target values of the design variables.

However, difficulty was encountered with two fuels that resulted in the need to accept values of the design variables that were different from the target values. These two fuels were the high-cetane, high-aromatic, and low- and high-T90 fuels (FD7A* and FD8A, respectively). Due to the desired high aromatic content, the blender experienced difficulties simultaneously achieving the correct values for the other design variables. Actual values of these variables will be discussed in more detail in the following sections of this report.

This report focuses on both the chemical and physical properties of the first production run of the FACE fuel set and the implementation of emerging state-of-the-art analytical tools for fuel analysis. The motivation behind the latter was to assess and take advantage of the capabilities of these new tools by leveraging from an existing U.S. Department of Energy (DOE) and National Resources Canada National Centre for Upgrading Technology (NCUT) collaboration focused on more complex fuels, such as those derived from oil sands and oil shales. Another motivation was to come up with a tractable parameter set, based on chemical composition, to relate to observed combustion behavior or physical properties such as lubricity. By having well-characterized chemistry for the fuels, it may be possible to develop predictive models for combustion behavior in both conventional and advanced combustion modes that could then be applied to much more complex fuels streams from nontraditional sources.

Several organizations contributed analyses that are included in this report. Each organization used different techniques to analyze the fuel set, and thus each analysis offers a different perspective on the makeup of the fuels. The report is organized into sections based on the different analytical techniques, with later sections focused on results drawn from combinations of the different techniques.

- Section 2 covers the traditional ASTM-type diesel fuel analyses and makes comparisons between fuels and the actual and targeted values.
- Section 3 covers ignition tests/characteristics of the FACE diesel fuels.
- Section 4 covers results from analysis by gas chromatography-mass spectrometry (GC-MS).
- Section 5 discusses results obtained from a two-dimensional (2-D) GC-MS (2-D GC-MS) technique that enhances separation of polar and nonpolar fractions.
- Section 6 discusses characterizing the fuels using gas chromatography-field ionization mass spectrometry (GC-FIMS).
- Section 7 discusses analyzing the fuels for paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) using ASTM D5443, a multidimensional gas chromatographic technique for hydrocarbons that boil below 200°C.
- Section 8 discusses the results of saturate-olefin-aromatic-polar (SOAP) solid phase extraction (SPE) analysis for hydrocarbons that boil above 200°C.
- Section 9 discusses the results of characterization by a combination of methods.
- Section 10 discusses detailed hydrocarbon analysis (DHA) of the nine FACE fuels.
- Section 11 covers characterization of the FACE fuels by nuclear magnetic resonance (NMR) spectroscopy.
- Section 12 compares the results from the various test methods.

*The FACE blends reported on in this report are referred to by “FD” numbers, for “FACE diesel.”

2. RESULTS FROM ASTM STANDARD TESTS

In this section we discuss the results of standardized ASTM tests for fuel characterization. Southwest Research Institute (SwRI) provided one set of results for these analyses, NCUT provided benchmark data for some of these analyses, and we also included the results provided on the CPChem certificates of analysis (CAs) for the drums of fuel purchased by members. It is worth noting that the formulation of the FACE diesel fuels sometimes falls outside of the envelope of fuel properties for which the ASTM tests were originally designed. This discrepancy likely leads to larger levels of variation in the results both from laboratory-to-laboratory and test-to-test than is typically experienced with marketplace fuels.

The following sections discuss the results for the ASTM tests; tabular data for all tests and all fuels are located in Table 2.2 at the end of this section and posted on the CRC Web site.

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

The CN for each fuel was measured by ASTM D613,[1] the engine-based determination for CN. Data from this test were available from both SwRI and the CPChem CAs. The values in the results from these two sources, summarized in Figure 2.1, differ by 1.5 units or less. Target values are indicated by the dashed lines across each group of columns. The low-cetane fuels (FD1A–FD4A) have CNs very close to the target value of 30, with some variation in the results from a D613 test expected at such a low CN. The values for fuels FD5A and FD6A were also very close to the target value of 55 for the high-cetane level. However, the values for fuels FD7A and FD8A (about 45 and 50, respectively) were significantly low compared to the target value of 55. This was accepted in order to preserve better agreement between the target and actual values of the two other design variables for these two fuels. FD9A, the center-point fuel, was produced on-target for a CN of 43.

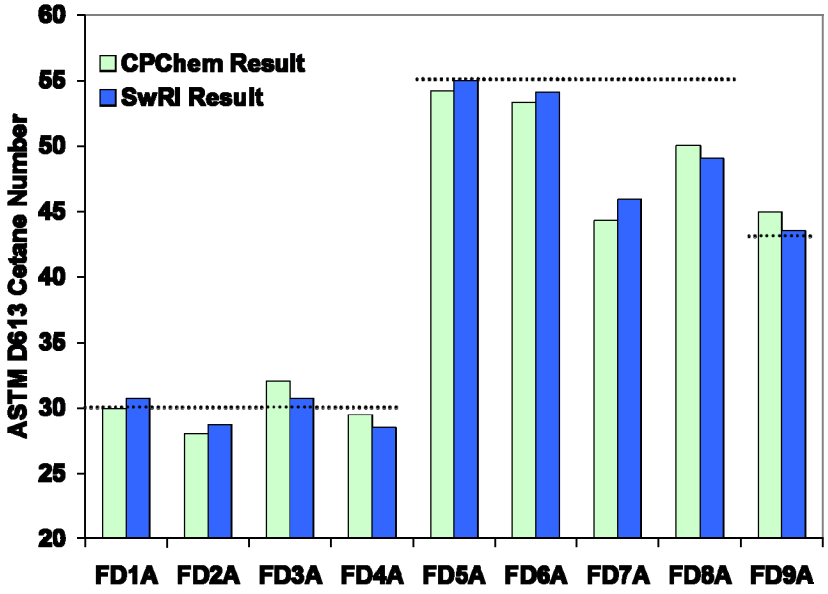

Figure 2.1. Fuel cetane number results from ASTM D613 tests.

The aromatic content for each fuel was determined by ASTM D1319.[2] Results from all three reporting organizations (SwRI, NCUT, and CPChem) as well as target values are shown in Figure 2.2. Target values are again indicated by dashed lines across each group of columns. For several of the fuels (FD4A, FD8A, and FD9A) the differences between results from different organizations were higher than the expected reproducibility value for this ASTM test, so retests were conducted by SwRI and NCUT; in these instances the values shown are the average of the two results. As mentioned above, this was not unexpected since these formulations fall somewhat outside the envelope of conventional fuel formulations for which the ASTM tests were designed. In general the low-aromatic fuels (FD1A, FD2A, FD5A, and FD6A) were all formulated very close to the target value of 20% aromatics. Of the high-aromatic fuels having a target of 45% aromatics, the measured aromatics content of fuels FD3A and FD4A were at or slightly above the target aromatic content while fuels FD7A and FD8A were formulated below the target aromatic content. FD9A was formulated at or slightly above the target aromatic content.

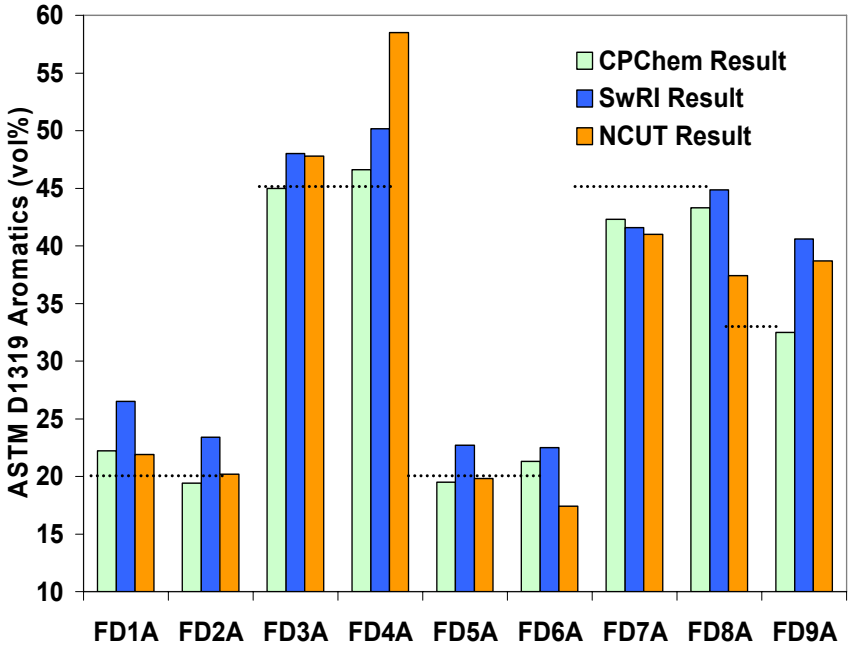

Figure 2.2. Fuel aromatic content results from ASTM D1319 tests.

T_{90} values were measured by ASTM D86.[3] Results from both CPChem and SwRI are shown in Figure 2.3. In general there is very good agreement in the results from both organizations, with noteworthy differences only with fuels FD1A and FD2A. Nevertheless, all nine fuels were formulated with the T_{90} value within 5–10 degrees of the target, with a separation between the high and low target of 126°F.

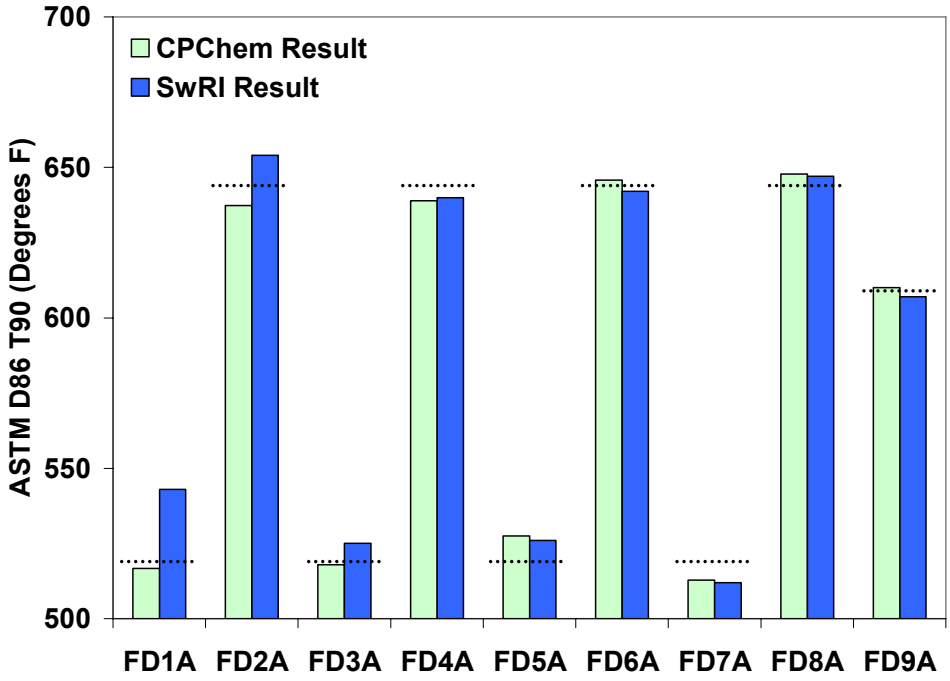

Figure 2.3. Fuel 90% recovery temperature results from ASTM D86 distillation tests.

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, and complete distillation curves of the nine fuels. These are summarized below.

2.2.1 Specific Gravity by ASTM 4052[4]

Tabulated values of the specific gravity are included in Table 2.2. There was good agreement in the results from all three organizations for all fuels. The maximum percent difference between the results from the three organizations for any fuel was 0.14%. Taking the average of the results from all three organizations, the minimum specific gravity was 0.8034 (FD2A) and the maximum was 0.8687 (FD8A). Specific gravity appeared to have a dependence on the aromatic content, as three of the four low-aromatic fuels had the lowest values of specific gravity, while the high-aromatic fuels tended to have higher specific gravities. Because of the breadth of fuel property targets that were designed, the specific gravity results for some of these research fuels exhibited values that were outside the range of the specification of 0.84–0.855 for U.S. number 2 diesel fuel. The center-point fuel (FD9A) that was designed as a near-marketplace-average fuel did fall within the limits of this specification.

2.2.2 Kinematic Viscosity by ASTM D445[5]

Measurements were carried out at 40°C by both SwRI and NCUT, and in general the results agreed well between the two laboratories. There were considerable differences in the kinematic viscosities of the various fuel formulations. The minimum kinematic viscosity was 1.319 cSt (FD3A) and the maximum was 3.218 cSt (FD8A). The combination of high-cetane and high-T_{90} values appeared to produce fuels that exhibited the highest values of kinematic viscosity. The wide range of fuel property

target values again resulted in a wider range of viscosities for this matrix of research fuels than the specification range for U.S. number 2 diesel fuel (2.0–3.0 cSt).

2.2.3 Cloud Point by ASTM D2500[6]

ASTM D2500 data were provided by both SwRI and NCUT. The laboratory-to-laboratory results agreed within a few degrees Celsius, with outliers for FD2A and FD4A, both of which are low-cetane, high-T_{90} fuels. All nine fuels had cloud points well below zero, with actual values spanning the range from −19.5 to −59°C (−3 to −74°F). A correlation between T_{90} and cloud point is not surprising; however, the variation in cloud point between high- and low-T_{90} blends was more pronounced for the low-cetane fuels than for the high-cetane fuels. Interestingly, the low-cetane fuels with high-T_{90} levels had the lowest cloud points. A dependence on the aromatic content was evident in the high-cetane fuels, though this had only a small effect. These trends may be explained by differences in fuel formulation and will be explored further in later sections of this report.

2.2.4 Flash Point by ASTM D93[7]

Measurements were made for all nine fuels at SwRI, while the CPChem CAs included data for some of the fuels. Where data were available from both sources, the average value is reported here. All nine fuels had flash points higher than 54°C (130°F), which is also the minimum specification for U.S. number 2 diesel fuel. In general, the low-cetane fuels had lower flash points than the high-cetane fuels. Of the low-cetane fuels, those with high aromatics tended to have slightly lower flash points; this trend was not evident for the high-cetane fuels.

2.2.5 Net Heat of Combustion by ASTM D240[8]

All data for this characteristic were obtained from SwRI. All nine fuels had values that were within 2.4% difference of the average. The maximum value was 18,553.1 Btu/lb (FD2A); the minimum was 18,120 Btu/lb (FD3A). There were no obvious correlations with the design parameters.

2.2.6 Cetane Index by ASTM D976[9]

CN was selected as a design variable; results for CN were discussed in Section 2.1. Cetane index was also characterized, and in this case all data were again obtained from SwRI. The maximum result was 52.1 (FD6A) and the minimum was 31.2 (FD3A). In some cases there was little difference in the cetane index results from a high-cetane and a low-cetane fuel. Nearly all fuels exhibited significant differences between their CN and cetane index results. This is not too surprising since D976 was primarily developed for and is applicable to straight run fuels, catalytically cracked stocks, and their blends, not for the special blends of the FACE diesel fuels matrix.

2.2.7 Distillation by ASTM D86 and D2887

ASTM D86[3] data were obtained from both CPChem and SwRI. Additionally, NCUT provided simulated distillation data (ASTM D2887[10]). These data generally showed the same trends as the D86 data. Special effort was required to complete D86 tests satisfactorily for FD1A and FD2A in particular. This is likely due to a large amount of narrow-boiling material in the first part of the distillation of the fuel and will be discussed further in the sections of this report detailing the chemistry of the fuels. Figure 2.4 shows the SwRI distillation results for the low-T_{90} fuels (FD1A, FD3A, FD5A, and FD7A) plus the center-point fuel (FD9A). The results for the high-T_{90} fuels (FD2A, FD4A, FD6A, and FD8A) are shown in Figure 2.5 along with those for the center-point fuel. A few of the fuels (notably FD1A and FD2A) exhibited shapes that were different from the others

with a very flat profile over a good portion of the curve and then a steep rise. This behavior is a result of a trade-off in formulating fuels with properties outside of the normal range for diesel fuels. In general, the majority of the fuel distillation curves for each of the low-T_{90} fuels fell below that of the center-point fuel. The results were mixed for the high-T_{90} fuels, however. Two of the high-T_{90} fuels (FD6A and FD8A, the high-cetane fuels) exhibited distillation curves that were higher than that of the center-point fuel. Two others (FD2A and FD4A, the low-cetane fuels) exhibited curves that had significant fractions below that of the center-point fuel. This was particularly evident for FD2A.

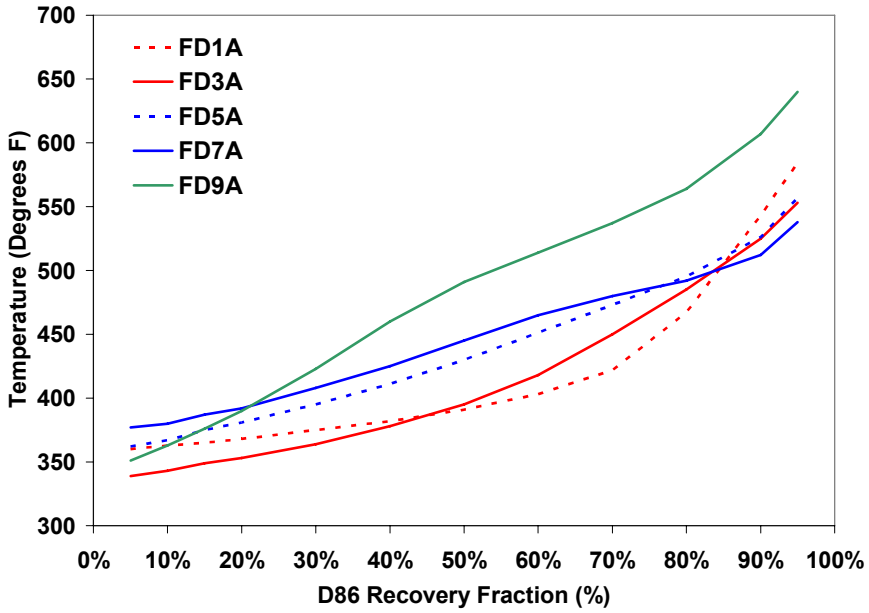

Figure 2.4. Distillation curves for the low-T_{90} fuels using ASTM D86.

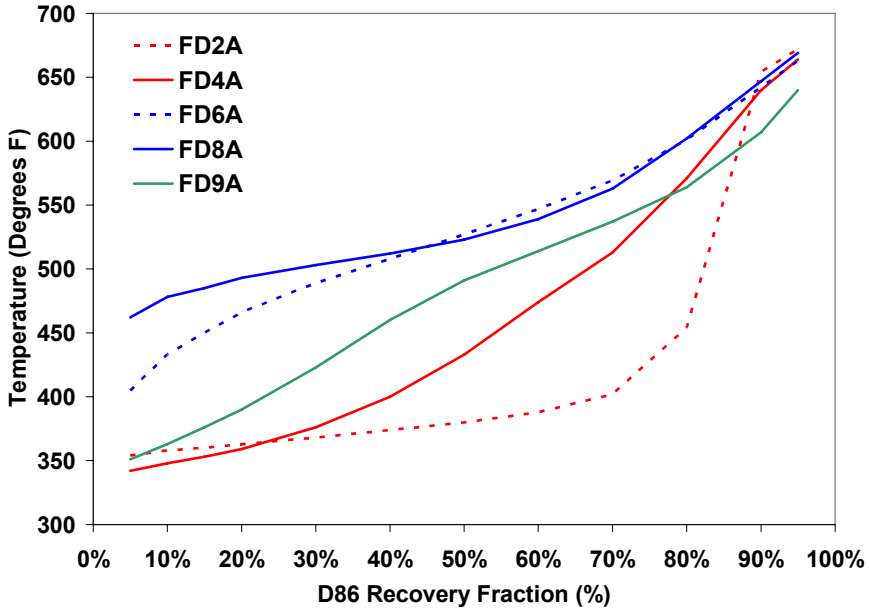

Figure 2.5. Distillation curves for the high-T_{90} fuels using ASTM D86.

ASTM D2887[10] covers the determination of the boiling point distribution of petroleum products for samples boiling between 55°C (100°F) and 538°C (1,000°F). The boiling range distribution determination by distillation is simulated by the use of GC (in this case, an Analytical Control Systems, Inc., simulated distillation custom analyzer based on the HP-6890 series), where a nonpolar capillary column is used to elute the hydrocarbon 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 hydrocarbons covering the boiling range expected in the sample. Simulated distillation data for the nine fuels showed similar curves to the D86[3] data. The data are presented in Figures 2.6 and 2.7 for the low-T_{90} and high-T_{90} fuels, respectively. The nature of the method allows for a smoother plot of temperature versus recovery fraction than D86, with the recovery fraction given as mass percent. However, it is clear that some of the fuels exhibit a step-change due to the trade-off in formulating diesel fuels outside of the normal range of fuel properties, as was described in the D86 section. The raw simulated distillation data are given in Appendix A. The T_{90} point is derived easily from D2887 data and is shown in Table 2.1. NCUT uses a number of gas chromatograph-based analytical methods to derive hydrocarbon type distributions in middle distillates. Many of the methods are reported separately for hydrocarbons boiling below and above 200°C (392°F), and the simulated distillation recovery fraction at 200°C (392°F) is used in the quantification of those hydrocarbon types (i.e., below and above 200°C). These data are also shown in Table 2.1. Clearly some samples such as FD1A and FD2A have a large proportion of hydrocarbons boiling below 200°C, and some, such as FD6A and FD8A, have a very small proportion boiling below 200°C.

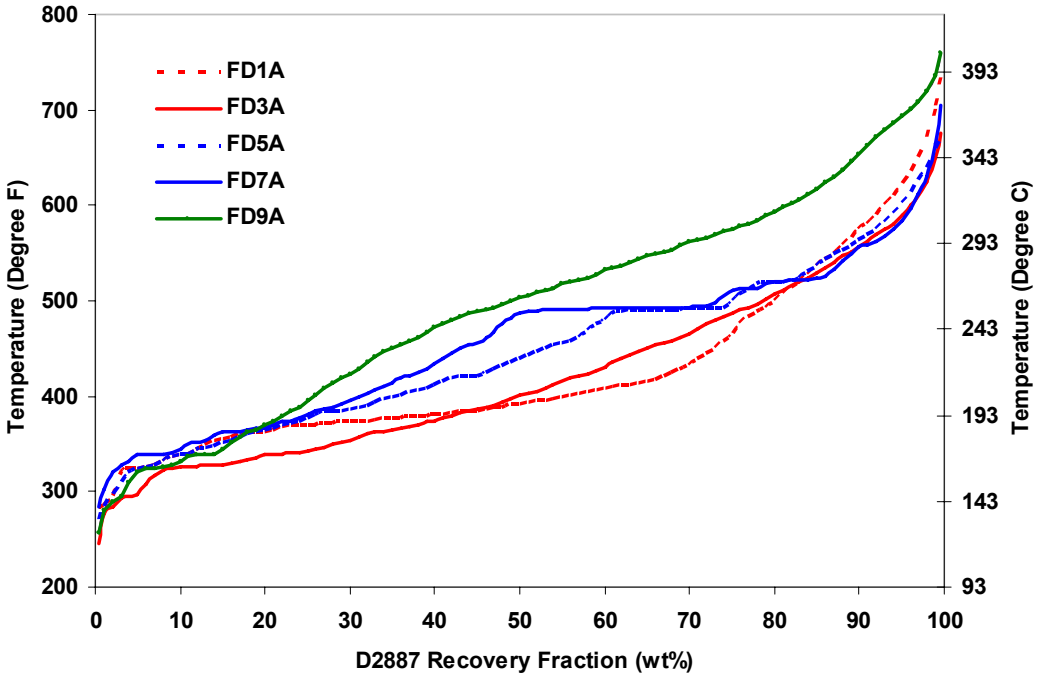

Figure 2.6. Low-T_{90} FACE diesel sample simulated distillation plots.

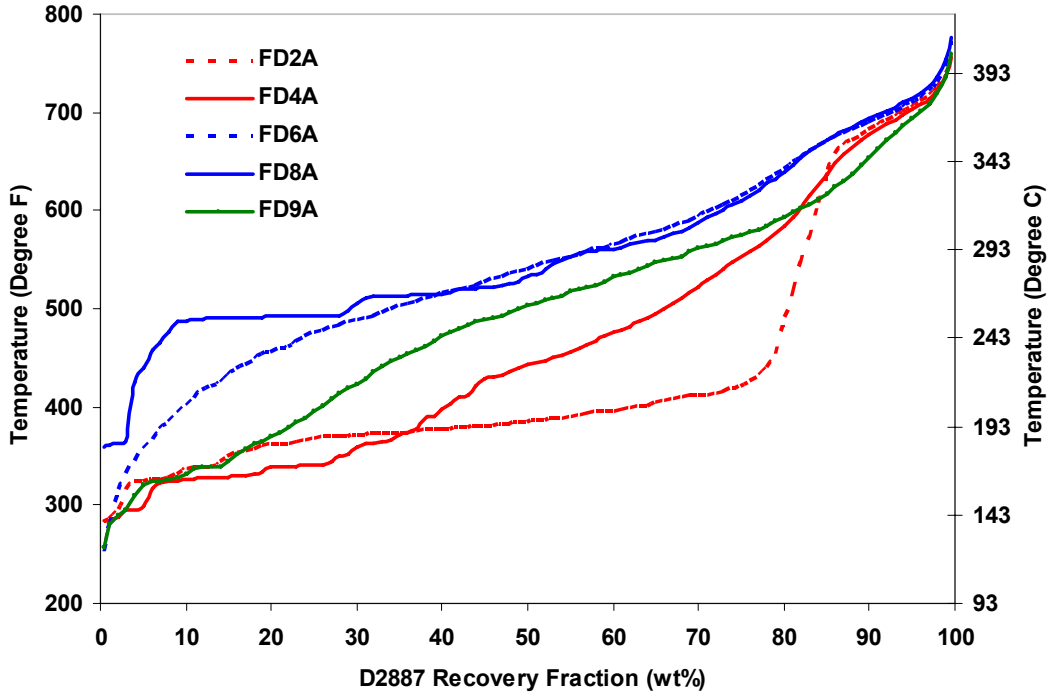

Figure 2.7. High-T_{90} FACE diesel sample simulated distillation plots.

Table 2.1. ASTM D2887 T_{90} Values and Fraction Recovery

Parameter	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
T_{90} target	270°C	340°C	270°C	340°C	270°C	340°C	270°C	340°C	305°C
	518°F	644°F	518°F	644°F	518°F	644°F	518°F	644°F	581°F
T_{90} measured	301°C	362°C	291°C	359°C	296°C	366°C	291°C	368°C	346°C
	575°F	684°F	556°F	678°F	564°F	690°F	556°F	694°F	654°F
Recovery Fraction up to 200°C (392°F) (wt %)	49.7	55.8	47.5	39.3	32.5	8.8	29.2	3.5	24.4
Recovery Fraction at more than 200°C (392°F) (wt %)	50.3	44.2	52.5	60.7	67.5	91.2	70.8	96.5	75.6

2.2.8 Lubricity by ASTM D6079[11]

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, ASTM developed what is known as the high frequency reciprocating rig test method (D6079) to determine lubricity. In this method 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. FACE fuel lubricity results, using ASTM D6079, are included in Table 2.2.

Only FD8A with a value of 492 μm had a WSD that met the ASTM U.S. No.1 and No.2 diesel specifications of 520 μm or less. The European EN 590 diesel specifications are even lower, with a maximum of 460 μm. The WSDs for the other fuels ranged from 571 μm for FD6A to 687 μm for FD5A. The fuels with the lowest cetane numbers (FD1A–FD4A) tended to provide poorer lubricity (larger WSDs) than the fuels with the highest cetane numbers. The exception appears to be FD5A, which has high cetane number but poor lubricity.

Based on the results of ASTM D6079, users of the FACE diesel fuels may want to consider adding a lubricity additive when performing engine tests.

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 MS. In addition, the carbon, hydrogen, nitrogen, and sulfur contents and bromine number were measured.

2.3.1 Hydrocarbons by ASTM D1319 (Fluorescent Indicator Adsorption)

ASTM D1319[2] characterizes the fuel composition in terms of three classes of hydrocarbons: saturates (also known as alkanes or paraffins), aromatics, and olefins (or alkenes). Results are expressed in volume percent. In developing the FACE diesel fuels matrix, aromatic content was selected as one of the design variables; olefin content was capped at 4% by volume. The saturates category includes not only normal (or straight chain) alkanes, but also isoparaffins (or branched alkanes) and cycloparaffins (or fully-saturated ring structures). Results were obtained by NCUT, SwRI, and CPChem. In general the results from the three organizations agreed reasonably well. Noteworthy exceptions to this were FD4A, FD8A, and FD9A, even after a repeat set of measurements for these fuels by NCUT and SwRI. In these cases the maximum and minimum reported values for aromatics differed by as much as 12%, with substantial disagreement in saturates and olefins content. The SwRI results (including a retest in each such case) reported olefins in excess of the 4% cap for fuels FD4A, FD6A, and FD9A, though results from both NCUT and CPChem found these fuels to have less than 4% olefins. Once again this demonstrates that the ASTM methods were designed to characterize more conventional fuels. Figure 2.8 shows the average results from analysis of each fuel using ASTM D1319.

Many compounds that can be present in fuel exhibit characteristics of more than one of these hydrocarbon categories. A good example of this is tetralin (also known as tetrahydronapthalene or benzocyclohexane). Tetralin has a naphthalene aromatic structure in which two of the double-bonds have been saturated. The resulting molecule has the appearance of a benzene ring structure fused to a cyclohexane ring structure. Oil-sands-derived blending streams are often high in these types of molecules because of the nature of the bitumen and the hydrotreating process used to create synthetic crude oil. Tetralin could be identified either as an aromatic or a saturate, depending upon the characterization technique used. For ASTM D1319, the separation of these classes of compounds is dependent upon the affinity of adsorption of the compounds to a silica gel. This may introduce some ambiguity into the interpretation of results when compounds such as tetralin or alkyl-substituted tetralins are included in the fuel formulation. For this reason, other less-common ASTM methods were additionally employed to provide more information about the hydrocarbon makeup of the fuels.

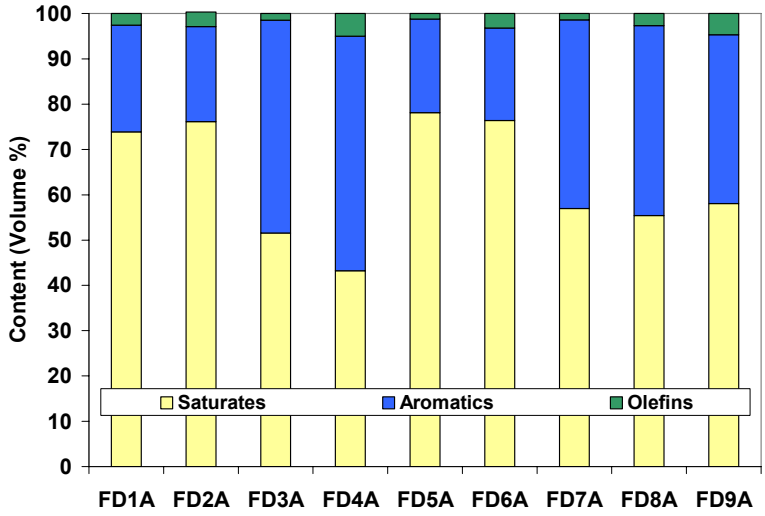

Figure 2.8. Hydrocarbons by fluorescent indicator absorption (ASTM D1319 results).

2.3.2 Aromatics by ASTM D5186 (Supercritical Fluid Chromatography)

ASTM D5186[12] has been purported to be statistically more precise than D1319 for determination of aromatic content of diesel fuels. This method separates hydrocarbons into three categories: nonaromatics, monoaromatics, and polynuclear aromatics. Results from ASTM D5186 are expressed in mass percent. The results from NCUT and SwRI agreed very well for all of the fuels; this is in contrast to a significant difference in the D1319 results observed for some fuels. Figure 2.9 shows the average results for each fuel from analysis by D5186. This leads to characterization of higher-boiling point aromatic compounds (such as diphenyl compounds) as polynuclear aromatic compounds. This is likely the reason that FD7A and FD8A exhibited high reported levels of polynuclear aromatics compared with the other fuels.

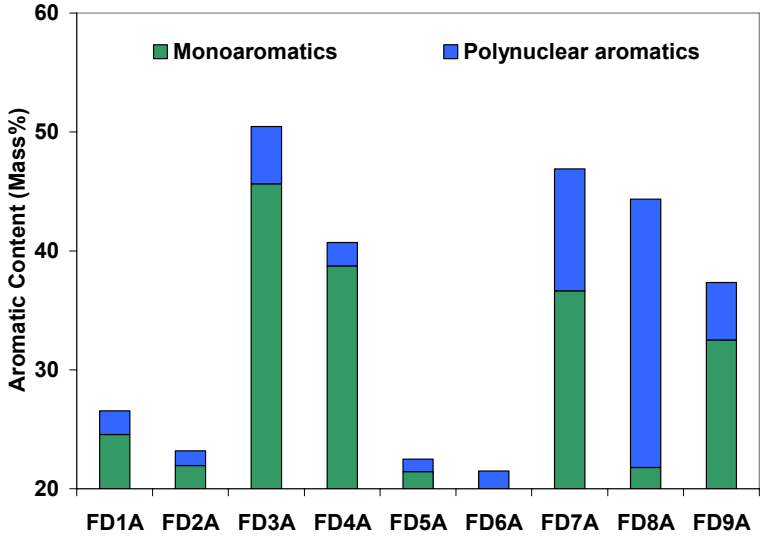

Figure 2.9. Aromatics by supercritical fluid chromatography (ASTM D5186 results).

2.3.3 Hydrocarbons by ASTM D2425[13] (Mass Spectrometry)

This method determines the hydrocarbon mass percent content of the fuel with considerably more specificity than ASTM D1319 or D5186. Figure 2.10 shows the saturates. Isoparaffins and normal paraffins (n-paraffins) are not separated by this method and are reported together as paraffins. The cycloparaffins are separated and are shown according to the number of rings in the molecular structure. Generally the results show that the saturates present in most of the FACE diesel fuels are n-paraffins, isoparaffins, and monocycloparaffins. Only fuels FD6A and FD8A were reported to also contain dicyloparaffins or tricycloparaffins. The ratio of cycloparaffins to n-paraffins and isoparaffins varied considerably.

Figure 2.11 shows the alkylbenzenes, indans/tetralins, and indenes. Figure 2.12 shows the polynuclear aromatics. Tricyclic polynuclear aromatics can be determined by this method but are not shown in the figure because none of the fuels were reported to contain these compounds.

The aromatics present in the fuels were composed primarily of alkylbenzenes. With the exception of fuel FD8A, naphthalene, alkylnapthalenes, and higher polycyclic aromatic hydrocarbon (PAH) compounds were present only at small levels, less than 3% of the fuel by mass. Alkylbenzenes made up the remainder of the aromatic content. Some fuels contained 5–8% by mass of indans/tetralins, and indenes were generally only present at small levels. FD8A had only a small amount of alkylbenzenes, and was reported to have a very high content of acenapthenes (biphenyl molecules).

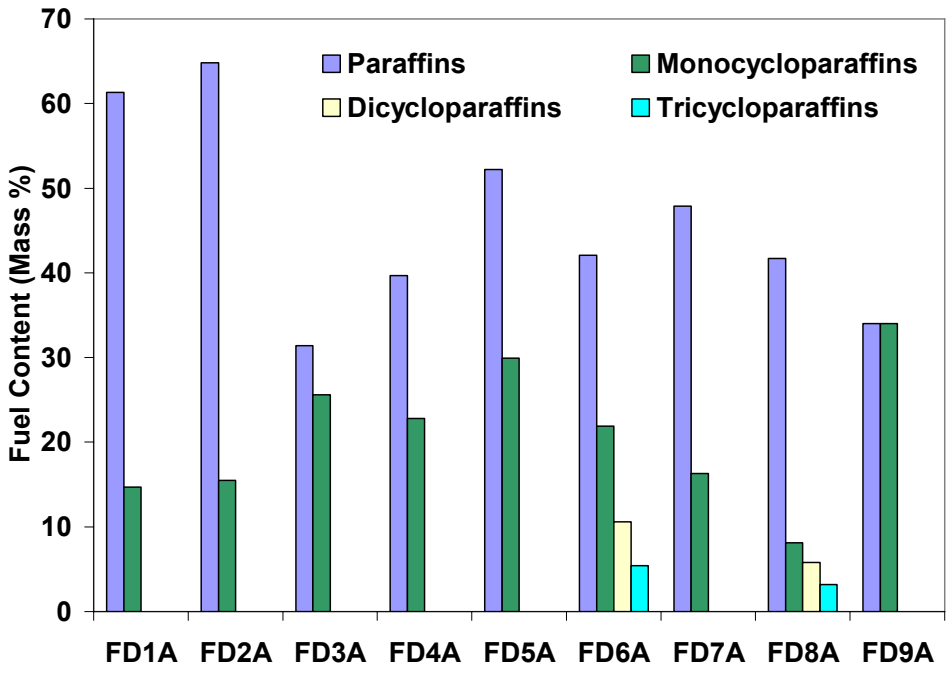

Figure 2.10. Saturates by mass spectrometry (ASTM D2425).

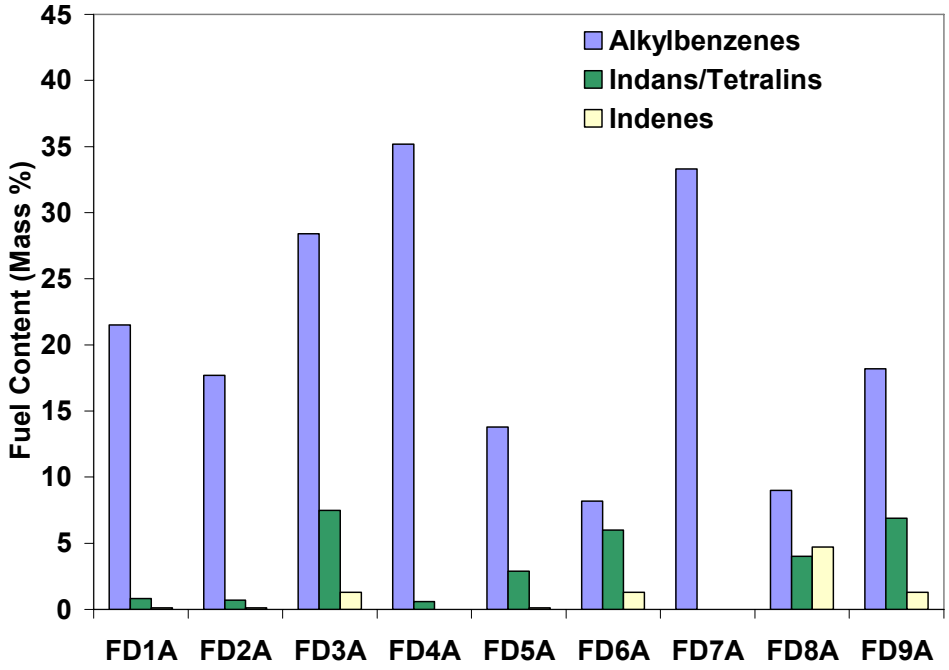

Figure 2.11. Alkylbenzenes, indans/tetralins, and indenes by mass spectrometry (ASTM D2425).

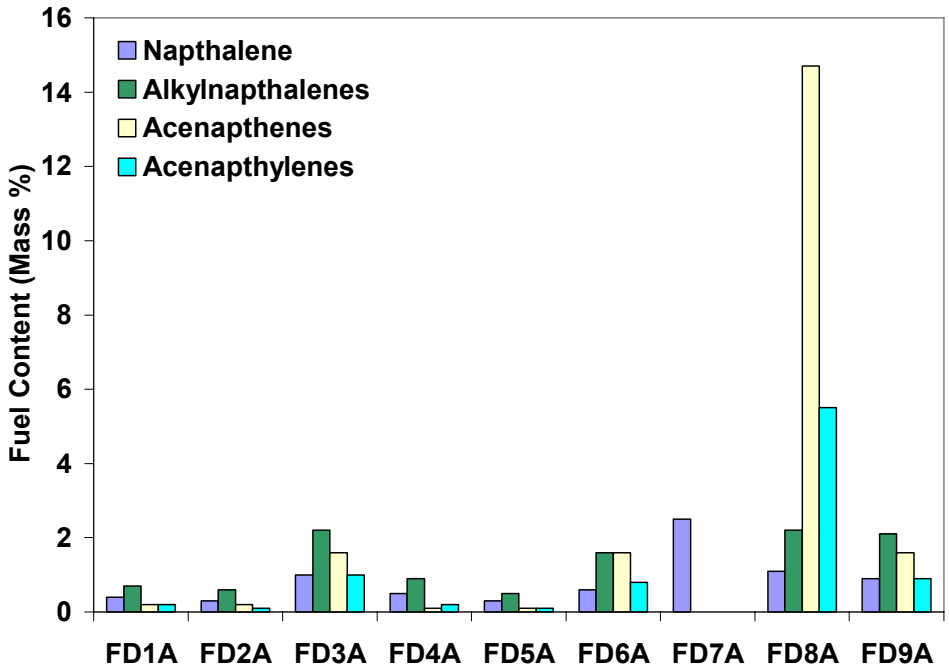

Figure 2.12. Polynuclear aromatics by mass spectrometry (ASTM D2425).

2.3.4 Elemental Analysis by ASTM D5291,[14] D5453,[15] D5623,[16] and D4629[17]

Carbon and hydrogen content were measured by both SwRI and NCUT using ASTM D5291. The values are tabulated separately in Table 2.2; however, since there was good agreement between the laboratories, this discussion will focus on the average values. The carbon content of the fuels varied from 85.5% to 87.4%. Hydrogen content varied from 12.4 to 14.2%. Viewed in a slightly different way, the H : C ratios for the fuels varied from 1.70 to 1.96. These results correlate to the aromatic content, as expected. The high-aromatic fuels consistently had lower H : C ratios than those with lower aromatic content.

Sulfur content was measured using ASTM D5453 by both CPChem and SwRI. Additionally, NCUT provided sulfur content data by ASTM D5623 and nitrogen content data by ASTM D4629. All of the fuels were found to contain less than 15 ppm sulfur, as specified in the formulation targets. Both ASTM methods affirmed general levels of sulfur of 0–4 ppm. CPChem reported FD6A to have a sulfur content of 13.6; however, both other reports for that fuel were lower than 3 ppm, so a typographical error is suspected in the CPChem reported value. The NCUT nitrogen content analyses showed that all of the fuels had less than 2.5 mg/l nitrogen content.

2.3.5 Bromine Number by ASTM D1159[18]

Determination of the bromine number is another means of examining the aliphatic unsaturation (olefin content) of a petroleum distillate. All of the fuels exhibited bromine numbers of 0.35 g BR/100 g sample or less. This indicates that all fuels had a very low level of unsaturation. Recall from the ASTM D1319 results that fuels FD4A and FD9A had reported olefin content above the 4% design cap in some, but not all, of the analyses. The bromine numbers for these fuels were not the highest result and were generally in line with the other fuels. This calls into question the accuracy of the D1319 results for these fuels. Again, because of the nature of the formulations for some of the FACE fuels, applicability of ASTM standard analyses to these fuels may be questionable.

Table 2.2. Summary Data for ASTM Standard Tests

Specific Tests	FACE Fuels (by FD/CPChem Designation)								
	FD1A/ FD-1-01	FD2A/ FD-2-01	FD3A/ FD-3-01	FD4A/ FD-4-01	FD5A/ FD-5-01	FD6A/ FD-6-01	FD7A/ FD-7-01	FD8A/ FD-8-01	FD9A/ FD-9-01
Design Variable Levels									
Cetane Number	Low	Low	Low	Low	High	High	High	High	Center
Aromatic Content (vol %)	Low	Low	High	High	Low	Low	High	High	Center
T_{90} (F)	Low	High	Low	High	Low	High	Low	High	Center
Cetane Number by Engine Method (ASTM D613)									
-CPChem C of A	29.93	28	32.02	28.44	54.2	53.3	44.3	50	44.95
-ORNL/SwRI	30.7	28.7	30.7	28.5	55	54.1	45.9	49	43.5
Distillation, T_{90} (F) (ASTM D86)									
-CPChem C of A	517	637	518	639	528	646	513	648	610
-ORNL/SwRI	543	654	525	640	526	642	512	647	607
Hydrocarbons by FIA (ASTM D1319)									
Aromatics, Volume % (Reproducibility = 1.4–1.6 vol %)									
-CPChem C of A	22.2	19.4	45	46.6	19.5	21.3	42.3	43.3	32.5
-ORNL/SwRI (& repeat)	26.5	23.4	48	51.2 (49.1)	22.7	22.5	41.6	45.7 (44.0)	41.6 (39.6)
-NCUT (& repeat)	21.9	20.2	47.8	57.0 (60.0)	19.8	17.4	41	35.1 (39.7)	37 (40.4)
Olefins (vol %) (Reproducibility = 1.7–5.1 vol %)									
-CPChem C of A	3.5	3.3	0.6	1.3	1.4	0.7	2.5	4.3	2.4
-ORNL/SwRI (and repeat)	1.2	2.8	3.2	12.4 (7.7)	1.1	4.8	1.2	1.5 (2.0)	8.9 (4.8)
-NCUT (and repeat)	3	3.5	0.6	3.6 (3.8)	1.2	4.1	0.5	1.3 (2.8)	0.7 (8.8)

Table 2.2. (continued)

Specific Tests	FACE Fuels (by FD/CPChem Designation)								
	FD1A/ FD-1-01	FD2A/ FD-2-01	FD3A/ FD-3-01	FD4A/ FD-4-01	FD5A/ FD-5-01	FD6A/ FD-6-01	FD7A/ FD-7-01	FD8A/ FD-8-01	FD9A/ FD-9-01
Saturates (Vol %) (Reproducibility = 5.6–4.8 vol %)									
-CPChem C of A	74.3	77.3	54.4	52.1	79.1	78	55.2	52.4	65.1
-ORNL/SwRI (and repeat)	72.3	73.8	48.8	36.4 (43.2)	76.2	72.7	57.2	52.8 (54.0)	49.5 (55.6)
-NCUT (and repeat)	75.1	77.3	51.6	39.4 (36.2)	79	78.5	58.5	63.6 (57.5)	62.3 (50.8)
Aromatics by SFC [ASTM D5186 (Reproducibility = 1.5-1.8 mass%)]									
Total Aromatics (mass %)									
-ORNL/SwRI	26.1	23.1	50	40.7	22.2	21.1	46.2	43.5	37
-NCUT	27	23.4	50.9	40.6	22.8	21.9	47.6	45.2	37.8
Monoaromatics (mass %)									
-ORNL/SwRI	24.2	21.7	45.5	38.8	21.1	17	37.8	22.7	32.3
-NCUT	24.9	22.2	45.8	38.7	21.8	17.2	35.5	20.9	32.7
Polynuclear Aromatics (mass %)									
-ORNL/SwRI	1.9	1.3	4.5	2	1.1	4.1	8.4	20.8	4.6
-NCUT	2.1	1.2	5.1	1.9	1	4.7	12.1	24.3	5.1
Hydrocarbon Types by Mass Spectrometry (vol %) [ASTM D2425 (ORNL/SwRI)]									
Paraffins (Reproducibility = 4.0%)	61.3	64.8	31.4	39.7	52.2	42.1	47.9	41.7	34
Monocycloparaffins (Reproducibility = 5.2%)	14.7	15.5	25.6	22.8	29.9	21.9	16.3	8.1	34
Dicycloparaffins (Reproducibility = 4.4%)	0	0	0	0	0	10.6	0	5.8	0
Tricycloparaffins (Reproducibility = 2.0%)	0	0	0	0	0	5.4	0	3.2	0
Total Napthenes	14.7	15.5	25.6	22.8	29.9	37.9	16.3	17.1	34
Total Saturates	76	80.3	57	62.5	82.1	80	64.2	58.8	68
Alkylbenzenes (Reproducibility = 1.4%)	21.5	17.7	28.4	35.2	13.8	8.2	33.3	9	18.2
Indans/Tetralins (Reproducibility = 0.5%)	0.8	0.7	7.5	0.6	2.9	6	0	4	6.9
Indenes (CnH2n-10)	0.1	0.1	1.3	0	0.1	1.3	0	4.7	1.3

Table 2.2. (continued)

Specific Tests	FACE Fuels (by FD/CPChem Designation)								
	FD1A/ FD-1-01	**FD2A/ FD-2-01**	**FD3A/ FD-3-01**	**FD4A/ FD-4-01**	**FD5A/ FD-5-01**	**FD6A/ FD-6-01**	**FD7A/ FD-7-01**	**FD8A/ FD-8-01**	**FD9A/ FD-9-01**
Napthalene (Reproducibility = 1.0%)	0.4	0.3	1	0.5	0.3	0.6	2.5	1.1	0.9
Alkylnapthalenes	0.7	0.6	2.2	0.9	0.5	1.6	0	2.2	2.1
Acenapthenes (CnH2n-14) (Reproducibility = 0.9%)	0.2	0.2	1.6	0.1	0.1	1.6	0	14.7	1.6
Acenapthylenes (CnH2n-16) (Reproducibility = 0.7%)	0.2	0.1	1	0.2	0.1	0.8	0	5.5	0.9
Tricyclic Aromatics (CnH2n-18) (Reproducibility = 0.4%)	0	0	0	0	0	0	0	0.1	0
Total PNAs	1.5	1.2	5.8	1.7	1	4.6	2.5	23.6	5.5
Total Aromatics	23.9	19.7	43	37.5	17.8	20.1	35.8	41.3	31.9
Net Heat of Combustion (BTU/lb) [ASTM D240 (Reproducibility = 0.40 MJ/kg = 172 Btu/lb)]									
-ORNL/SwRI	18,402	18,553.1	18,120	18,269.4	18,442.6	18,399.4	18,211.3	18,140.9	18,256.5
API Gravity (ASTM D4052)									
API°:									
-ORNL/SwRI	43.5	44.6	37	37.8	43.5	36.7	37.5	31.3	35.7
Specific Gravity (Reproducibility = 0.0005 g/ml)									
-CPChem C of A	0.8084	0.8037	0.8401	0.8355	0.8086	0.8411	0.8375	0.8682	0.8465
-ORNL/SwRI	0.8084	0.8037	0.84	0.8359	0.8086	0.8412	0.8375	0.8694	0.8464
-NCUT	0.8076	0.803	0.8393	0.8352	0.8078	0.8401	0.8366	0.8684	0.8457
Elemental Analysis (ASTM D5291)									
Carbon, wt% [Reproducibility = (Mean Value + 48.48)*0.018]									
-ORNL/SwRI	85.71	86.12	86.49	86.9	86.11	86.22	86.57	87.52	86.97
-NCUT	85.76	85.29	86.94	86.68	85.48	86.28	86.88	87.28	86.9
Hydrogen, wt% [Reproducibility = 0.2314* (Mean Value)^0.5]									
-ORNL/SwRI	13.56	13.64	12.56	12.77	13.85	13.66	12.59	12.33	13.1
-NCUT	14.08	14.23	12.76	13.23	14.11	13.55	12.93	12.48	13.04
Bromine Number (grams Br/100g)	0.27	0.15	0.35	0.29	0.22	0.23	0.25	0.14	0.32

Table 2.2. (continued)

Specific Tests	FACE Fuels (by FD/CPChem Designation)								
	FD1A/ FD-1-01	FD2A/ FD-2-01	FD3A/ FD-3-01	FD4A/ FD-4-01	FD5A/ FD-5-01	FD6A/ FD-6-01	FD7A/ FD-7-01	FD8A/ FD-8-01	FD9A/ FD-9-01
(ASTM D1159—NCUT)									
Cloud Point (°C) (ASTM D2500)									
-ORNL/SwRI	-27	-51	-35	-50	-29	-25	-21	-20	-30
-NCUT	-25	-59	-38	-59	-28	-28	-22	-19	-30
Kinematic Viscosity at 40°C (cSt) [ASTM D445 (Reproducibility = 0.8%)]									
-CPChem C of A						3.09	1.55		
-ORNL/SwRI	1.741	1.96	1.32	1.785	1.795	3.097	1.759	3.278	2.107
-NCUT	1.56	1.652	1.317	1.781	1.587	3.099	1.581	3.158	2.104
Sulfur by Ultraviolet Fluorescence (ppm) (ASTM D5453)									
-CPChem C of A	1.7	0.3	2.8	0.1	1.2	13.6	2	1.7	3.4
-ORNL/SwRI	1.9	0.4	2.6	<1	1.2	2.8	1.4	1.6	2.5
Sulfur (ppm) (ASTM D5623—NCUT)	1.2	<0.5	1.7	<0.5	<0.5	2	<0.5	0.9	1.9
Nitrogen (mg/L) (ASTM D4629—NCUT)	0.8	1.68	2.1	0.87	1.35	2.3	0.9	0.81	2.2
Cetane Number by Engine Method (ASTM D613)									
-CPChem C of A	29.9	28	32	28.4	54.2	53.3	44.3	50	45
-ORNL/SwRI	30.7	28.7	30.7	28.5	55	54.1	45.9	49	43.5
Cetane Index (calculated) (ASTM D976)									
-CPChem C of A							41.5		
-ORNL/SwRI	40.1	39	31.2	40.7	49.7	52.1	41.9	42.9	46.1
Flash Point by Closed Cup (°F) (ASTM D93)									
-CPChem C of A	140.4	134.4		130.4	138.1		150.3		
-ORNL/SwRI	135	128	141	139	131	166	149	158	140

Table 2.2. (continued)

Specific Tests		FACE Fuels (by FD/CPChem Designation) FD1A/ FD-1-01	FD2A/ FD-2-01	FD3A/ FD-3-01	FD4A/ FD-4-01	FD5A/ FD-5-01	FD6A/ FD-6-01	FD7A/ FD-7-01	FD8A/ FD-8-01	FD9A/ FD-9-01
Distillation (°F) [ASTM D86 (Reproducibility dependent on apparatus and setup used)]										
-CPChem C of A										
IBP		174	307.4	315.3	331.7	327.6	364.3	354.7	433.9	320.5
	5%	286.9	352.6	332	345.6	363.2	414.3	379.8	459.5	359.8
	10%	313.5	362.8	341.2	350.1	369.1	440.6	385.5	475.5	372.9
	15%									
	20%	351.8	365.2	344.5	360.7	382.3	471.4	395.6	493	398.1
	30%	365.5	366.6	356	376.7	395.8	494.1	409.3	503.6	429.8
	40%	366.8	366.6	368.6	400.5	412.3	512.8	426.2	513.5	466.3
	50%	373.8	371.1	384.4	437.5	430.2	530.2	446.2	524.8	494.6
	60%	385	379.4	408.2	477.9	451.4	550.9	466	541.9	516.7
	70%	400.8	390.2	438.8	518.4	473.7	575.2	481.3	567.1	538.3
	80%	430.2	415.6	475.5	574.7	496.8	607.3	493.5	605.7	565.9
	90%	516.7	637.3	518	639	527.5	645.8	512.8	647.8	610
	95%	570.4	665.8	548.2	664	561.7	667.4	539.4	675.1	644.9
FBP		610.5	673	583.2	675.1	591.6	674.4	594	687.4	667.6
	Recovered (mL)	98.5	97.9	98.3	98.5	98.5	97.6	98.3	99	98.5
	Residue (mL)	1	1	1	1	1	0.8	1	1	1
	Loss (mL)	0.5	1.1	0.7	0.5	0.5	1.6	0.7	0	0.5
-ORNL/SwRI										
IBP		344	345	317	324	341	369	357	435	315
	5%	360	354	339	342	362	405	377	462	351
	10%	363	358	343	348	367	433	380	478	363
	15%	365	360	349	353	375	450	387	485	376
	20%	368	363	353	359	381	466	392	493	390
	30%	375	368	364	376	395	489	408	503	423
	40%	382	374	378	400	411	508	425	512	460
	50%	391	380	395	433	430	527	445	523	491
	60%	403	388	418	474	451	547	465	539	514

Table 2.2. (continued)

Specific Tests	FACE Fuels (by FD/CPChem Designation)								
	FD1A/ FD-1-01	**FD2A/ FD-2-01**	**FD3A/ FD-3-01**	**FD4A/ FD-4-01**	**FD5A/ FD-5-01**	**FD6A/ FD-6-01**	**FD7A/ FD-7-01**	**FD8A/ FD-8-01**	**FD9A/ FD-9-01**
70%	422	402	450	513	473	569	480	563	537
80%	467	454	485	571	495	601	492	602	564
90%	543	654	525	640	526	642	512	647	607
95%	584	672	553	664	557	663	538	669	640
FBP	616	679	582	674	591	673	583	687	661
Recovered (mL)	97.6	98.3	97.3	97.7	98	97.5	98.2	97.3	97.7
Residue (mL)	1.5	1.2	1.1	1.4	1.1	1.7	1.1	1	1.3
Loss (mL)	0.9	0.5	1.6	0.9	0.9	0.8	0.7	1.7	1
Simulated Distillation (°F) (mass %) [ASTM D2887—NCUT (Reproducibility—1.4 F @ 10%; 2.2 F @ 95%; 5.8 F @ FBP)]									
0.50%	283.3	284.7	245.5	283.3	271.0	253.8	284.7	359.6	257.4
5%	325.0	325.0	297.0	298.4	325.0	357.1	338.7	440.2	321.1
10%	338.7	337.3	326.1	326.1	338.7	402.1	344.8	487.8	331.2
15%	356.0	349.5	328.6	328.6	351.0	433.0	362.1	490.3	344.8
20%	363.2	362.1	338.7	338.7	364.6	456.1	366.8	492.4	369.3
30%	373.3	371.8	354.6	359.6	386.6	488.8	396.0	505.4	423.3
40%	380.5	378.0	374.4	397.0	411.4	516.2	434.1	514.8	471.9
50%	392.4	385.5	400.6	442.8	440.2	541.0	487.8	532.8	503.2
60%	408.9	396.0	430.5	475.5	480.6	565.2	492.4	560.8	532.8
70%	433.0	412.5	465.8	522.0	492.4	594.0	493.5	587.1	561.9
80%	500.7	491.4	506.8	584.6	520.9	643.3	519.8	639.7	592.9
90%	574.5	683.6	556.2	677.5	564.1	690.4	556.2	694.0	654.1
95%	622.8	705.6	590.4	703.4	601.9	710.2	584.6	714.9	694.0
99.50%	739.8	757.0	675.3	756.0	674.2	772.2	705.6	776.8	759.2
HFRR Lubricity [WSD (µm)] (ASTM D6079)									
	662	673	671	636	687	571	625	492	589

2.4 REFERENCES

1. ASTM International, *Standard Test Method for Cetane Number of Diesel Fuel Oil,* ASTM D613-08 (ASTM International, Pennsylvania, 2008).

2. ASTM International, *Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption,* ASTM D1319-08 (ASTM International, Pennsylvania, 2008).

3. ASTM International, *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure,* ASTM D86-09e1 (ASTM International, Pennsylvania, 2009).

4. ASTM International, *Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter,* ASTM D4052-96(2002)e1 (ASTM International, Pennsylvania, 2002).

5. ASTM International, *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity),* ASTM D445-06 (ASTM International, Pennsylvania, 2006).

6. ASTM International, *Standard Test Method for Cloud Point of Petroleum Products,* ASTM D2500-09 (ASTM International, Pennsylvania, 2009).

7. ASTM International, *Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester,* ASTM D93-08 (ASTM International, Pennsylvania, 2008).

8. ASTM International, *Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter,* ASTM D240-02(2007) (ASTM International, Pennsylvania, 2007).

9. ASTM International, *Standard Test Method for Calculated Cetane Index of Distillate Fuels,* ASTM D976-06 (ASTM International, Pennsylvania, 2006).

10. ASTM International, *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography,* ASTM D2887-08 (ASTM International, Pennsylvania, 2008).

11. ASTM International, *Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR),* ASTM D6079-04e1 (ASTM International, Pennsylvania, 2004).

12. ASTM International, *Standard Test Method for Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography,* ASTM D5186-03(2009) (ASTM International, Pennsylvania, 2009).

13. ASTM International, *Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry,* ASTM D2425-04 (ASTM International, Pennsylvania, 2004).

14. ASTM International, *Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants,* ASTM D5291-02(2007) (ASTM International, Pennsylvania, 2007).

15. ASTM International, *Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence,* ASTM D5453-09 (ASTM International, Pennsylvania, 2009).

16. ASTM International, *Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection,* ASTM D5623-94(2009) (ASTM International, Pennsylvania, 2009).

17. ASTM International, *Standard Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection,* ASTM D4629-09 (ASTM International, Pennsylvania, 2009).

18. ASTM International, *Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration,* ASTM D1159-07 (ASTM International, Pennsylvania, 2007).

3. IGNITION CHARACTERIZATION OF FACE DIESEL FUELS USING THE IGNITION QUALITY TESTER

3.1 INTRODUCTION

Diesel fuel ignition quality is commonly measured via two standard methods, the ASTM D613[1] engine method and the ASTM D6890[2] ignition quality tester (IQT) method. The FACE diesel fuels were tested by both methods. Initially, ASTM D613 was conducted for all nine FACE diesel fuels by both SwRI, under contract to ORNL, and by CPChem. The National Renewable Energy Laboratory (NREL) then tested all nine FACE diesel fuels using an IQT. The IQT is a constant volume combustion apparatus developed specifically as a standard test device for fuel ignition delay (ID),[3–8] and ASTM D6890 was developed around this apparatus.[2] NREL tested all fuels according to ASTM D6980 and also performed additional experiments to further study ignition quality. These additional experiments were conducted to provide data which further characterize the ignition quality of the FACE fuels. The following discussions are divided into two sections.

- The first section covers ASTM D6890 analysis.
- The second section covers additional fuel ignition characterization to allow predictions of ID time under a range of combustion conditions.

3.2 DERIVED CETANE NUMBER

3.2.1 Experimental

NREL tested samples of all nine FACE diesel fuels using its IQT—laboratory model constant volume combustion device. NREL's IQT (Figure 3.1.) was manufactured by Advanced Engine Technology, Ltd. The NREL IQT uses an S-type, ISO-4010 delay pintle fuel injector instrumented with a needle lift sensor injecting into a preheated combustion air charge held in a constant volume chamber instrumented with a high-speed pressure transducer. Fuel ID is measured as the elapsed time between start of injection as indicated by the needle lift sensor to a time of specific combustion pressure rise, as defined by Ryan and Callahan.[4] This is illustrated in Figure 3.2.

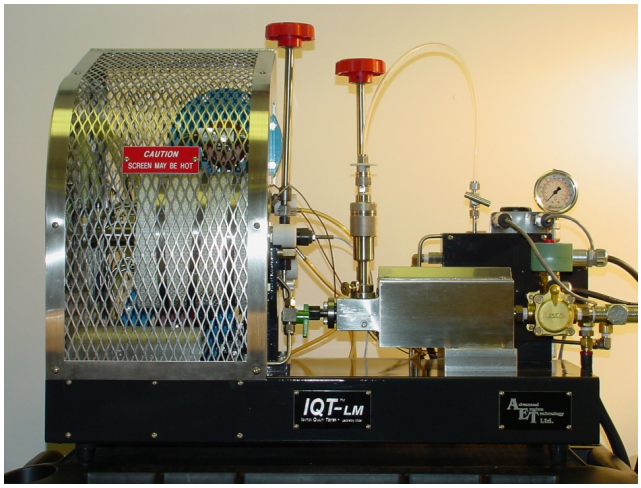

Figure 3.1. NREL's IQT.

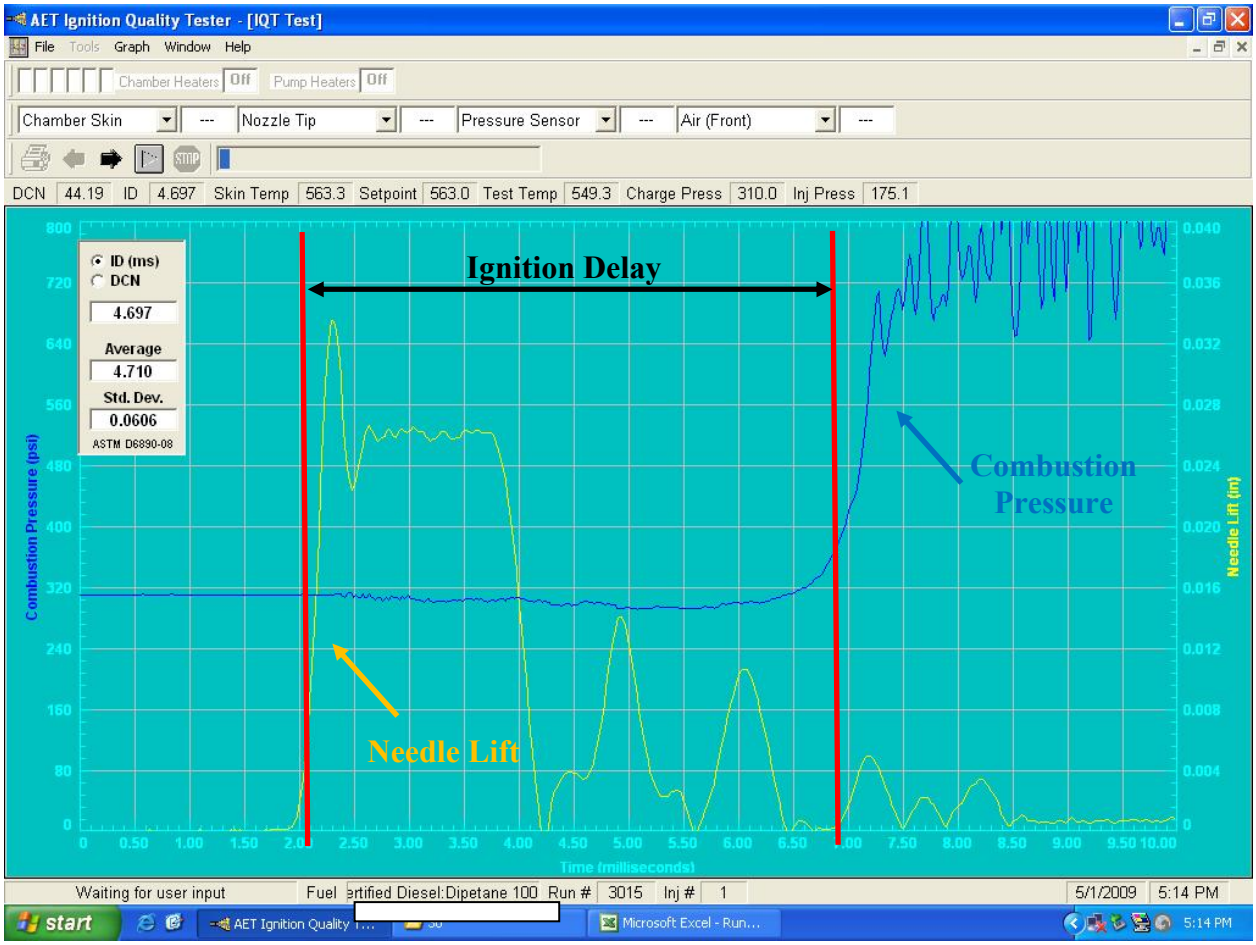

Figure 3.2. Sample screen shot output of IQT ID measurement.

While the IQT device allows the user to set charge combustion air pressure and temperature arbitrarily, the standard settings used for derived cetane number (DCN) measurements according to ASTM D6890 are 2.137 ± 0.007 MPa gauge (referenced to 1 atmosphere, 0.101 MPa, at sea level) and 545 ± 30°C, with charge air containing 20.9 ± 1.0 volume percent oxygen.[2] The user calibrates the device using n-heptane and methylcyclohexane, adjusting combustion chamber surface temperature (and therefore charge air temperature) until IDs with these reference fuels fall within specified limits. The IQT system is fully automated and performs an experiment of 15 preinjections to equilibrate system temperatures followed by 32 recorded injections. After screening for acceptable test limits, the average value of 32 IDs is calculated and correlated to a DCN value. The ASTM D6890 standard procedure was used by NREL to determine the DCN of all nine FACE diesel fuels. Note, the pressure transducer calibration is referenced to sea level and the combustion chamber is sealed during operation; therefore the experiments are not affected by NREL's high-altitude laboratory location.

The average fuel ID of the 32 recorded test injections is converted into a DCN value according to empirical relationships defined by ASTM D6890, illustrated in Figure 3.3. These relationships between ID and DCN have been correlated over time with various fuels against ASTM D613 CN (engine test) by an ASTM committee[9–11] and incorporated into ASTM D6890-08. As illustrated in Figure 3.3, two empirical relationships are used in ASTM D6890 to calculate DCN from average ID,

recorded in milliseconds.[2] For average ID times between 3.3 and 6.4 ms, DCN is calculated according to Eq. (3.1):

$$DCN = 4.460 + \frac{186.6}{ID} \quad . \tag{3.1}$$

Equation (3.1) covers a DCN range of 61 to 34, the range of DCN for which ASTM D6890 was initially developed. For average ID times outside the range of 3.3 and 6.4 ms, DCN is calculated according to Eq. (3.2):

$$DCN = 83.99 \cdot (ID - 1.512)^{-0.0668} + 3.547 \quad . \tag{3.2}$$

The empirical calculation for DCN in Eq. (3.2) is intended for lower cetane fuels and was derived from a correlation test program comprising ASTM National Exchange Group test fuels, 2,2,4,4,8,8 heptamethylnonane, cetane, and an in-house check fuel.[2,9] No precision for Eq. (3.2) is specified by ASTM. Note, a slight discontinuity exists between the functions for an ID of 6.4 ms (DCN ~ 33.1 to 33.6).

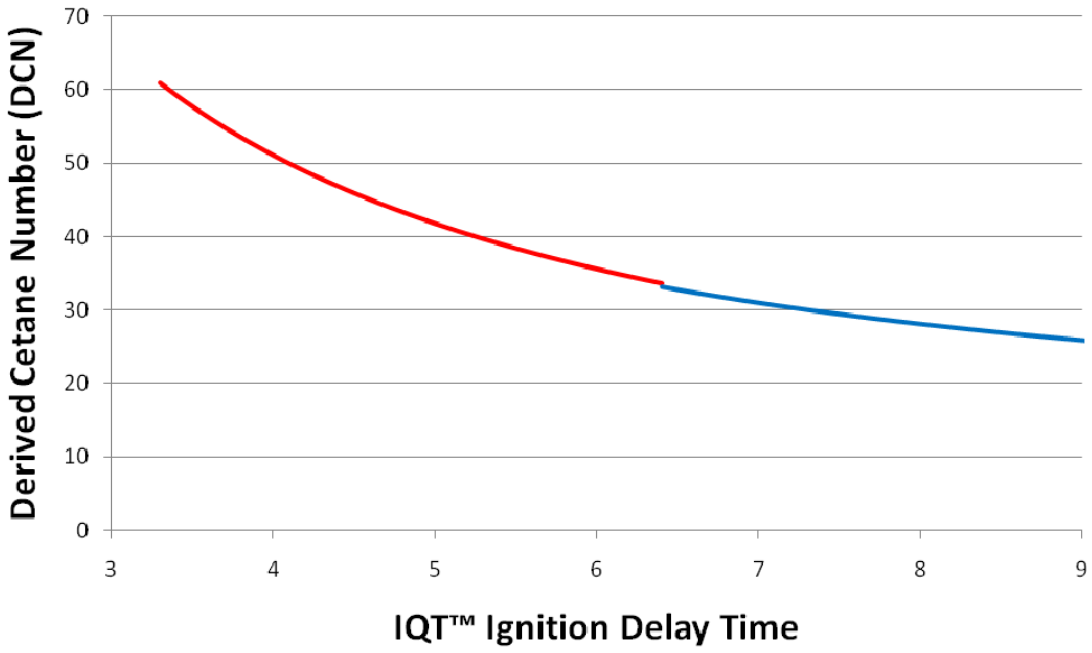

Figure 3.3. ASTM D6890 empirical relationship for DCN vs IQT ignition delay time.

3.2.2 Results

The results of testing the FACE diesel fuels according to ASTM D6890 appear in Table 3.1. The average ID time (in milliseconds) listed is the average taken from the 32 recorded test injections following 15 preinjections for stabilization. The coefficient of variation for each set of 32 test injections was calculated, showing variation between 1.46 and 2.15 % for each of the FACE diesel fuel experiments. The empirical correlation equation used to convert ID time to DCN is shown for each fuel. FD3A and FD4A had ID times extremely close to the transition between the two correlations, at −0.5% and +0.8% of the 6.4 ms limit, respectively. Since the two correlation equations are discontinuous at that point, Table 3.1 also lists alternate DCN calculations using the

alternate equations. The discontinuity between the two correlations results in a difference of about 0.5 DCN.

Table 3.1. ASTM D6890 Results for FACE Diesel Fuels

FACE diesel fuel	Average Ignition Delay (ID) Time (ms)	ID Time Coefficient of Variation (%)	Derived Cetane Number (DCN) Equation Applied	DCN
FD1A	6.044	1.56	Eq. (3.1)	35.3
FD2A	6.196	1.81	Eq. (3.1)	34.6
FD3A	6.369	1.46	Eq. (3.1)	33.8[a]
FD4A	6.454	1.60	Eq. (3.2)	32.9[b]
FD5A	3.696	1.68	Eq. (3.1)	54.9
FD6A	3.801	2.03	Eq. (3.1)	53.6
FD7A	4.563	1.75	Eq. (3.1)	45.4
FD8A	4.082	1.94	Eq. (3.1)	50.2
FD9A	4.645	2.15	Eq. (3.1)	44.6

[a]DCN = 33.2 when Eq. (3.2) is applied.

[b]DCN = 33.4 when Eq. (3.1) is applied.

3.2.3 Discussion

As indicated in Table 3.2, the IQT–based ASTM D6890 DCNs agree fairly well with the ASTM D613 engine-based CNs, except for the lower cetane fuels. FD5A–FD9A generally showed differences of DCN-CN around 0.1-1.2 CNs. These differences fall within the same order of magnitude for DCN-CN data differences shown in ASTM's empirical model validation studies.[9–12] FD1A–FD4A demonstrate a greater DCN-CN difference, and the DCN values are consistently higher than the engine-based CNs, by as much as 24%. There may be several reasons for these differences. In general, the ASTM D613 CN test is not typically performed for CNs below 30,[1] but CPChem and ORNL/SwRI results agree fairly well with each other for FD1A, FD2A, and FD4A. As discussed in the results, FD3A and FD4A demonstrated ID times corresponding to the transition between correlation Eqs. (3.1) and (3.2), yielding an additional possible uncertainty of about 0.5 DCN. A likely explanation for the larger differences between ASTM D6890 and ASTM D613 for these low-cetane fuels is due to the correlation equations themselves.

A review of ASTM D6890 test method development[2] and subsequent research reports validating the empirical models[9–12] show the majority of experiments conducted to develop the empirical relations involved fuels with CNs between 40 and 60, which is reasonable considering the ASTM test was primarily concerned with testing the traditional range of commercial diesel fuels. Only two fuels with lower CNs were studied, an ASTM in-house check fuel (CN = 33.4) and the anchor point using 2,2,4,4,8,8 heptamethylnonane (CN = 15). As the model used to develop and validate the ASTM D6890 DCN in comparison to the ASTM D613 CN was not widely correlated for CNs lower than 40, it is not surprising the empirical correlations do not yield close agreement for the low-cetane FACE

diesel fuels. [9–12]In summary, it appears that while the IQT was able to precisely determine ID times for the low-cetane FACE diesel fuels, the current ASTM D6890 empirical conversions may not yield DCNs which accurately match D613 engine-based CNs. Further investigation of DCN correlations at low CNs is planned at NREL.

Table 3.2. ASTM D6890 Results Compared to ASTM D613 Results

FACE diesel fuel	D 613 CN (CPChem)[a]	D 613 CN (ORNL/SwRI)[a]	D 6890-08 DCN (NREL)	DCN-CN (CPChem)	DCN-CN (ORNL/SwRI)
FD1A	29.9	30.7	35.3	5.4	4.6
FD2A	28	28.7	34.6	6.6	5.9
FD3A	32	30.7	33.8	1.8	3.1
FD4A	28.4	28.5	32.9	4.5	4.4
FD5A	54.2	55	54.9	0.7	−0.1
FD6A	53.3	54.1	53.6	0.3	−0.5
FD7A	44.3	45.9	45.4	1.1	−0.5
FD8A	50	49	50.2	0.2	1.2
FD9A	45	43.5	44.6	−0.4	1.1

[a]Significant figures as reported in Coordinating Research Council, "ASTM Test Analysis of FACE Diesel Fuels," August 2008 (http://www.crcao.com/news/FACE%20Diesel%20Fuels%20ASTM%20Results-%20Final.pdf).

3.3 PREDICTIVE ID TIME

3.3.1 Experimental

In addition to using the IQT to measure DCN for a given fuel, NREL has developed techniques to further characterize ignition characteristics of diesel fuels using this device.[12–14] Although the IQT is typically used only to measure DCN according to ASTM D 6890, it can also measure how ID varies with temperature, pressure, and charge composition (e.g., oxygen fraction). Prior work at NREL studied ID over a range of temperatures (450°–550°C), pressures (10–30 bar), and oxygen mole fractions (15–21%), simulating exhaust gases by using compressed gas bottles with reduced concentrations of oxygen, balanced with nitrogen.[14,15] The oxygen compositions for these experiments effectively modeled exhaust gas recirculation (EGR) rates of 0–28%.[15] Because the IQT does not operate using compressive heating (unlike a shock tube or rapid compression facility, where differing heat capacities affect the end-of-compression thermodynamic conditions), there is no thermodynamic effect of substituting N_2 for CO_2 and H_2O present in exhaust gas. The chemical effect of substituting N_2 for CO_2 and H_2O present in exhaust gas is considered negligible, based on prior Rapid Compression Facility experiments with isooctane.[15] A full factorial design of the conditions was developed, resulting in a 27-test-point matrix to complement the standard ASTM D6890 measurement. The experimental relationships of temperature, pressure, and oxygen concentration affecting ID time were calculated according to a simplified global rate model. The resulting Arrhenius relationships yield the apparent activation energy and oxygen order factor for a given fuel.[15] This allows for predictive calculations of ID time as a function of pressure, temperature, and oxygen mole

fraction over the range studied, which provide more ignition behavior insight than DCN alone. Later development at NREL resulted in a reduced eight-test-point matrix which yields the same information; the reduced matrix requires a smaller quantity of test fuel, which is advantageous for experimental research fuels that may only be available in limited quantities. This eight-test-point matrix was applied to the nine FACE diesel fuels using the IQT and spanning the following conditions.

- Combustion air charge temperatures of 450°C and 550°C.
- Combustion air charge pressures of 15 and 30 bar (vs 21.37 bar for ASTM D 6890-08).
- Oxygen volume fractions of 15.0% and 20.9% (balance nitrogen).

3.3.2 Results

The parametric study ID data were plotted as a natural log of the ignition rate (inverse of ID) versus the inverse of temperature in Arrhenius form to determine how the ID rate varies with temperature, resulting in a slope indicating activation energy. Although the spray ignition in the IQT is not a single elementary reaction (instead involving spray, evaporation, mixing, and ignition chemistry), some justification exists for plotting IQT ID results in Arrhenius form.[14] A simplified global model may consider the IQT ignition event in reaction kinetic terms including the time from initial fuel spray to the time the reaction has produced sufficient concentration of chain branching reactions with reactive intermediate species (such as OH), consuming sufficient fuel to register a threshold pressure rise. In terms of this lumped ID, incorporating both physical delay (with spray, evaporation, and mixing) and chemical delay, the slope of the Arrhenius plot is analogous to an "apparent" activation energy for ignition.[14]

This simplified global rate model was fit to the parametric study data to deconvolute the effects of temperature and oxygen concentration on the measured ID. In this model, the effects of charge pressure and oxygen fraction are both coupled into a molar concentration of oxygen rather than treating them separately.[15] The rate expression is shown in Eq. (3.3):

$$\text{Rate} = \frac{1}{ID} = A \cdot \exp\left(\frac{E_a}{R \cdot T}\right) \cdot [O_2]^b \quad , \tag{3.3}$$

where A is the preexponential constant, E_a is the apparent activation energy (kilojoule per mole), R is the universal gas constant (8.314E-5 m^3 bar mol^{-1} K^{-1}), and b is the reaction order for oxygen concentration. In Eq. (3.3), the concentration of oxygen is calculated by Eq. (3.4):

$$[O_2] = \frac{P}{R \cdot T} \cdot \chi_{O_2} \quad , \tag{3.4}$$

where χ_{O_2} is the mole fraction of oxygen in the charge combustion air.

By applying this rate model to Eq. (3.3), the ID of a given fuel can be characterized by a three-parameter fit, solving for A, E_a, and b. The value for oxygen order, b, for each fuel was regressed initially on a modified Arrhenius plot to collapse the data onto one line, with regression by maximizing the R-squared value of the linear fit, shown in Figure 3.4.[15] Apparent activation energy,

E_a, was determined from the slope of the best fit line. It is clear from Figure 3.4 that the model is sufficient to allow for a good fit to the data, resulting in an R-squared value of 0.996 for FD9A. Data regression for other FACE fuels resulted in similarly high R-squared values, as indicated in Table 3.3. Table 3.3 also lists the calculated ignition characterization parameters for the diesel FACE fuel set.

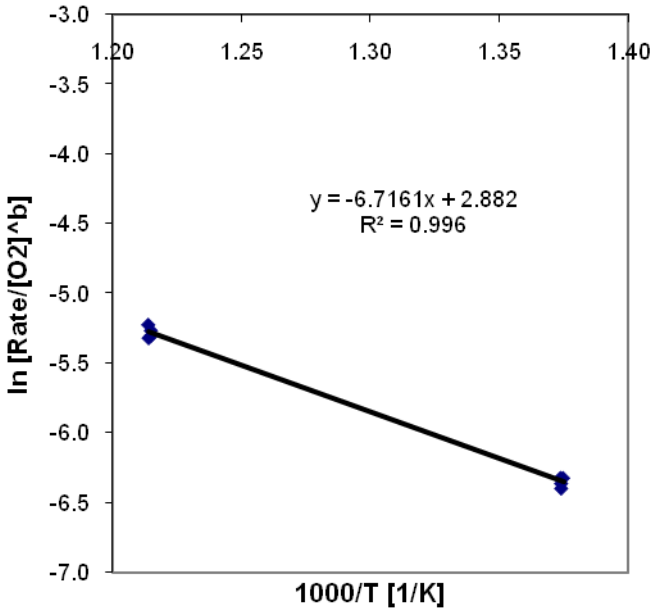

Figure 3.4. Modified Arrhenius plot showing best linear fit to solve for oxygen order and apparent activation energy for FACE fuel FD9A.

Table 3.3. Arrhenius Relation Regression Results

FACE diesel fuel	Regression R^2 value	A	Apparent activation energy (kJ/mol)	Oxygen order (b)
FD1A	0.990	4.800	50.34	0.95
FD2A	0.986	2.059	46.34	1.00
FD3A	0.992	14.338	56.22	0.87
FD4A	0.988	2.254	48.11	1.03
FD5A	0.998	22.489	54.12	0.83
FD6A	0.998	19.064	54.00	0.85
FD7A	0.997	25.897	56.62	0.83
FD8A	0.997	18.830	54.09	0.85
FD9A	0.996	17.850	55.84	0.88

3.3.3 Discussion

This ignition characterization parametric study results in data to allow predictions of ID time under a useful range of combustion conditions:

- combustion air charge temperatures between 450°C and 550°C,
- combustion air charge pressures between 15 and 30 bar, and
- oxygen volume fractions between 15.0% and 20.9% (balance nitrogen).

By applying Eqs. (3.3) and (3.4) with the experimentally determined values for A, apparent activation energy (E_a), and oxygen reaction order (b), ID time for each FACE fuel can be predicted. As a check of predictive accuracy, the experimentally measured ID time was compared to the predicted value using the observed ASTM D6890 test conditions as inputs for each of the diesel FACE fuels, as shown in Table 3.4. The ID prediction errors for this test point are quite low, varying between 0.73% fast and 1.46% slow.

Table 3.4. Measured Ignition Delay Compared to Arrhenius Relation Predictive Ignition Delay for ASTM D 6890 Test Conditions

FACE diesel fuel	Measured average ignition delay (ID) time (ms)	Predicted ID time (ms)	ID prediction error (%)
FD1A	6.044	6.132	+1.46
FD2A	6.196	6.206	+0.16
FD3A	6.369	6.459	+1.41
FD4A	6.454	6.428	−0.41
FD5A	3.696	3.745	+1.33
FD6A	3.801	3.804	+0.08
FD7A	4.563	4.615	+1.14
FD8A	4.082	4.052	−0.73
FD9A	4.645	4.619	−0.56

As indicated by these predictive results, the parameters in Table 3.3 for A, E_a, and b are quantitative metrics of how the fuel ignition responds to changes in temperature, pressure, and EGR. These relationships provide more ignition behavior insight than DCN alone and may be used for fuel modeling for engine control in advanced combustion regimes such as homogeneous charge compression ignition (HCCI). The apparent activation energy can be used to adjust the gain value on an intake air temperature controller for a given fuel to control combustion phasing.[15] Similarly, oxygen reaction order (b values) can be used to adjust relative intake air pressure boost or EGR levels.[15] Furthermore, using the rate expression in Eq. (3.3) and correcting the preexponential value (A) for engine specific conditions, it is feasible that this type of formulation can be used to predict ignition timing over a wide range of conditions in an HCCI engine model.[15]

This additional fuel ignition characterization leads to some interesting observations. Inspection of Table 3.5 shows that three of the four lowest CN fuels (FD1A, FD2A, and FD4A) have the highest oxygen reaction orders (b values). Additionally, both the preexponential value (A) and oxygen order (b) for FD3A, which has the best DCN agreement to engine CN among the low-CN fuels, are close to the related values for FD5A–FD9A (which also have good DCN-CN agreement). A similar pattern exists for apparent activation energy results. NREL plans to further investigate these relationships.

Table 3.5. Comparison of Cetane Number (CN) and Derived Cetane Number (DCN) with Arrhenius Ignition Delay Predictive Parameters

FACE diesel fuel	ASTM D613 CN (CPChem)***	ASTM D613 CN (ORNL/SwRI)***	ASTM D6890 DCN (NREL)	A	Apparent activation energy (kJ/mol)	Oxygen order (b)
FD1A	29.9	30.7	35.3	4.800	50.34	0.95
FD2A	28.0	28.7	34.6	2.059	46.34	1.00
FD3A	32.0	30.7	33.8	14.338	56.22	0.87
FD4A	28.4	28.5	32.9	2.254	48.11	1.03
FD5A	54.2	55.0	54.9	22.489	54.12	0.83
FD6A	53.3	54.1	53.6	19.064	54.00	0.85
FD7A	44.3	45.9	45.4	25.897	56.62	0.83
FD8A	50.0	49.0	50.2	18.830	54.09	0.85
FD9A	45.0	43.5	44.6	17.850	55.84	0.88

3.4 REFERENCES

1. ASTM International, *Standard Test Method for Cetane Number of Diesel Fuel Oil,* ASTM D 613-08 (ASTM International, Pennsylvania, 2008).

2. ASTM International, *Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber,* ASTM D6890-08 (ASTM International, Pennsylvania, 2008).

3. Ryan III, T. W., and Stapper, B., *Diesel Fuel Ignition Quality as Determined in a Constant Volume Combustion Bomb,* Technical Paper 870586 (Society of Automotive Engineers, Warrendale, Pennsylvania, 1987).

4. Ryan III, T. W., and Callahan, T. J., *Engine and Constant Volume Bomb Studies of Diesel Ignition and Combustion,* Technical Paper 881626 (Society of Automotive Engineers, Warrendale, Pennsylvania, 1988).

5. Allard, L. N., et al., *Diesel Fuel Ignition Quality as Determined in the Ignition Quality Tester (IQT™),* Technical Paper 961182 (Society of Automotive Engineers, Warrendale, Pennsylvania, 1996).

6. Allard, L. N., et al, *Diesel Fuel Ignition Quality as Determined in the Ignition Quality Tester (IQT™)—Part II,* Technical Paper 971636 (Society of Automotive Engineers, Warrendale, Pennsylvania, 1997).

7. Allard, L. N., et al., Analysis of the Ignition Behaviour of the ASTM D-613 Primary Reference Fuels and Full Boiling Range Diesel Fuels in the Ignition Quality Tester (IQT™)—Part III, Technical Paper 1999-01-3591 (Society of Automotive Engineers, Warrendale, Pennsylvania, 1999).

8. Allard, L. N., et al., "Diesel Fuel Ignition Quality as Determined in the Ignition Quality Tester (IQT™)—Part IV," Technical Paper 2001-01-3527 (Society of Automotive Engineers, Warrendale, Pennsylvania, 2001).

9. ASTM International, *Diesel Fuel Ignition Quality Tester (IQT™)—Development of the IQT™ Model to Calculate the Derived Cetane Number (DCN),* Research Report D02-1531 (ASTM International, Pennsylvania, 2002).

10. ASTM International, Research Report D02-1532, *Ignition Quality Tester—Summer 2001 Interlaboratory Study,* Research Report D02-1532 (ASTM International, Pennsylvania, 2002)

11. ASTM International, *Diesel Fuel Ignition Quality Tester (IQT™) Spring 2000 Round Robin,* Research Report D02-1534 (ASTM International, Pennsylvania, 2002).

12. Taylor, J., McCormick, R., and Clark, W., *Develop In-House Laboratory Capability for Fuel Screening Relevant to CIDI and Advanced Combustion Concepts,* Report NREL/MP-540-34904 (National Renewable Energy Laboratory, Golden, Colorado, September 2003).

13. Taylor, J., McCormick, R., and Clark, W., *Report on the Relationship between Molecular Structure and Compression Ignition Fuels: Both Conventional and HCCI,* Report NREL/MP-540-36726, (National Renewable Energy Laboratory, Golden, Colorado, August 2004); available at http://www.nrel.gov/vehiclesandfuels/pdfs/mp36726.pdf.

14. Taylor, J., *Fuels Performance Technologies: Milestone FY06 9.1—Using IQT Measurements, Develop Simplified Kinetic Expressions for Ignition of Fuels That Could Be Used in HCCI Engine Models,* Milestone Report NREL/MP-540-40755 (National Renewable Energy Laboratory, Golden, Colorado, November 2006); available at http://www.nrel.gov/vehiclesandfuels/apbf/pdfs/40755.pdf.

15. He, X., et al., "An Experimental and Modeling Study of Iso-octane Ignition Delay Times under Homogeneous Charge Compression Ignition Conditions," *Combustion and Flame*, **142**, pp. 266–275 (2005).

4. ANALYSIS OF FUELS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

In an effort to more fully characterize the fuel chemistry, the fuel compositions were analyzed by a number of nontraditional analysis techniques. This section focuses on the results of analyses of the fuels by a gas chromatograph equipped with a mass-selective detector (GC-MS). The first analyses were accomplished with a traditional GC-MS instrument; a 2-D GC-MS was also used in an effort to add further separation between polar and nonpolar compounds in addition to separation by volatility. The traditional one-dimensional (1-D) GC-MS analysis is discussed first.

4.1 ONE-DIMENSIONAL GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSES

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 4.1 through 4.9 show the results of GC-MS analysis for fuels FD1A–FD9A. The plots show the abundance of the compounds (in arbitrary units) plotted versus the boiling points of the compounds, as calculated by the procedure outlined in ASTM D2887.[1] The vertical broken lines and accompanying labels show the 10%, 50%, and 90% recovery values from the ASTM D86[2] characterizations. Commercial diesel fuels typically exhibit a normal distribution of straight-alkanes, generally centered about carbon number 15 (C_{15}), and with aromatics well-distributed among many compounds. The bulk aromatic content of most typical diesel fuels is made up of naphthalene and alkyl-substituted naphthalene. Aromatic compounds typically are not present individually at the same levels as the straight-alkanes in diesel fuels.

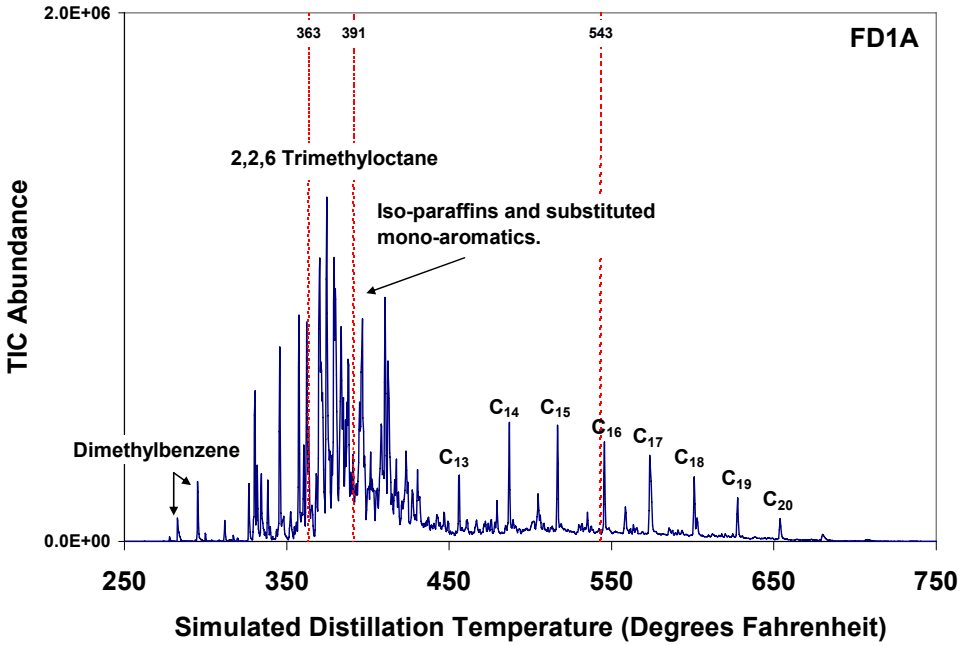

Figure 4.1. 1-D GC-MS chromatogram of FD1A, including D86 10%, 50%, and 90% reference lines.

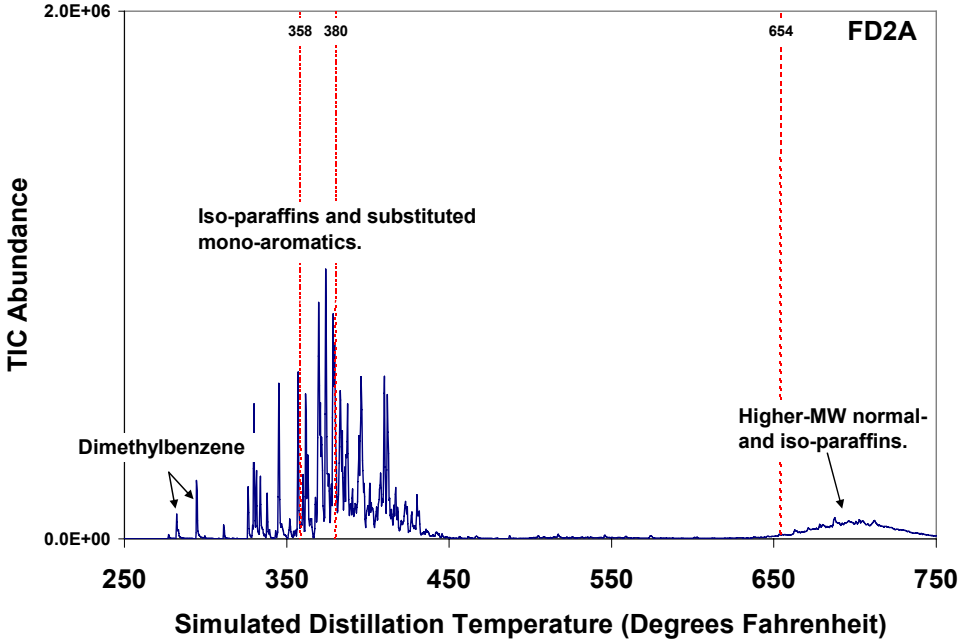

Figure 4.2. 1-D GC-MS chromatogram of FD2A, including D86 10%, 50%, and 90% reference lines.

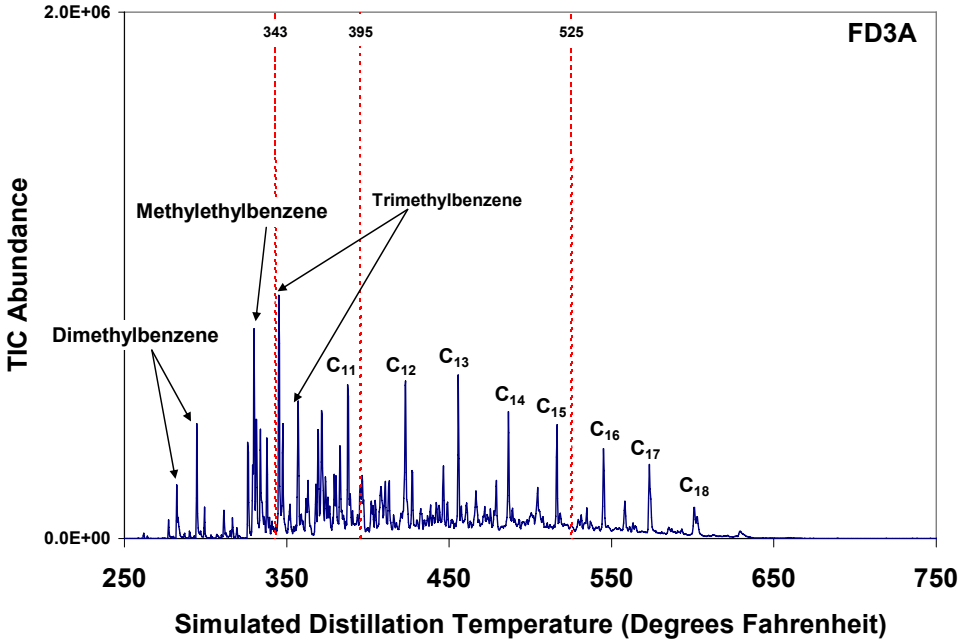

Figure 4.3. 1-D GC-MS chromatogram of FD3A, including D86 10%, 50%, and 90% reference lines.

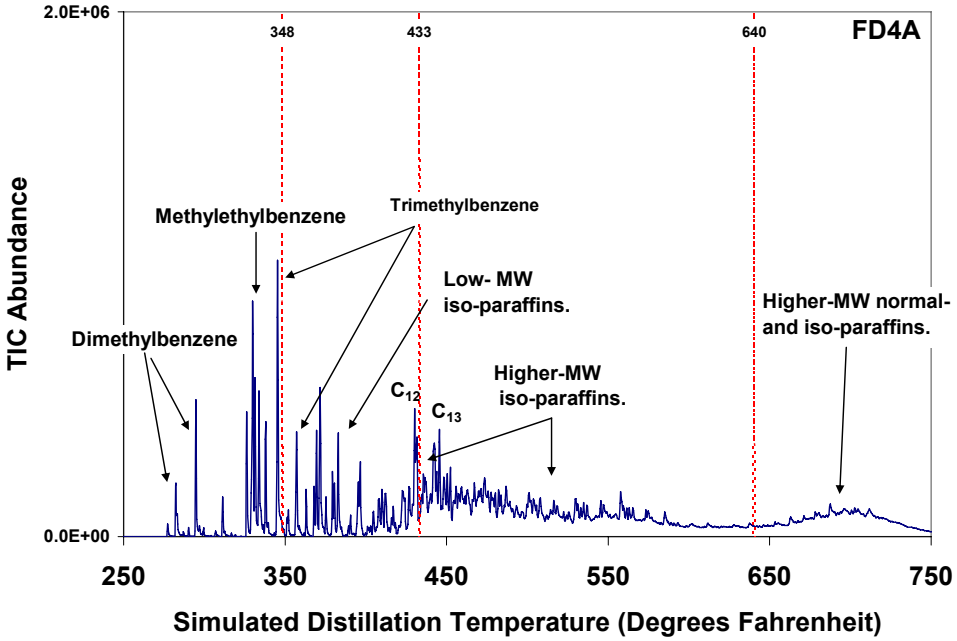

Figure 4.4. 1-D GC-MS chromatogram of FD4A, including D86 10%, 50%, and 90% reference lines.

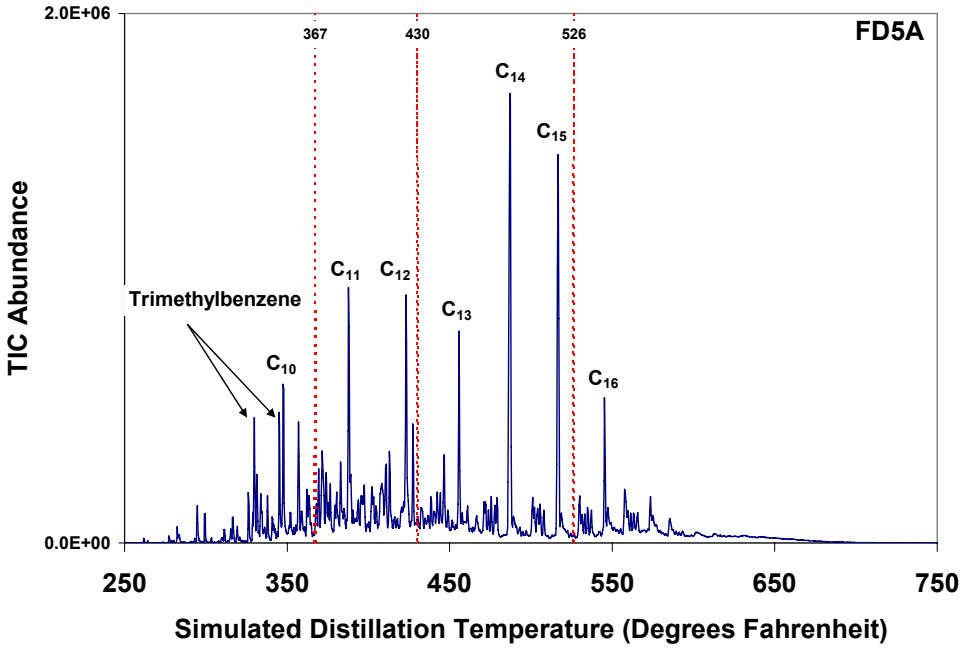

Figure 4.5. 1-D GC-MS chromatogram of FD5A, including D86 10%, 50%, and 90% reference lines.

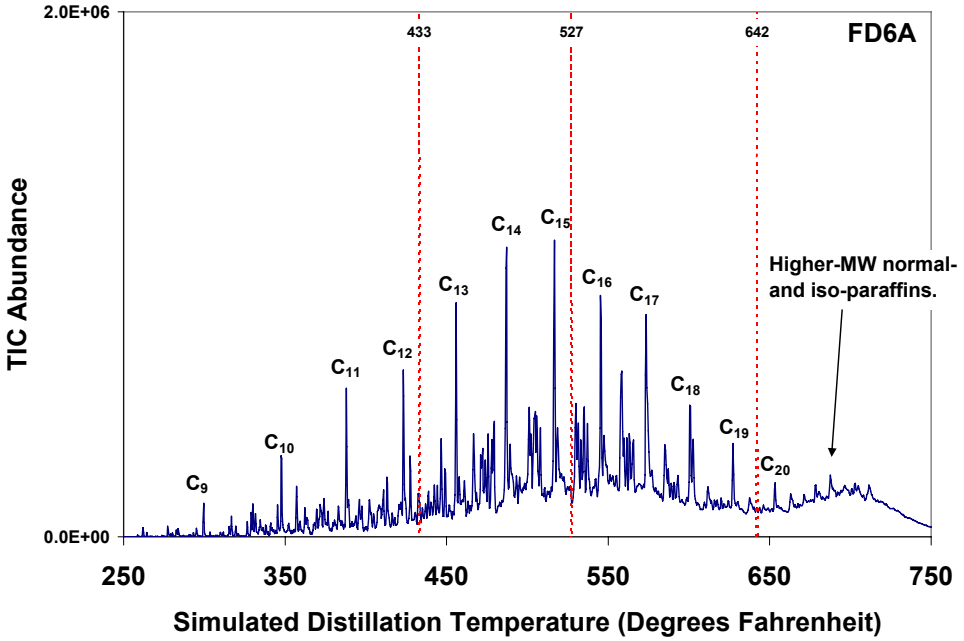

Figure 4.6. 1-D GC-MS chromatogram of FD6A, including D86 10%, 50%, and 90% reference lines.

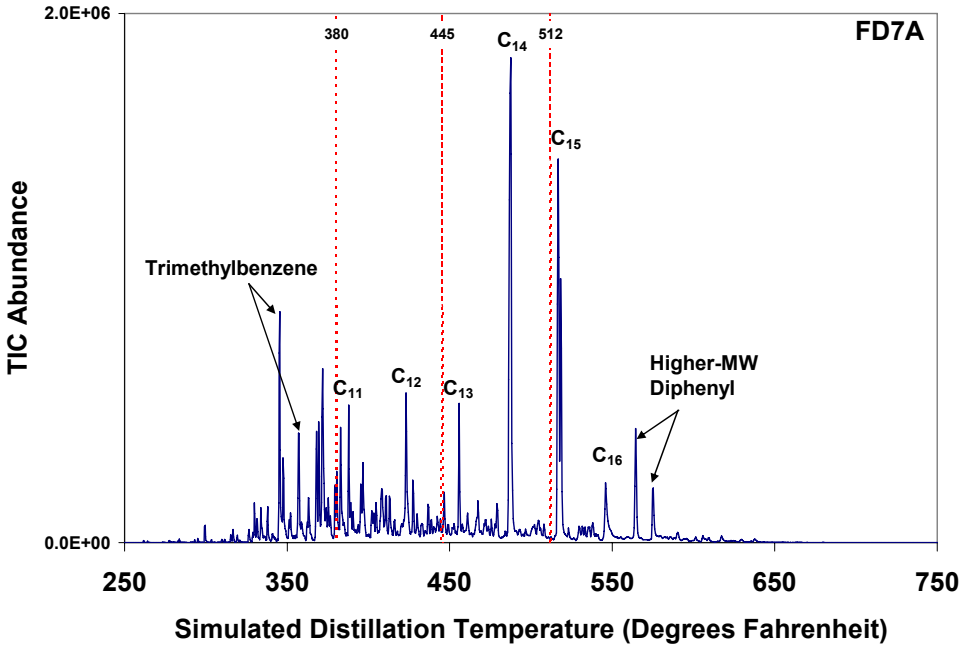

Figure 4.7. 1-D GC-MS chromatogram of FD7A, including D86 10%, 50%, and 90% reference lines.

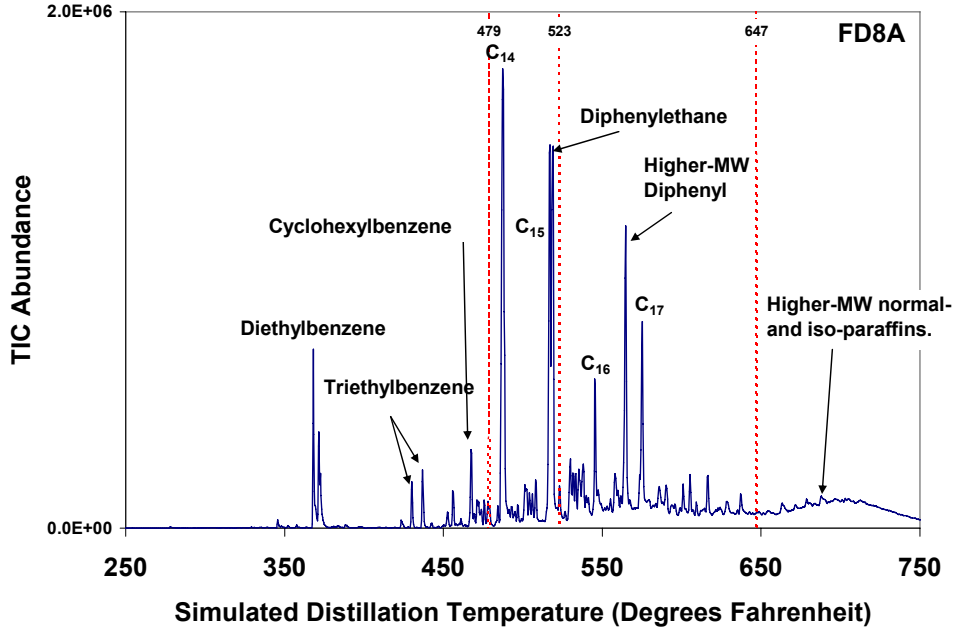

Figure 4.8. 1-D GC-MS chromatogram of FD8A, including D86 10%, 50%, and 90% reference lines.

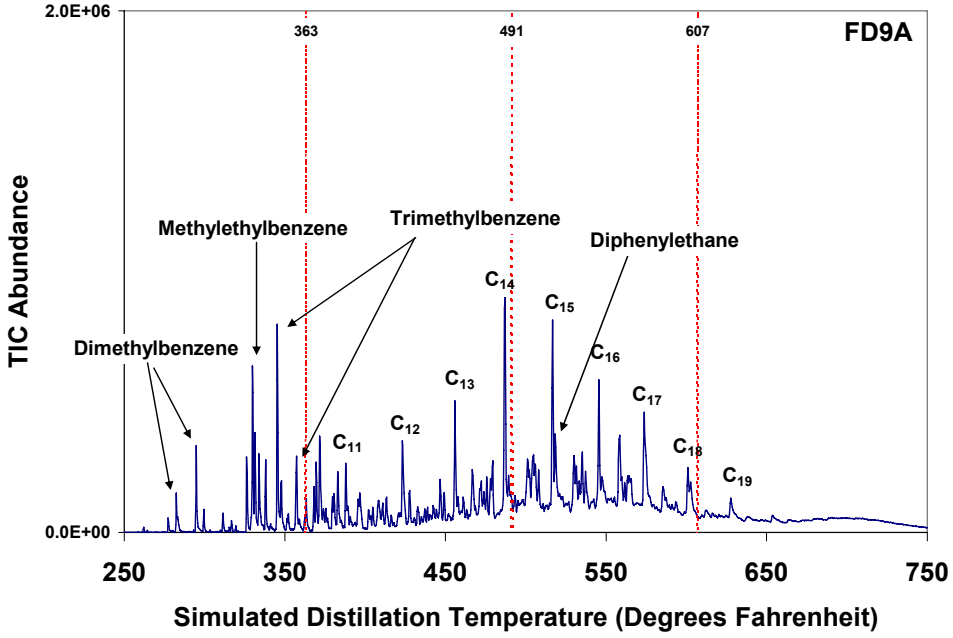

Figure 4.9. 1-D GC-MS chromatogram of FD9A, including D86 10%, 50%, and 90% reference lines.

4.1.1 Center-Point Fuel (FD9A)

FD9A (the center-point fuel) has an alkane profile that is typical of a middle-distillate fuel. The distribution is more-or-less normal and centered about C_{14} with lesser amounts of isoparaffins. However, the substituted monoaromatics at the low end of the boiling range are atypical for commercial diesel fuels. FD9A has an aromatic content that is typical of most of the FACE diesel fuels in that most of the aromatic content is made up of very volatile substituted monoaromatics with very little napthalenic content. Some aromatic content is also derived from diphenylethane, which is used commercially as a heat transfer fluid. FD9A exhibits a hydrocarbon distribution that essentially ends at C_{19} and contains little, if any, material that boils above 650°F. Given the relative high volatility (low distillation temperature) of the monoaromatics present, FD9A exhibits a distillation in which the first 10% volume distilled off is made up of molecules typically exhibiting a low-cetane character. The remainder of the fuel distillation has a higher cetane character because of the higher levels of normal alkanes present.

4.1.2 Low-Cetane Fuels (FD1A–FD4A)

FD1A and FD3A are the low-T_{90}, low-CN fuels. Both of these fuels exhibit a normal alkane profile that is skewed toward lower carbon numbers compared with the distribution exhibited by FD9A. This reflects the low-T_{90} formulation of these fuels. The monoaromatics for these fuels are present at levels similar to or greater than the individual normal alkanes; this is atypical of marketplace fuels. In both cases the first 50% of the distillation is made up of compounds typically thought of as low-cetane, with normal alkanes typical of middle-distillate fuels in the upper half of the boiling range. FD1A has a distillation that continues to C_{20}, while the FD3A distillation ends at C_{18}.

FD2A and FD4A are the high-T_{90}, low-CN fuels. Neither fuel bears much resemblance to marketplace fuels. 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 between 450 and 650°F. FD4A has a similar hydrocarbon distribution, but with the addition of isoparaffins in the boiling range from 450 to 650°F. There is some n-paraffin content from C_{12} and C_{13}, but this is minor compared with the isoparaffin content. These hydrocarbon distributions explain the odd distillation behavior observed for these fuels from the ASTM D86 results.

4.1.3 High-Cetane Fuels (FD5A–FD8A)

FD5A and FD7A are the low-T_{90}, high-cetane fuels. Both 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. FD7A also contains higher-molecular weight diphenyl compounds near the end of the distillation.

FD6A and FD8A are the high-T_{90}, high-cetane fuels. FD6A exhibits a broad distribution of n-paraffins and isoparaffins, from C_9 to C_{20} and including the higher molecular weight paraffin stream that is common to the high-T_{90} fuels. The substituted monoaromatic stream is present but is not pronounced as with many of the other fuels. FD8A is an unusual formulation. It is characterized by a narrow cut of n-paraffins and isoparaffins from C_{14} to C_{17}. There are also very high concentrations of diphenyl compounds, including diphenylethane and higher molecular weight diphenyls. Substituted monoaromatics make up the majority of the first 10% of the distillation, and the last 10% of the distillation is made up of the higher molecular weight paraffinic stream typical of the high-T_{90} fuels.

This fuel, in particular, is reminiscent of the fuels formulated several years ago for the Diesel Emissions Control Sulfur Effects program.

4.2 TWO-DIMENSIONAL GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSES

4.2.1 Introduction

Fuel composition will affect the physical properties of the fuel as well as combustion characteristics. Oils from petroleum sources, and nonpetroleum sources such as oil sands and shales, consist of thousands of compounds, which makes analysis for individual fractions challenging. While the detailed analysis of "straight run" gasoline to C_{12} is well known, the analysis of middle distillates like jet fuel and diesel can be very challenging. The chemistry of the fuel may also influence fuel properties such as lubricity, so the molecular description of new fuels is critical. With new challenges from both the sources of oil and end uses, the new methods that are being developed for the analysis of fuels such as GC-FIMS and 2-D GC are particularly important. The results of these analyses are often validated by comparison with standard methods such as the PIONA method, although PIONA was developed for gasolines and is typically not performed for higher boiling fuels such as diesel. GC-FIMS and 2-D GC with FID detection are discussed elsewhere. This section focuses on 2-D GC with mass spectrometric detection (2-D GC-MS).

Advances in mass spectroscopy, high-speed data acquisition, and GC have led to the development of a powerful tool for analysis of complex organic mixtures: 2-D GC-MS, which combines two-dimensional GC with TOFMS. The particular instrument used in our experiments (Pegasus 4D GC×GC-TOFMS) is commercially produced (LECO Corporation, St. Joseph, Michigan) and has been used in the analysis of complex mixtures such as fuels, environmental samples, and pesticide residues.

4.2.2 Two-Dimensional Time-of-Flight Mass Spectrometry Description

After the sample is injected into the instrument, it travels down column 1 and all of the compounds that exit the column in 6 s are held in a cryogenic switching trap (referred to as the "Thermal Modulator"). At the end of 6 s, the trap delivers its collection to column 2, and these compounds are then separated and delivered to the TOF mass spectrometer for analysis. The most polar compounds have the highest retention times (RTs) in column 2, so they end up with a longer RT2 and visually are higher in the y-dimension. Figure 4.10 shows a typical three-dimensional plot produced by the software, where the z-dimension shows the relative abundance of a particular compound. (The fuel shown in Figure 4.10 is FD9A.)

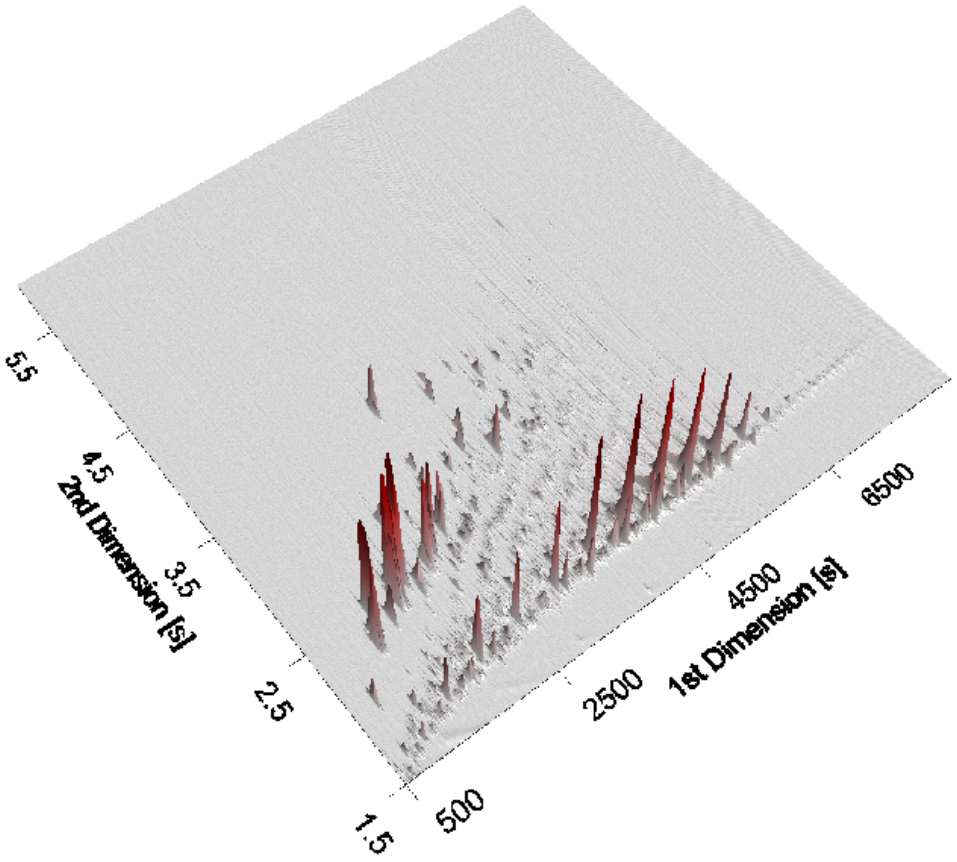

Figure 4.10. Three-dimensional map of FD9A. The column 1 (x-) dimension is to the right and up. The column 2 (y-) dimension is up and to the left. The largest peaks along the x-axis are the n-alkanes, and the large peaks on the left are monoaromatics.

4.2.3 Analysis software

The analysis software is very complex and, coupled with a powerful search library, allows for much flexibility in peak assignment and identification. For example, in the first run 3,000 compounds were identified for FD9A. Many of these compounds are of little consequence; compounds associated with bleed of the siloxane phase on the column, for instance, are identified and counted. Another issue that was difficult in particular with the FACE fuels is the problem of abundance sensitivity. In this situation a large amount of a given compound [e.g., n-tetradecane (C_{14})] will create a wide peak (>6 s) in column 1 that is split more than once by the cryogenic trap. Thus, column 2 receives two or more "loads" of C_{14}, and the result is separate peaks for the same compound. The software allows one to combine these split peaks into the same peak by matching spectra, but in complex mixtures like fuels with normal and branched alkanes, that may result in a 2-methyltridecane being lumped in with a big n-tetradecane peak. The approach taken with the FACE fuels has been more conservative but manually intensive: peaks are matched by inspection of the spectra and then their areas are added together to form the result for a particular compound. This was especially true with the peaks associated with the C_9 monoaromatics, which were very abundant in some of the FACE fuels The software parameters for the analysis of FACE fuels are given in Table 4.1.

Table 4.1. LECO Software Analysis Parameters

Baseline offset	0.5
Peak smoothing	Auto
Peak width	0.1
Maximum number of peaks to find	1,000
Segmented processing Start of run—500s 500s—end of run	 Peak find off Peak find on S/N = 100 Number of apexing masses = 2
GC×GC parameters—match to combine Peak widths broaden throughout run	600 10 at 776s (retention time 1) 30 at 3620s
Library search Number library hits to return Range of masses to search Minimum molecular weight Maximum molecular weight Mass threshold Minimum match to assign name Libraries to search	Normal, not quick Reverse (forward done manually if no good match found) 20 library hits 30 to 400 50 amu 500 amu 10 600 Mainlib, replib
Masses to use for area calculations	Apexing
Classifications	Preliminary based on diesel standard

Preliminary classification into groups was done based on analysis of a standard mixture run on the same day as the FACE fuels. The groups included the even-numbered n-alkanes from C_{10} to C_{28}, decalin, and PAHs. Peaks due to the solvents and peaks that were not coming from the sample being analyzed were also identified, at second retention times less than 1.4 minutes. From the mass spectral analysis, it is likely that these arose from column bleed. At very long second retention times, some carryover was seen for some of the samples. This carryover represented only a minor portion of the signal and so was not included in the analysis.

4.2.4 Results

For the analysis, the peaks were sorted first by percent of the total peak area, calculated to identify the most common compounds. At this point, all compounds that made up less than 0.1% of the total peak area were set aside. This left anywhere from ~100–250 identified compounds for each FACE fuel. These select peaks represented from 83 to 92% of the total peak area. Contaminant peaks such as the Si-containing column bleed were typically less than 0.05%. Table 4.2 gives the number of peaks and the percent of total area calculated for each FACE fuel. A major drawback of this approach, of course, is the exclusion of potentially important compounds if they are part of a refinery mixture stream. Indeed, it was found that a complex mixture of C_{21} and C_{22} paraffins was added to FD2A, FD4A, FD6A, and FD8A to increase their T_{90} values. This mixture did not contain a single compound greater than 0.02% of the total area but was too important to ignore. In this instance, the mixture was relatively easy to define by an upper and lower retention time, so these compounds were included in the analysis of the high T_{90} fuels.

Table 4.2. Number of Significant Compounds in the Nine FACE Fuels

Fuel	Number of peaks greater than 0.1%	Percent of total peak area
FD1A	196	89.2
FD2A	181	91.8
FD3A	221	83.8
FD4A	208	88.6
FD5A	231	83.4
FD6A	202	82.9
FD7A	189	86.2
FD8A	97	91.3
FD9A	163	89.5

After setting aside the peaks that made up less than 0.1% of the peak area, the remaining compounds were sorted again by retention time in column 1 (RT1). Using the standard mixture run as a guide, the boiling point vs RT1 relationship was established just as was done in Sect. 4.1 with the 1-D GC-MS results. A map of the compounds was then plotted with boiling point on the x-axis, and polarity, or RT2, on the y-axis. The results are presented visually in the form of color-coded bubble charts so that the interrelationships of the different compound classes can be observed (see even numbered figures from 4.12 to 4.30).

One way of thinking about polarity, or the RT2 dimension, in fuel mixtures that do not contain oxygen is in terms of the carbon to hydrogen (C/H) ratio. The higher the C/H ratio, the more aromatic the species. Naphthalene ($C_{10}H_8$; C/H = 1.2) has the highest C/H ratio of the compounds in the FACE fuels, octane (C_8H_{18}; C/H = 0.444) the lowest. Thus, for the most prevalent compounds in each fuel, the C/H ratio was calculated and then plotted against the carbon number for that compound. Compound classes were again color-coded. Carbon number is often useful in modeling combustion. The carbon number of each compound was determined, often manually, because of the misidentification of the longer chain n-alkanes and branched alkanes. In some cases, there was too much fragmentation to discern a molecular ion for an alkane, so a C number was determined based on position relative to the corresponding n-alkane. For example, all unidentifiable isoparaffins were assigned $C_{16}H_{34}$ if they eluted between n-C_{15} and n-C_{16}. In all likelihood, highly branched C_{17} isoparaffins are also eluting between n-C_{15} and n-C_{16}, so this approach is likely to under weight the heavier C-number branched alkanes.

The two plots for each FACE fuel and two plots for a commercial California ultralow sulfur diesel for comparison are on the following pages (Figures 4.11–4.30).

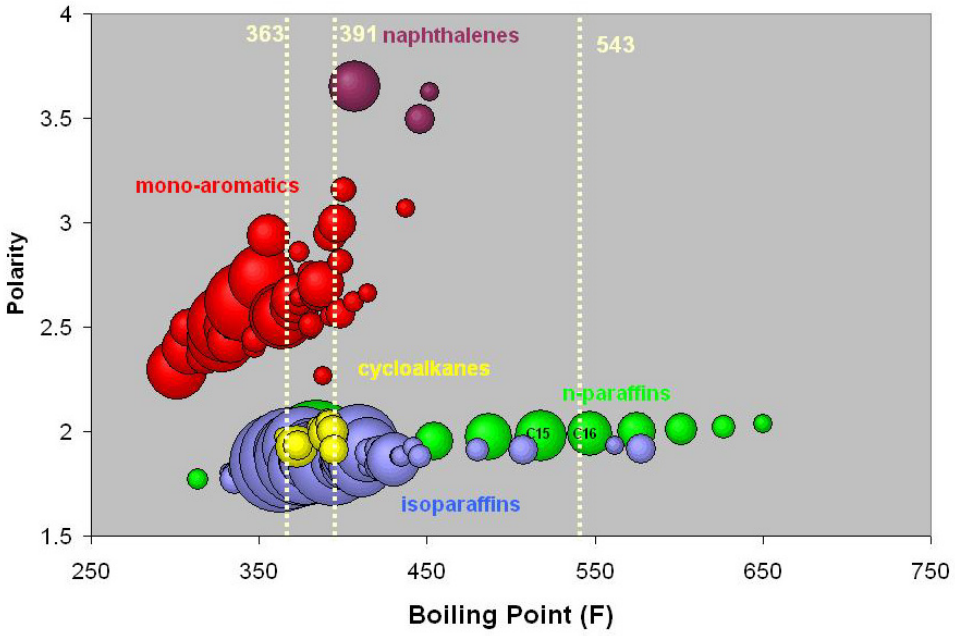

Figure 4.11. FD1A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1-D GC-MS work.

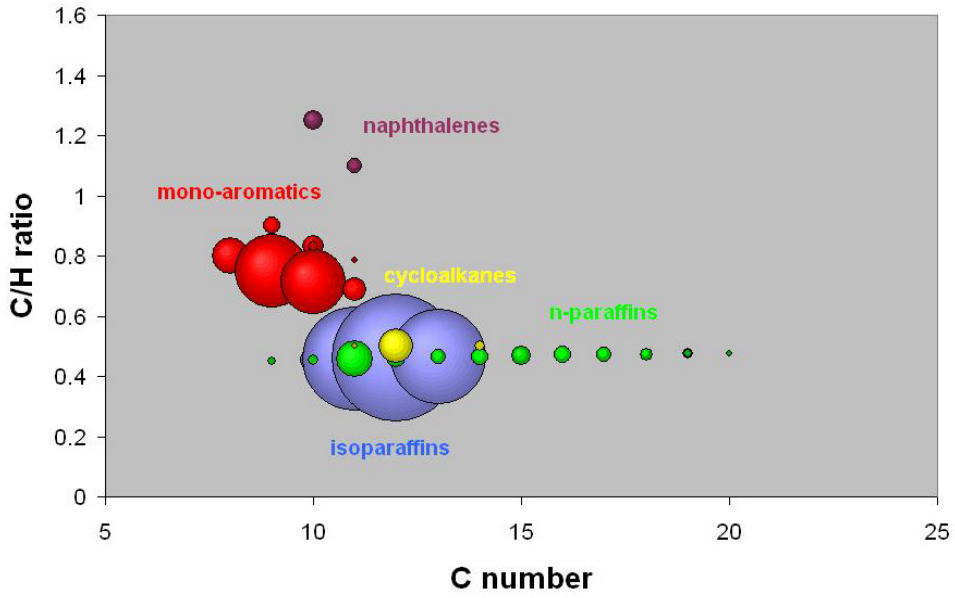

Figure 4.12. FD1A fuel compound C/H ratio as a function of carbon number.

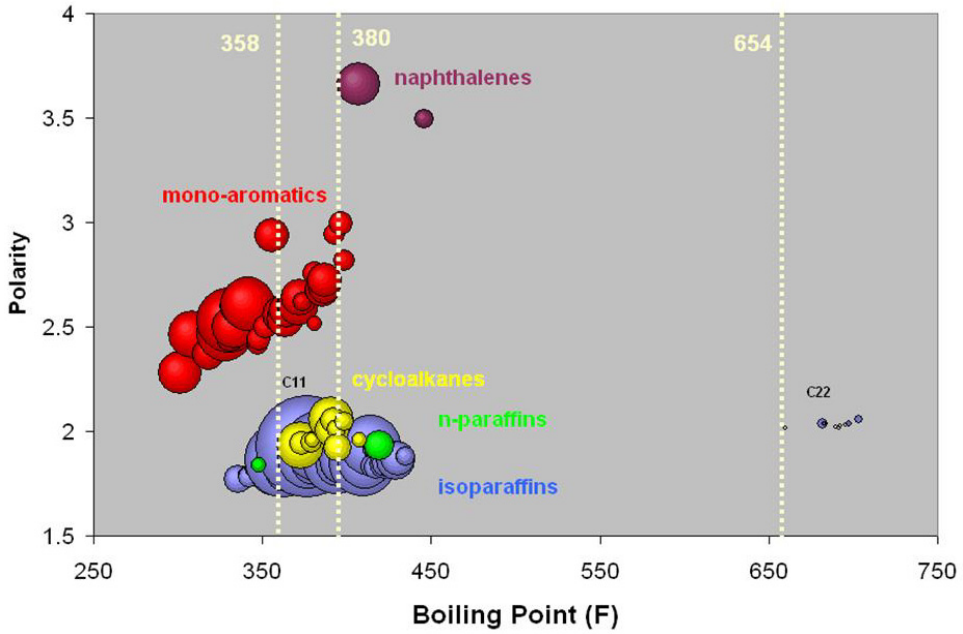

Figure 4.13. FD2A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1-D GC-MS work.

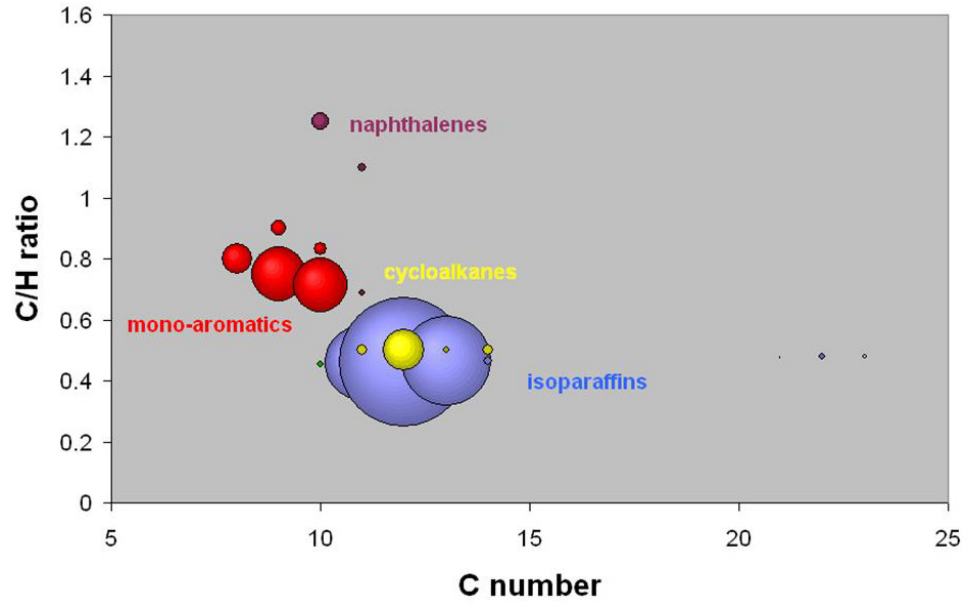

Figure 4.14. FD2A fuel compound C/H ratio as a function of carbon number.

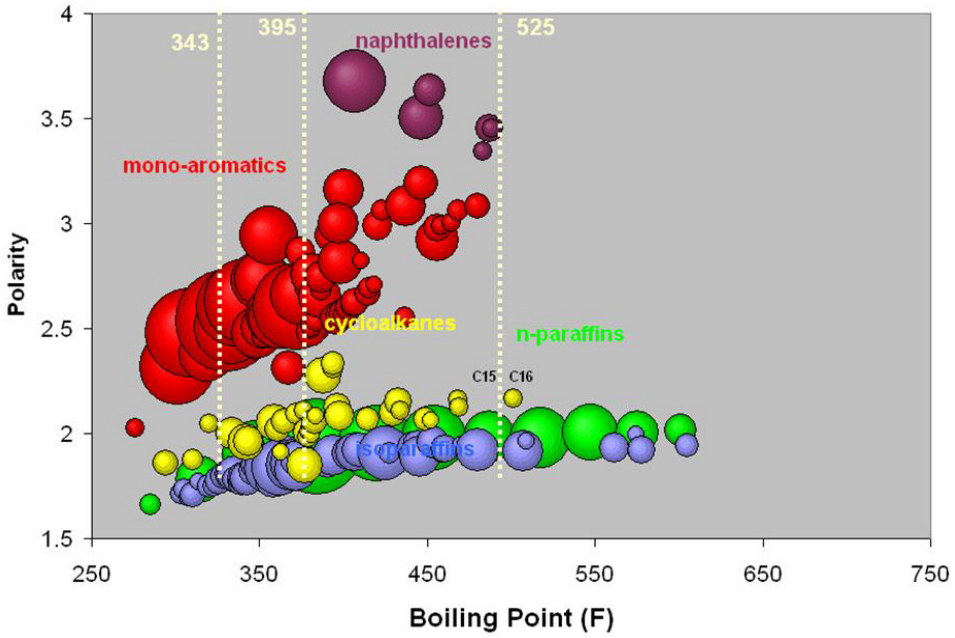

Figure 4.15. FD3A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1-D GC-MS work.

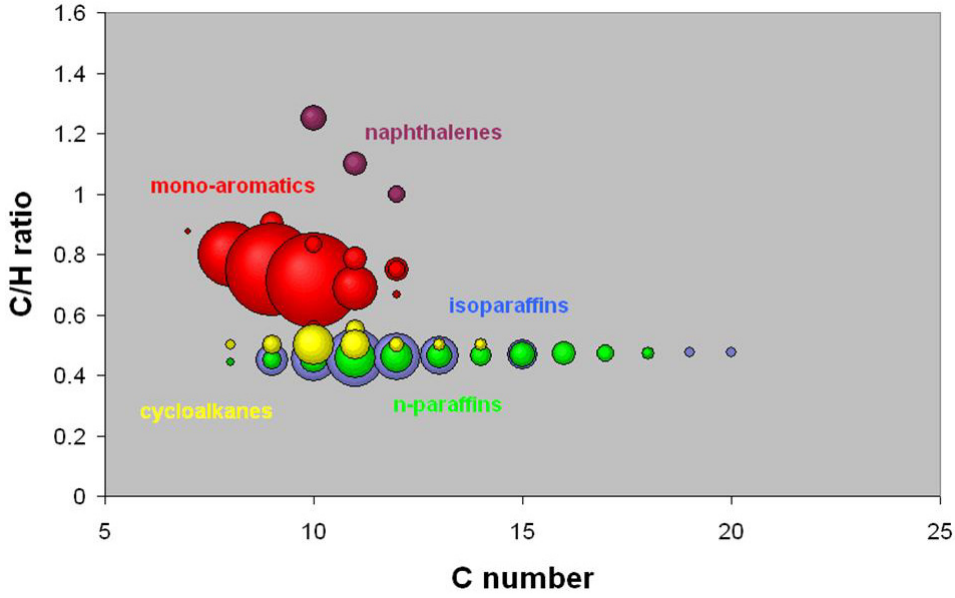

Figure 4.16. FD3A fuel compound C/H ratio as a function of carbon number.

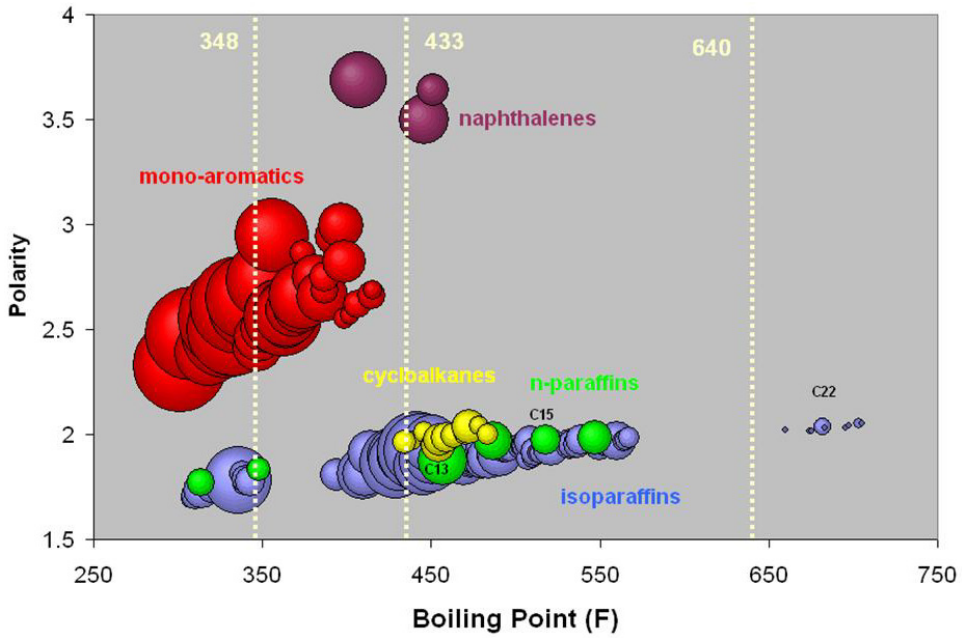

Figure 4.17. FD4A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1-D GC-MS work.

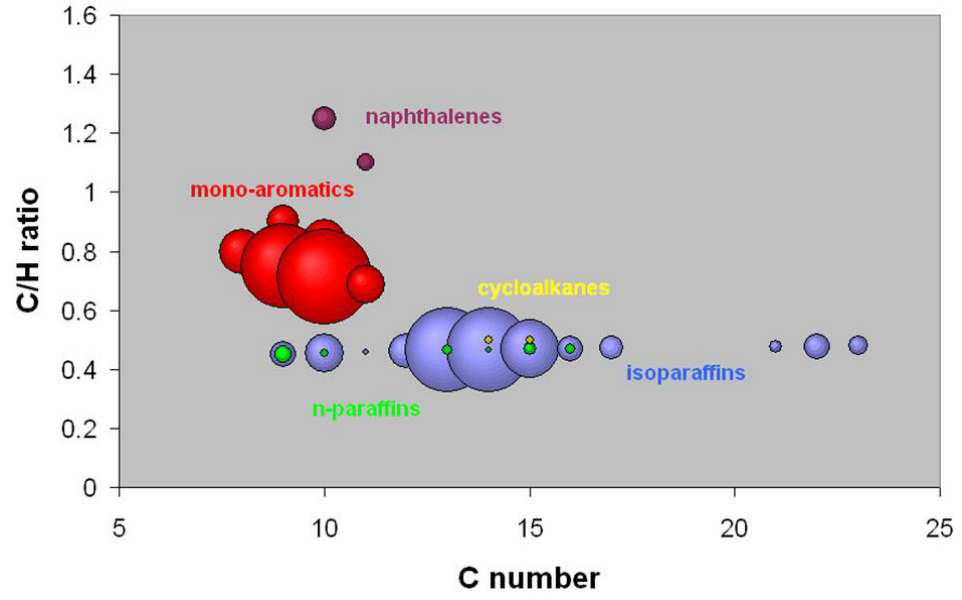

Figure 4.18. FD4A fuel compound C/H ratio as a function of carbon number.

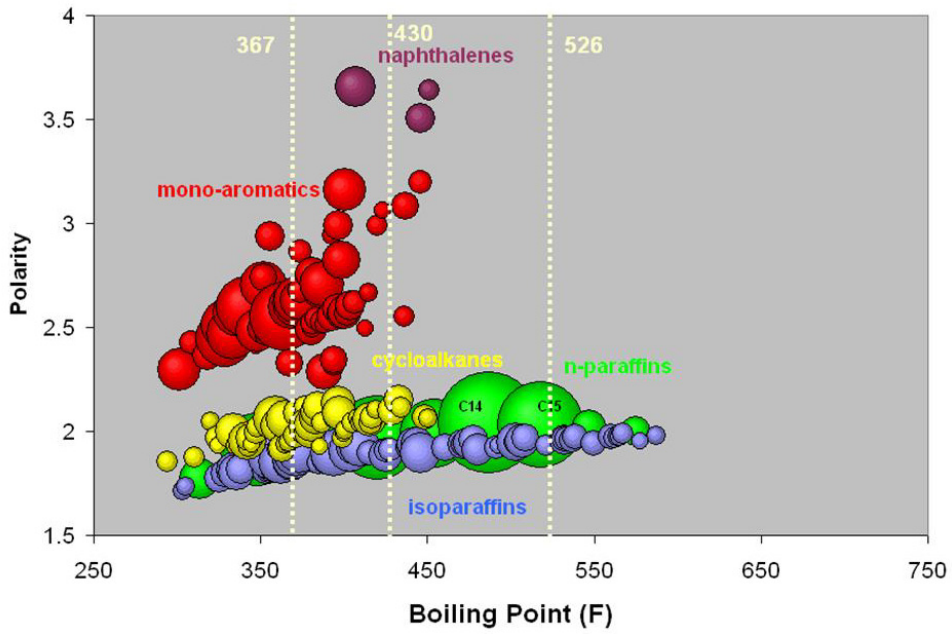

Figure 4.19. FD5A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1-D GC-MS work.

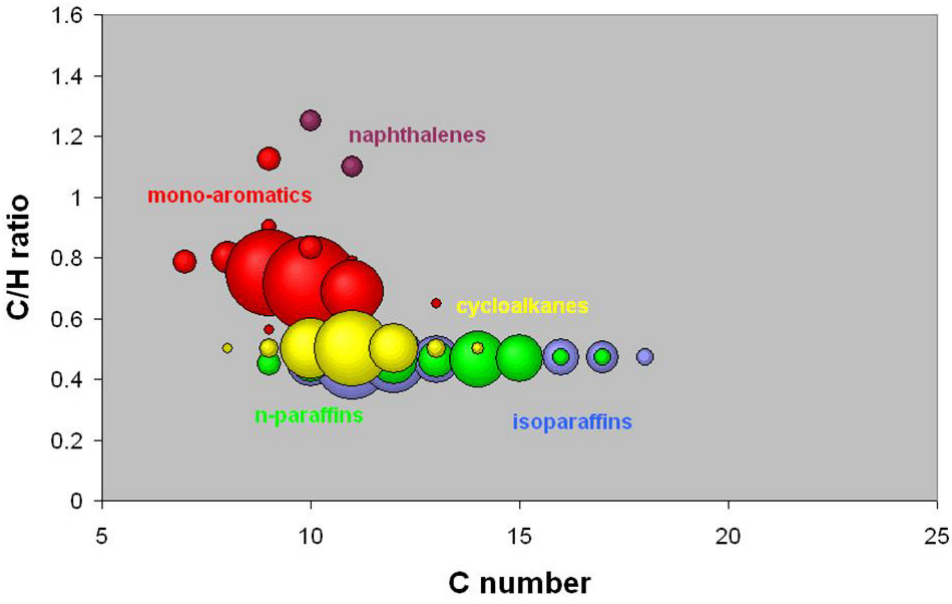

Figure 4.20. FD5A fuel compound C/H ratio as a function of carbon number.

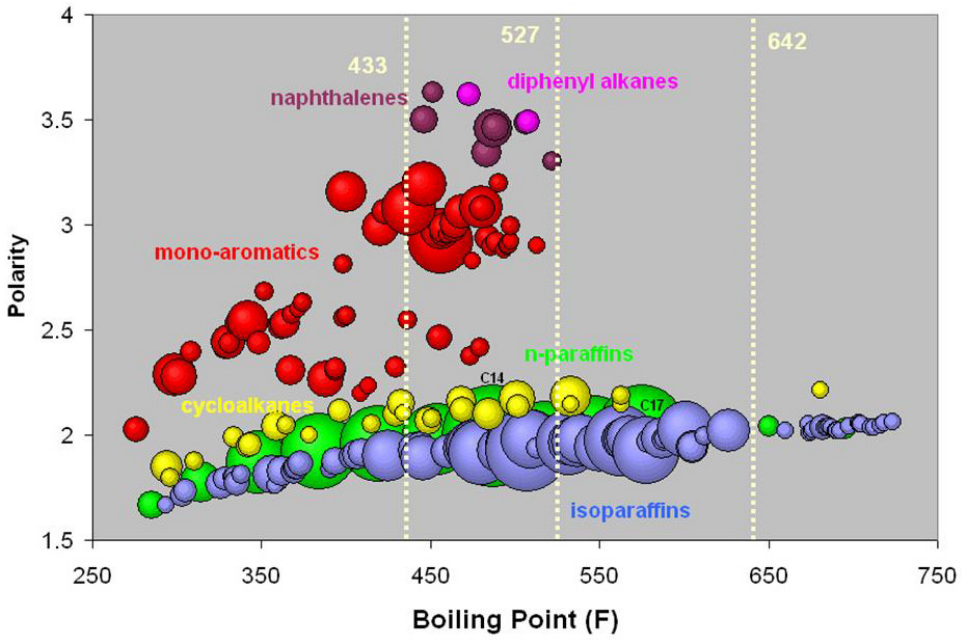

Figure 4.21. FD6A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1-D GC-MS work.

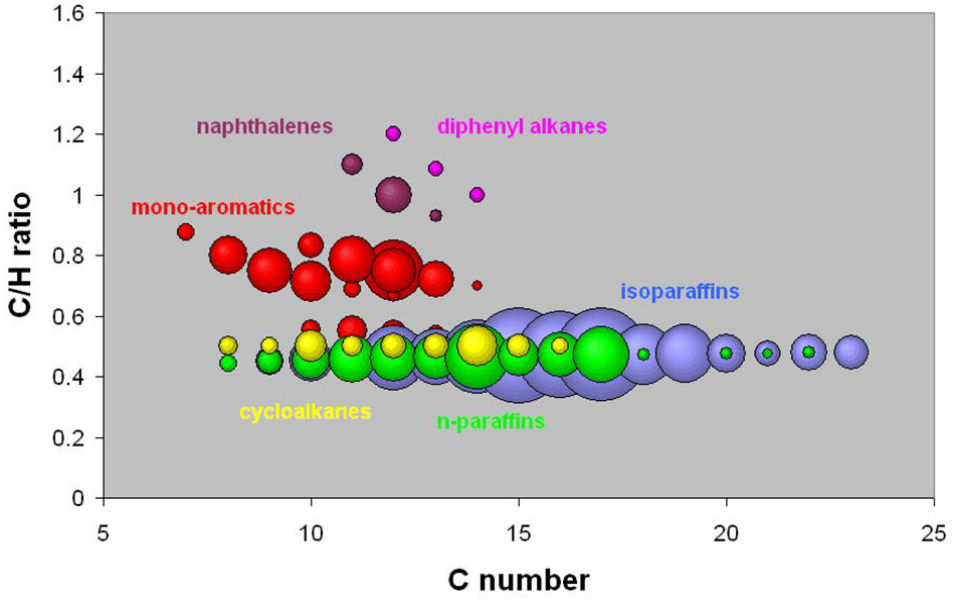

Figure 4.22. FD6A fuel compound C/H ratio as a function of carbon number.

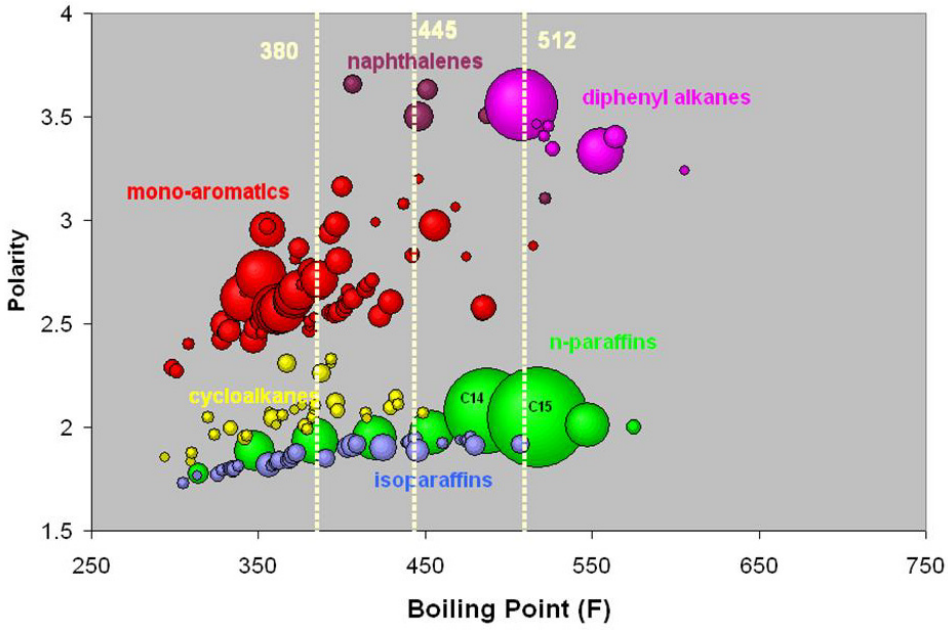

Figure 4.23. FD7A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1-D GC-MS work.

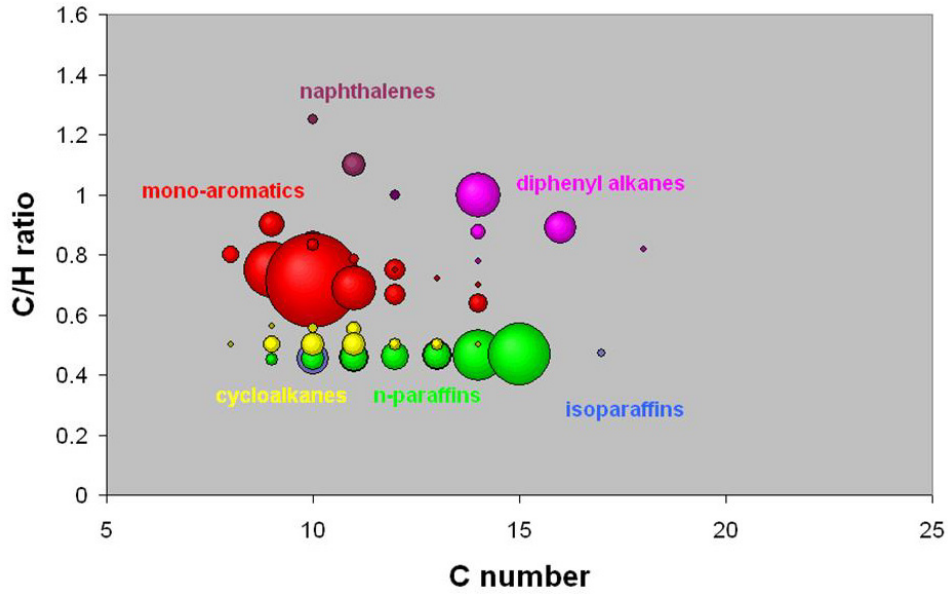

Figure 4.24. FD7A fuel compound C/H ratio as a function of carbon number.

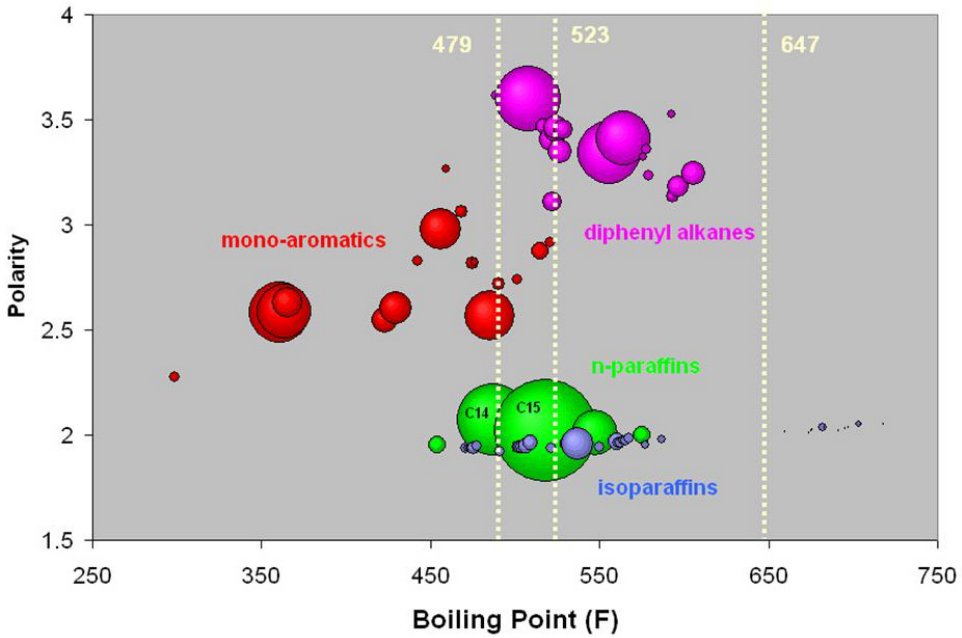

Figure 4.25. FD8A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1-D GC-MS work.

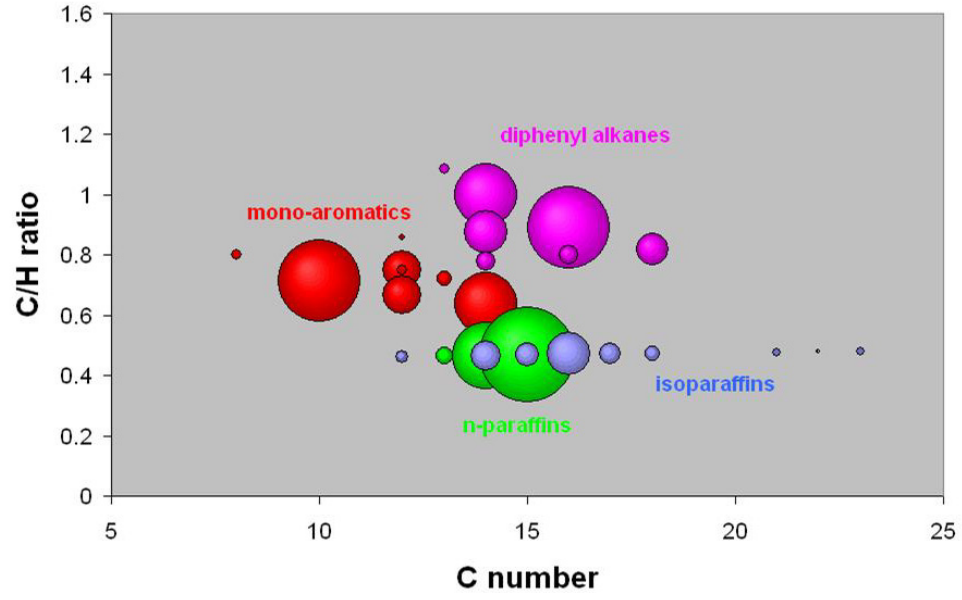

Figure 4.26. FD8A fuel compound C/H ratio as a function of carbon number.

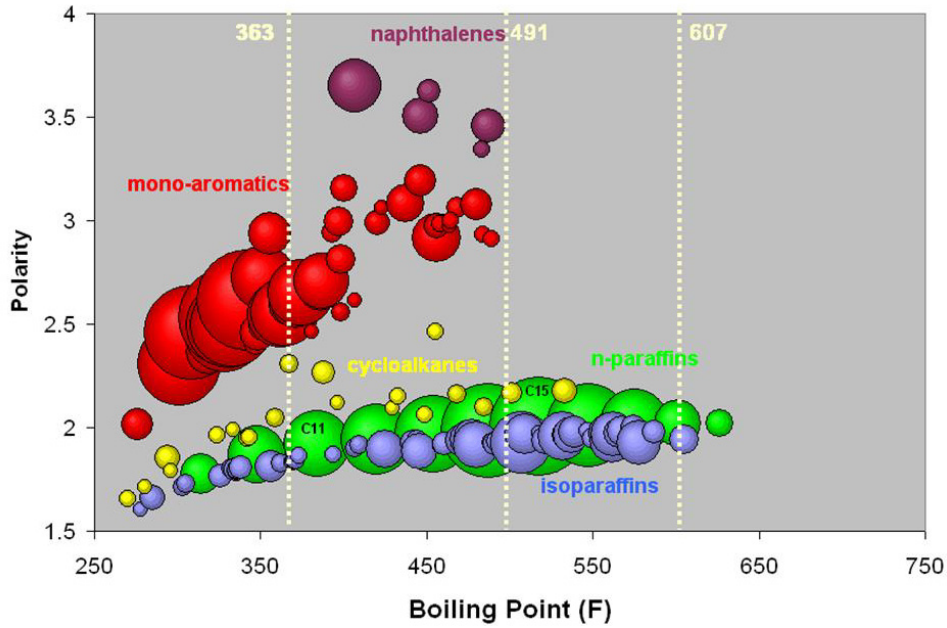

Figure 4.27. FD9A compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on the 1D GC-MS work.

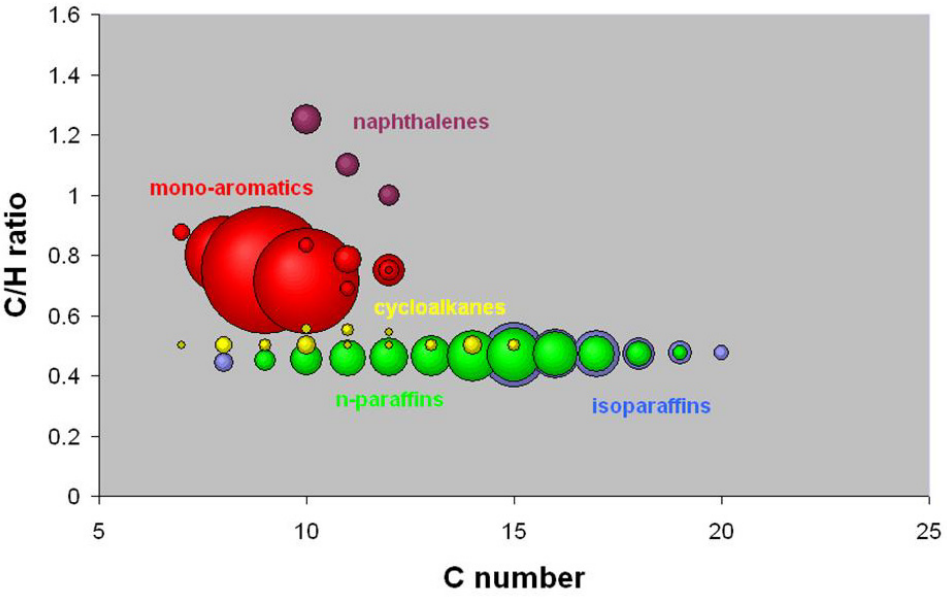

Figure 4.28. FD9A fuel compound C/H ratio as a function of carbon number.

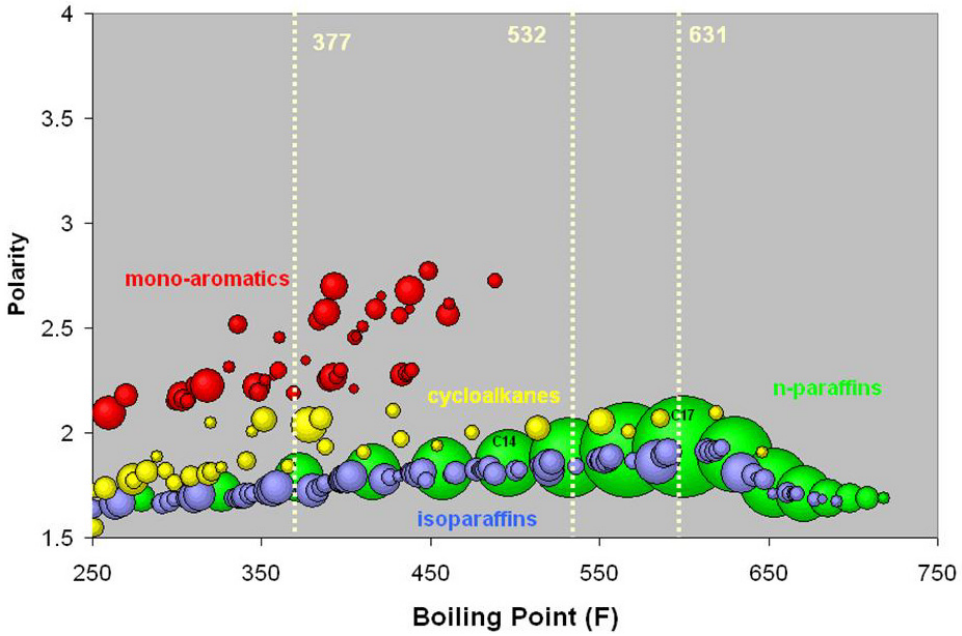

Figure 4.29. Commercial California ultralow sulfur diesel fuel compounds as a function of boiling point. The dashed lines, left to right, represent T_{10}, T_{50}, and T_{90} based on data provided by the manufacturer. (Note smaller bubbles.)

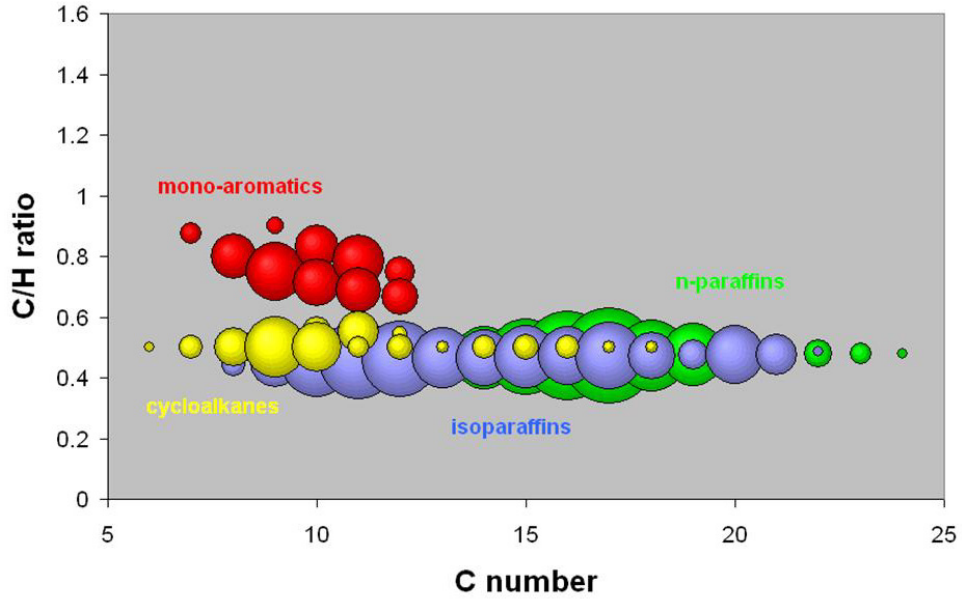

Figure 4.30. Commercial California ultralow sulfur diesel fuel compound C/H ratio as a function of carbon number.

4.2.5 Discussion

The data show the wide variation in the composition of the FACE fuels, although several distinct blending streams seem evident. For instance, a large amount of similar C_{10} monoaromatics is added to FD3A, FD4A, FD7A, and FD8A to make them higher in aromatics. Isoparaffins appear to be used to lower cetane number in the low cetane fuels. FD1A, FD2A, FD3A, and FD4A have isoparaffins, mostly around C_{11} in size, as a large proportion of their volume. In fact, FD2A is devoid of virtually all n-paraffins and typical diesel range paraffins. T_{90} appears to be controlled by the addition of the C_{22} and C_{23} paraffins as a separate stream. The cycloalkane component also varies. Presumably these compounds are created from monoaromatics and naphthalenes when the hydrogen is added to remove S-containing benzothiophenes. In FD9A and the commercial fuel, the size of these compounds reaches C_{15} and C_{18}, respectively. Cyclohexanes with alkyl "tails" and decahydronaphthalenes and octahydroindenes were found. Figure 4.31 illustrates examples of these compounds.

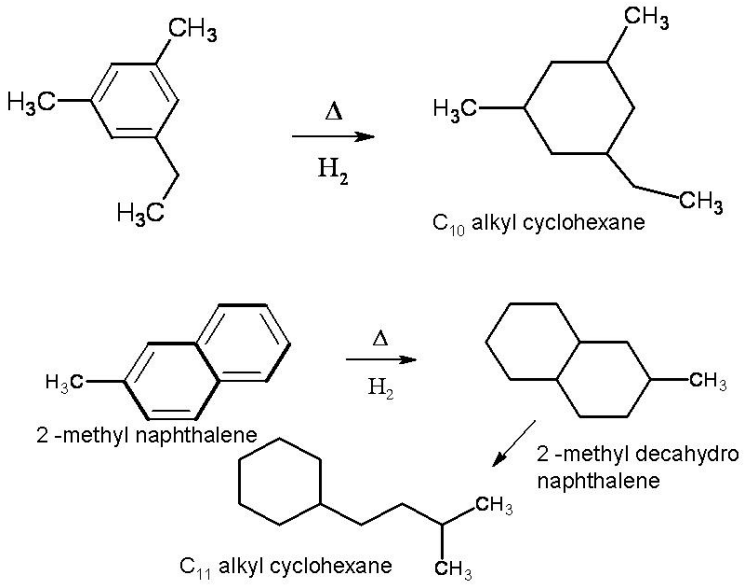

Figure 4.31. Hydrogenation of feedstocks can lead to numerous cycloalkanes. Cyclohexanes with long "tails" can arise both from the transformation of strained decahydronaphthalene molecules and from multisubstituted cyclohexanes.

Also, although the individual compounds were not more than 0.1% of the total area, the high molecular weight paraffin stream that was added to FD2A, FD4A, FD6A, and FD8A (high T_{90}) was identified. These compounds appear on the right side of the plots for these fuels, and while specific individual isoparaffins were difficult to identify, the general structures and retention times were consistent with C_{21} to C_{23} isoparaffins.

Naphthalenes (including methyl and dimethyl varieties) were present in most of the fuels with the exception of FD8A and the commercial fuel, neither of which had any significant heavy aromatics. California limits the aromatic content of diesel fuel, so this result was not unexpected. FD7A and FD8A, and to a limited extent FD6A, used a heavy aromatic stream which has been labeled diphenylalkanes to enhance aromatic content and boost T_{90}. Examples of this family of compounds are illustrated in Figure 4.32, with the most prevalent compound being diphenylethane.

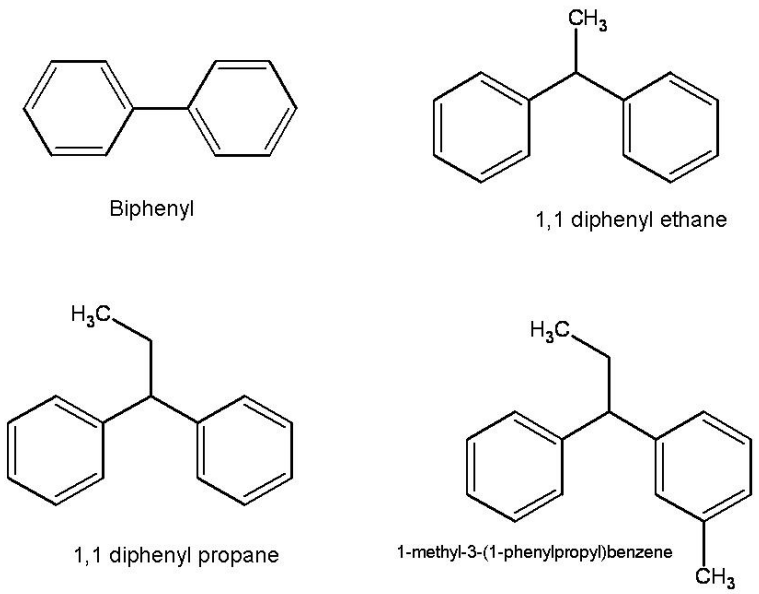

Figure 4.32. Examples of compounds in the diphenylalkane blending stream.

These compounds are similar to naphthalenes in their C/H ratio but have a higher boiling point, so it is not clear whether they behave similarly in the engine. Commercially, mixtures of these compounds are often sold as heat transfer fluids because they have good stability below 250°C. Ten years ago in a previous DOE program, Diesel Emissions Control—Sulfur Effects, the base 3 ppm sulfur fuel contained these compounds. The purpose then was to boost the aromatic content of "future" ultralow sulfur fuels while maintaining the distillation properties of the current diesel fuel.

Carbon number and C/H ratio are often critical fuel parameters for combustion modeling. By plotting the C vs C/H ratio, one obtains a "flatter" description of the fuel that bins similar molecules. It may be possible, then, to use such a matrix description of each of the fuels in models.

Finally, one of the key assumptions that this analysis makes is that the peak area is representative of the amount of that compound in the mixture. The items in Table 4.1 highlighted in yellow show that the apexing masses are used for area calculations. What this means is that the largest mass fragment or two fragments are used to calculate the area of a given peak. This is important because n-alkanes will have an m/z = 57 fragment as the apexing fragment, but much of the area will be contained in the other fragments. In the current analysis method, the reported peak area for each compound is added to the peak areas for the other compounds to get a total area, and then the fraction of that total represented by an individual compound is calculated as a percent. If we are ignoring the additional peak area represented by the fragments of the alkanes, it will have the effect of decreasing the total area for the compound and thus decreasing the relative amounts of the alkanes. The monoaromatic compounds are typically quantified from the ion m/z = 77, which is the dominant fragment, and the area of the side chains is relatively small, so the peak areas of the monoaromatics are going to be closer to the true proportion.

In contrast to the MS detector, FID is more quantitative in terms of carbon but does not identify the individual species. For the FACE fuels, it may be possible to match the peaks obtained with the 2-D GC-FID to the peaks obtained with the 2-D GC-MS and thus obtain a quasi-quantitative result for

each compound. This will help resolve the differences in the bulk numbers obtained with the different methods.

Two-dimensional GC-MS has proven to be a powerful tool for the analysis of these fuels. Because these initial data analyses were very time intensive, work in the future will focus on opportunities for incorporating rules into the data analysis software that would streamline the process. Work will also continue on the comparison between the 2-D GC-FID data and the 2-D GC-MS data.

4.3 REFERENCES

1. ASTM International, *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography,* ASTM D2887-08 (ASTM International, Pennsylvania, 2008).

2. ASTM International, *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure,* ASTM D86-09e1 (ASTM International, Pennsylvania, 2009).

5. TWO-DIMENSIONAL GAS CHROMATOGRAPHIC ANALYSIS OF FACE FUELS WITH FLAME IONIZATION DETECTOR

5.1 INTRODUCTION

Two-dimensional GC analysis with an FID (2-D GC-FID) uses instrumentation similar to that of 2-D GC-time-of-flight MS (TOFMS), but an FID is used instead of the mass spectrometer. The FID response is linear over a very wide range of concentrations and mainly proportional to the mass flow rate of carbon. It therefore may be considered a general hydrocarbon detector.

This detector can determine peak concentrations more accurately than the mass spectrometer, and the peak identification and classification capability is based completely on retention coordinates.

5.2 EXPERIMENTAL CONDITIONS

The 2-D GC-FID system used in our experiments was provided by LECO Corporation and included a cryogenically cooled modulator.

The column features and operating conditions for the 2-D GC-FID experiments are listed in Table 5.1.

Table 5.1. Operating Conditions for 2-D GC-FID Analysis

1st column	Varian Factor 4 VF5-HT, 30 m × 0.32 mm, df: 0.1
Main oven program	50–340°C; 5°C/min
2nd column	Varian Factor 4 VF17-MS, 1.5 m × 0.1, df: 0.2
Secondary oven program	40°C offset from main oven
Inlet temperature	350°C
Injection size	0.2 μL
Split ratio	40 : 1
Carrier gas	He; constant flow, 1.5 mL/min
Modulator temperature	55°C offset from main oven
Detector	FID, 350°C
Acquisition rate	100 Hz
Modulation period	8 s

5.3 EXPERIMENTAL RESULTS

Data handling such as contour plotting, 2-D GC peak collection, retention time measurements, and peak volume calculation were performed using ChromaTOF software provided by LECO Corporation.

The ChromaTOF software enables the creation of class and subclass regions inside an acquired chromatogram based on retention times. The classes could be created by drawing shapes around the groups of peaks of interest, producing what is called a template. After a template with the drawn classes is created, it can be applied to other samples. Figure 5.1 shows a class template together with one of the FACE fuels.

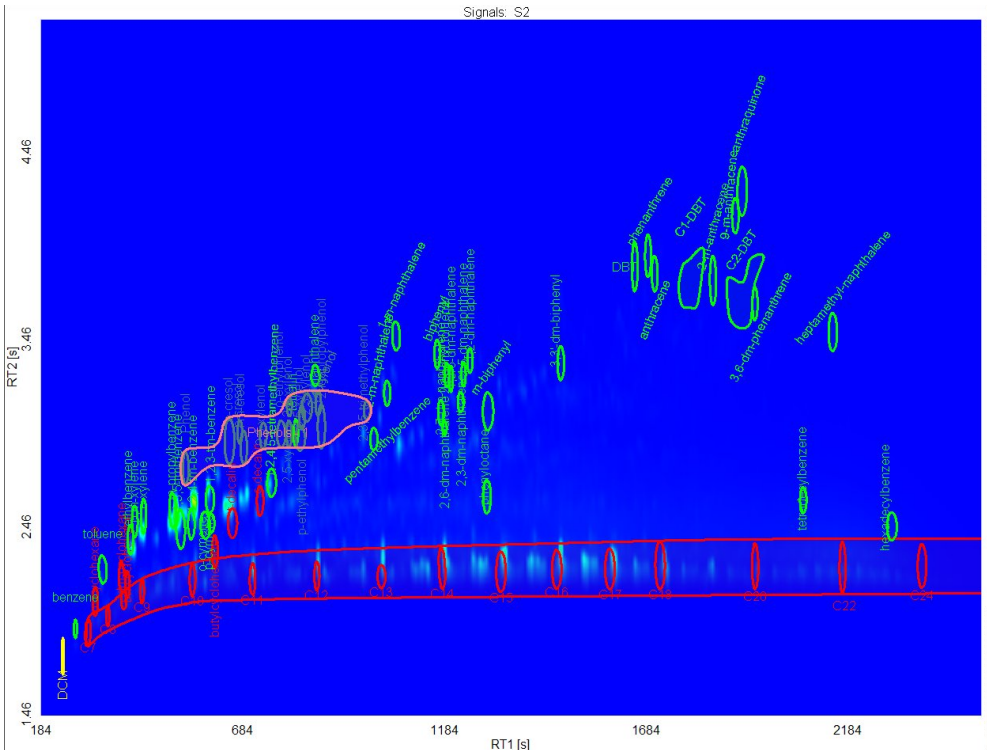

Figure 5.1. Contour plot chromatogram of FD9A sample with selected class of compounds.

Classification using the above mentioned technique grouped the compounds into structure-based chemical classes and quantified the peak/compound groups precisely by peak areas. Peak areas obtained after data preprocessing with ChromaTOF were transferred to Microsoft Excel, and the final classification report (see Table 5.2) was created there.

Table 5.2. Quantitative Group Type 2-D GC-FID Separation

Sample	n-Paraffins	Paraffins	Isoparaffins	Cycloalkanes	Known aromatics	Unknown aromatics	Total aromatics	Total
FD1A	6.78	59.06	52.28	12.17	8.08	19.97	28.05	99.28
FD2A	3.32	61.85	58.53	14.66	9.58	13.36	22.94	99.45
FD3A	10.49	37.97	27.48	6.19	6.55	48.01	54.56	98.72
FD4A	4.36	52.88	48.52	3.38	11.53	31.15	42.68	98.94
Face5	31.39	63.18	31.79	7.97	7.18	19.72	26.90	98.04
FD6A	13.45	62.58	49.12	7.78	1.56	26.01	27.57	97.92
FD7A	30.32	46.95	16.63	4.25	9.40	38.73	48.13	99.33
FD8A	23.00	45.57	22.57	3.02	1.10	48.73	49.83	98.42
FD9A	10.96	46.85	35.89	7.65	11.76	32.04	43.80	98.30

The highly structured chromatograms obtained from the analysis of all nine FACE fuels using 2-D GC-FID are shown on the following figures (Figure 5.2–Figure 5.10). 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. Signal intensity is illustrated on a color scale—light gray represents the baseline, and red (dark gray in black and white copies) represents the most intense peaks in the chromatogram. Additionally, primary retention times for compounds found in 2-D GC-FID were converted into boiling temperature scale and were presented in bubble plot form. This type of data visualization allows comparing results between 2-D GC-FID and 2-D GC-TOFMS maps.

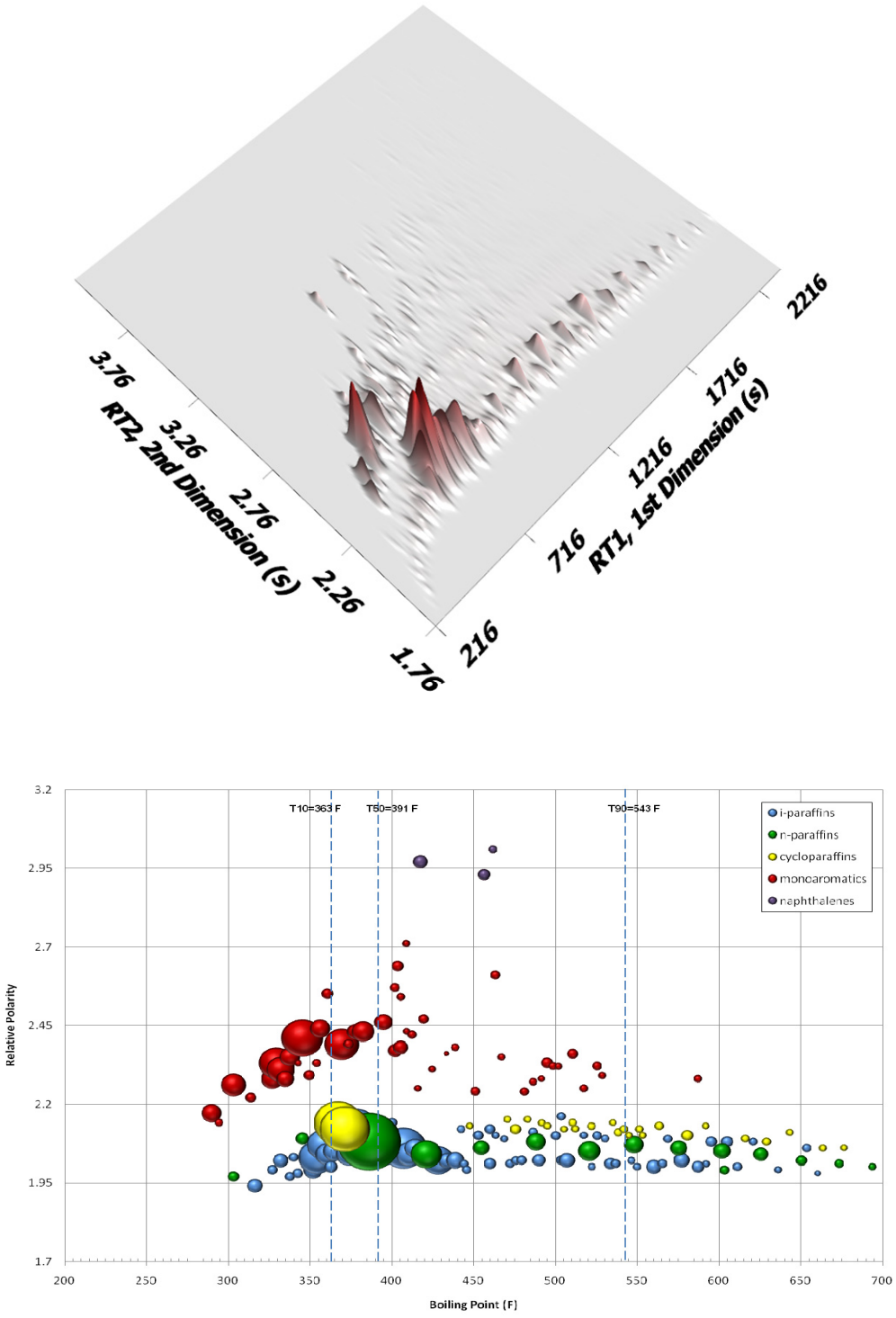

Figure 5.2. FD1A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

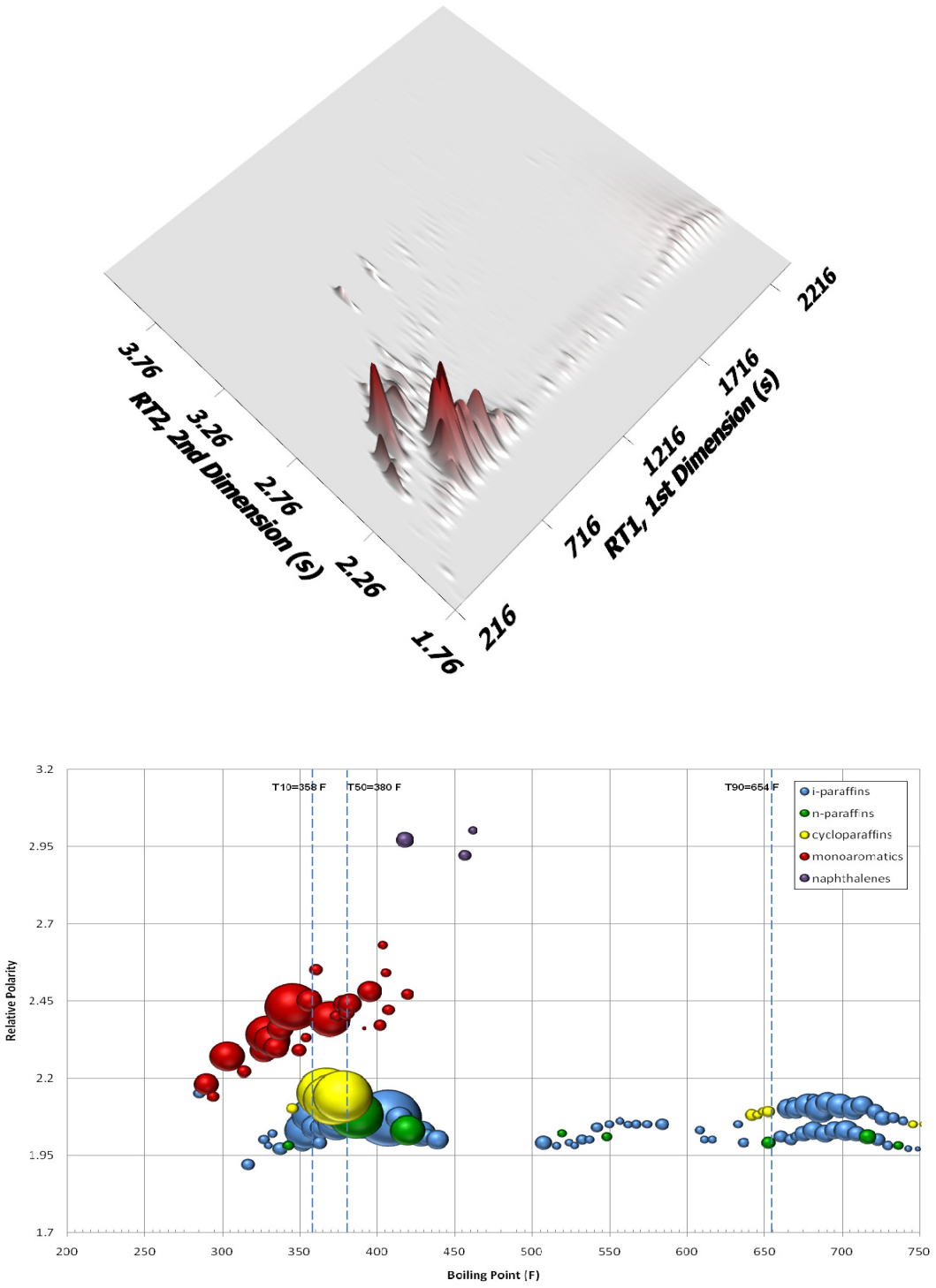

Figure 5.3. FD2A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

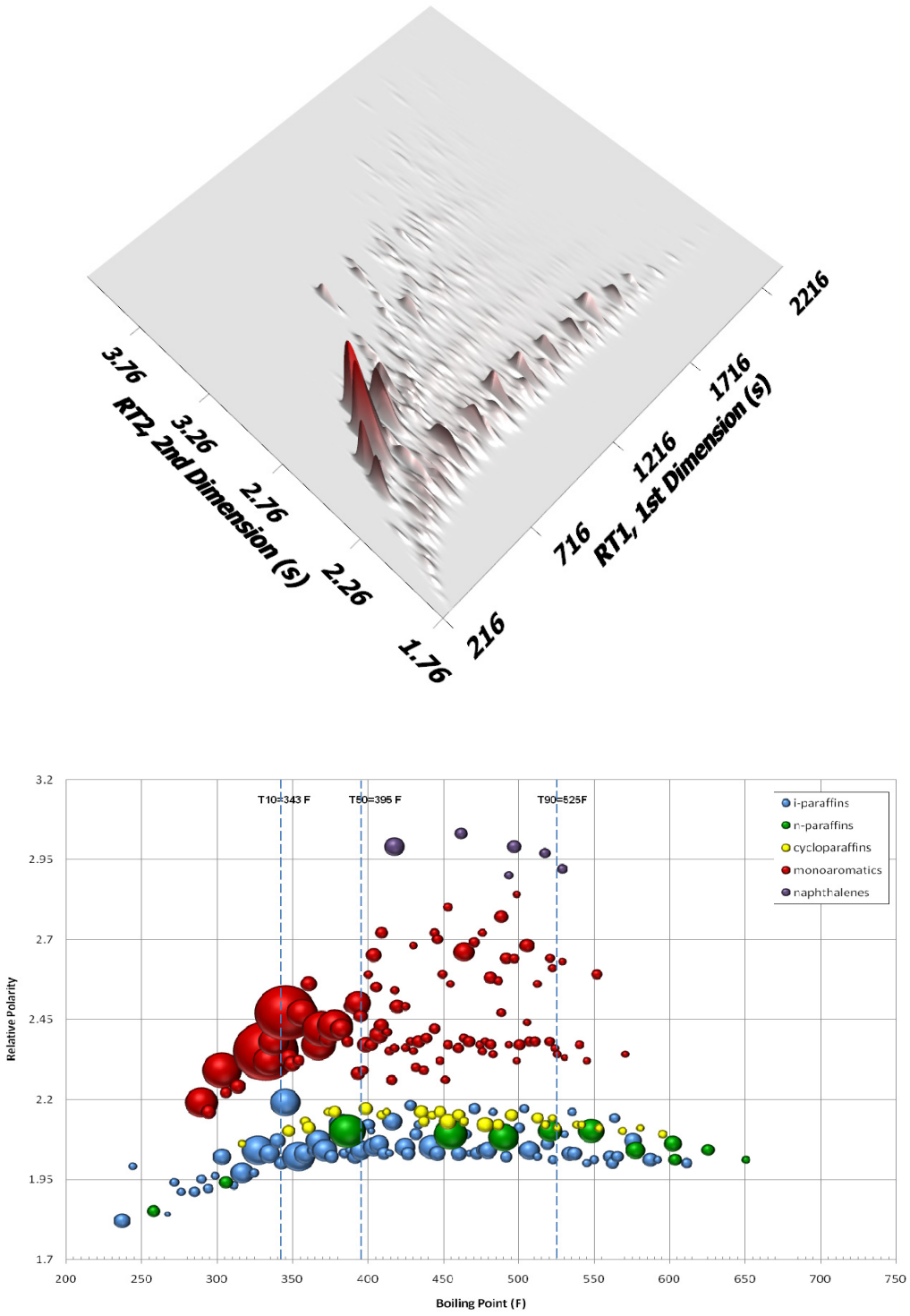

Figure 5.4. FD3A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

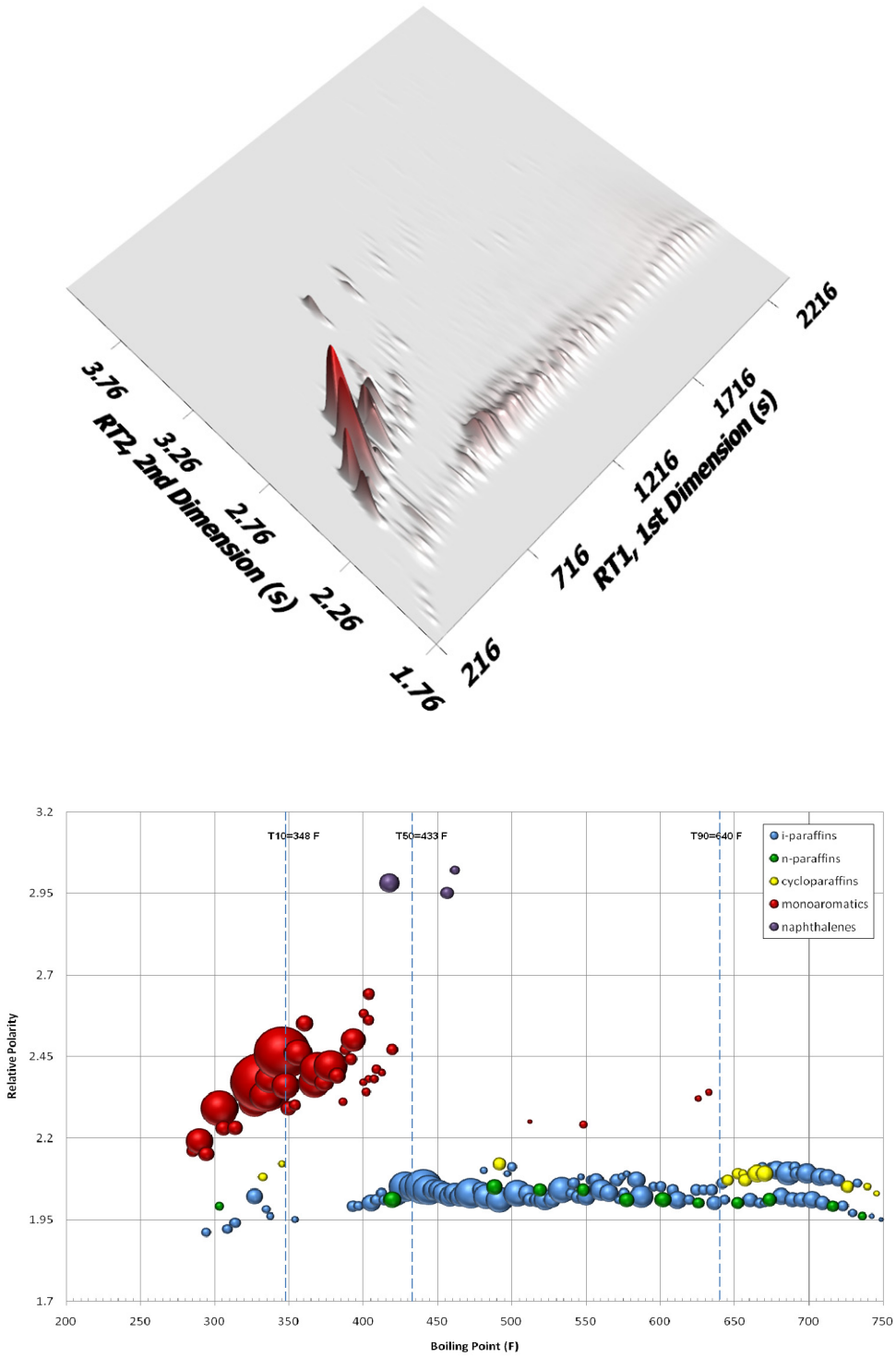

Figure 5.5. FD4A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

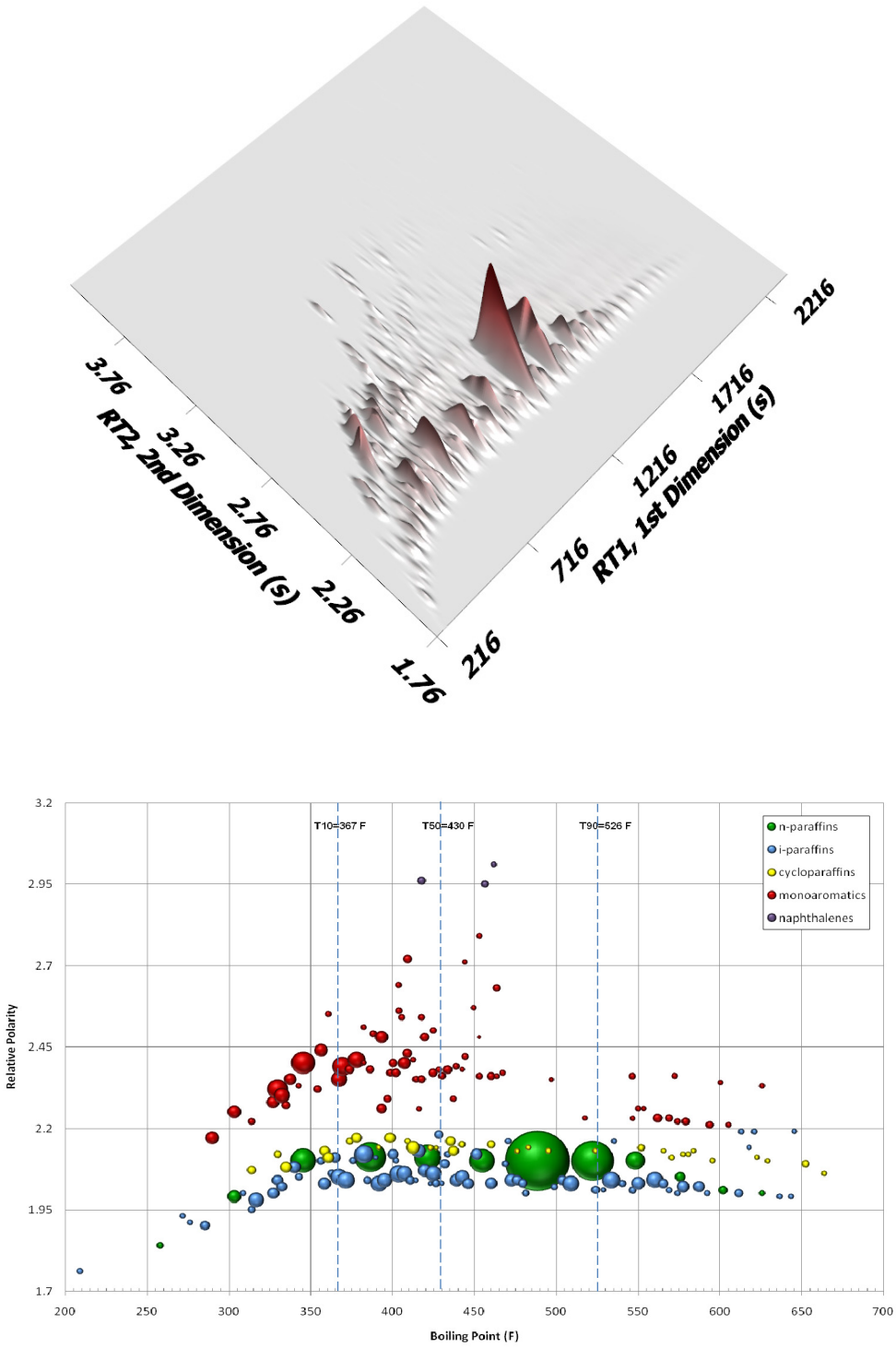

Figure 5.6. FD5A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

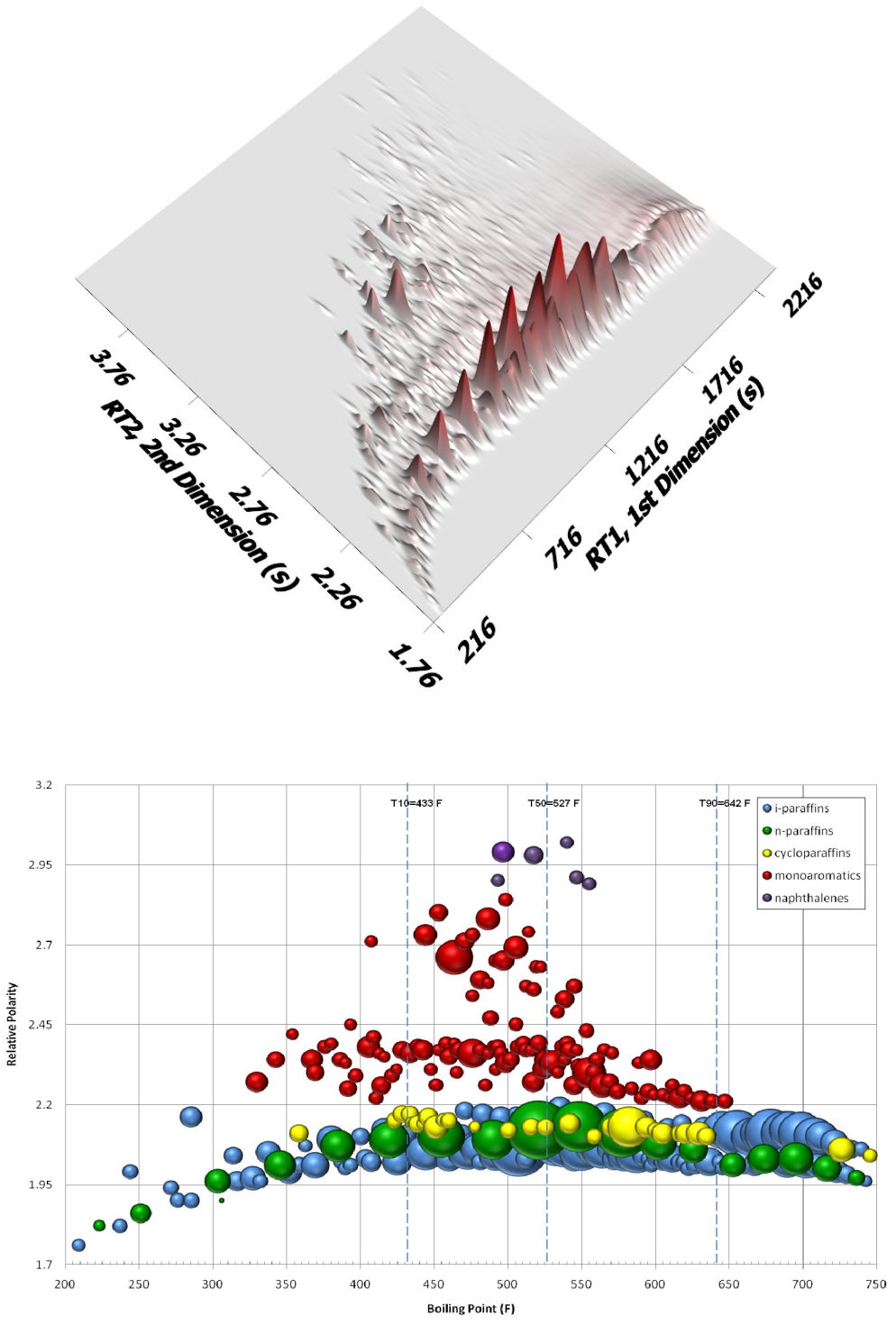

Figure 5.7. FD6A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

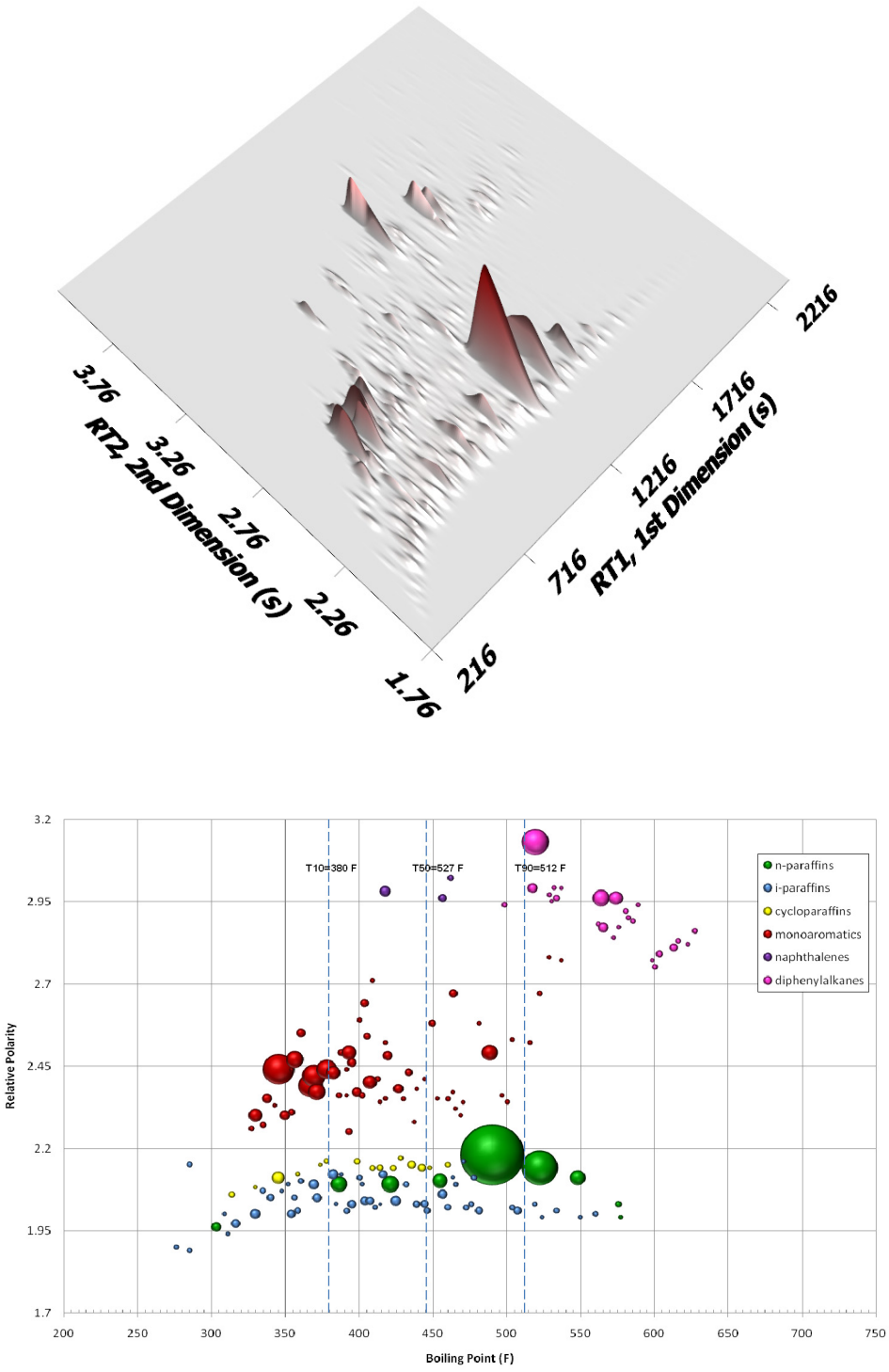

Figure 5.8. FD7A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

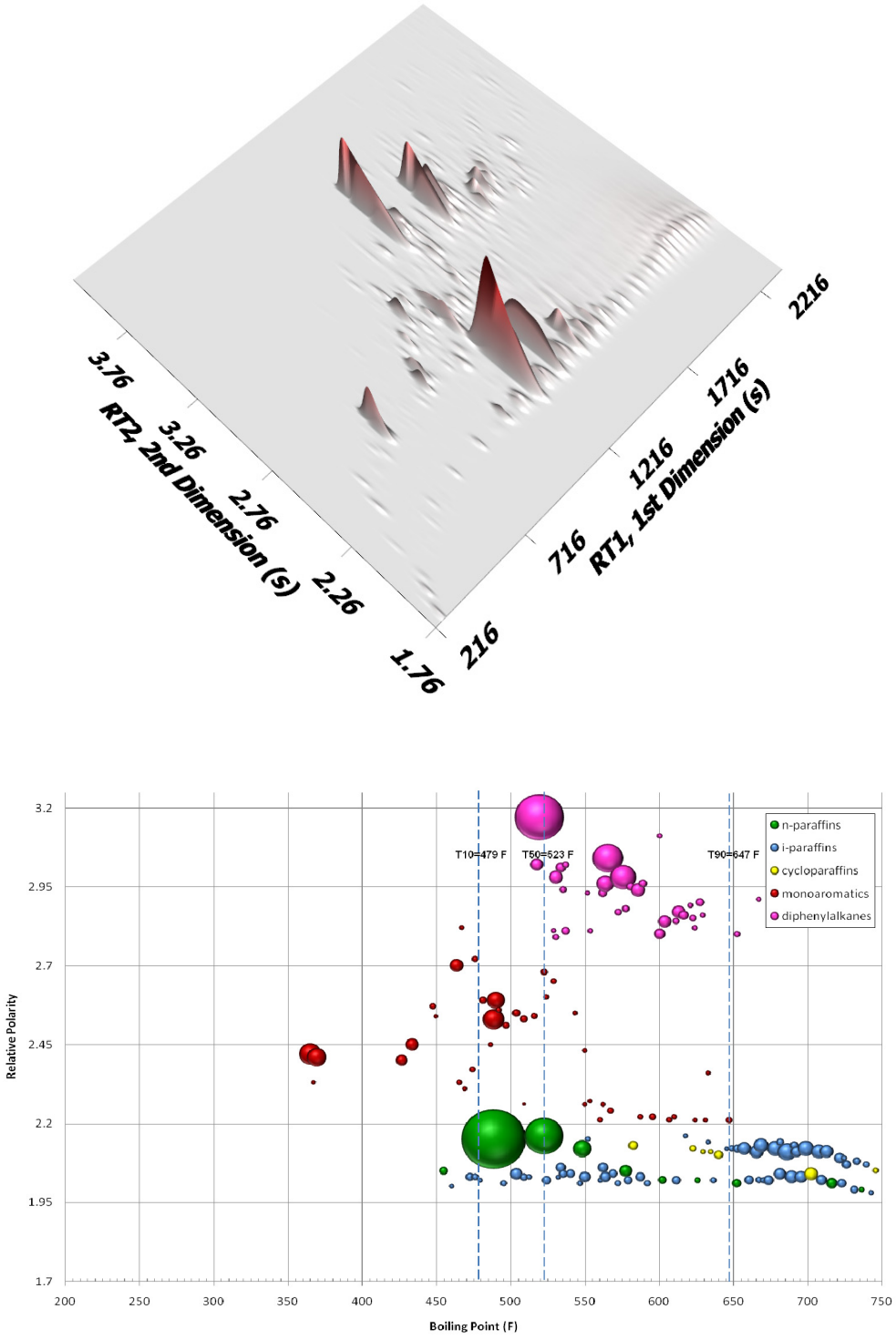

Figure 5.9. FD8A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

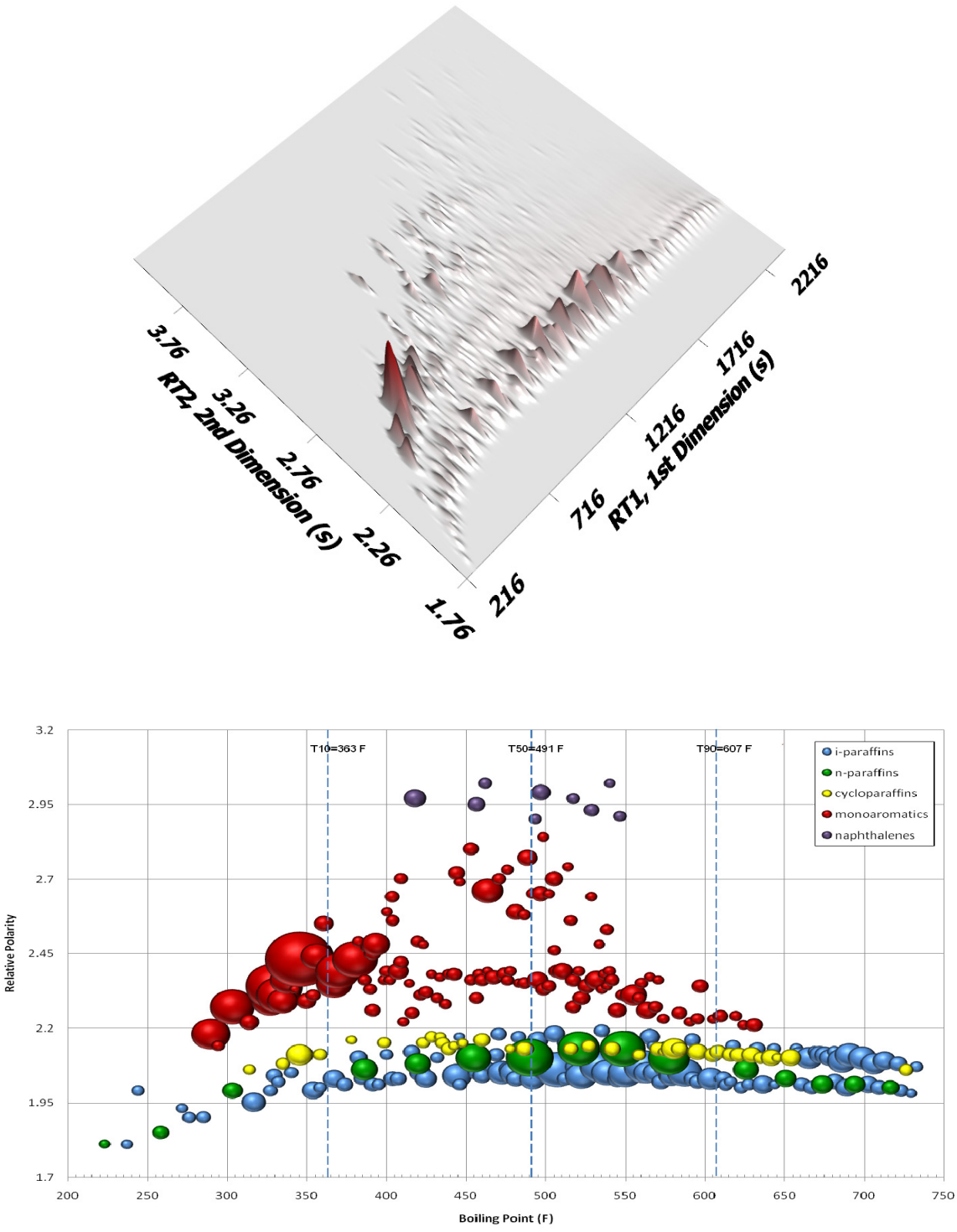

Figure 5.10. FD9A. Two-dimensional GC-FID surface map (upper plot) and types of compounds found during 2-D GC experiment as a function of boiling point presented as a bubble plot (bottom plot).

6. GAS CHROMATOGRAPHY-FIELD IONIZATION MASS SPECTROMETRY

GC-FIMS determines the characterization of saturated and aromatic hydrocarbons for diesel fuels in the boiling range of 200–343°C (392 to 649°F). This method provides detailed characterization for up to five saturates (including isoparaffins and n-paraffins), six aromatics, and two aromatic thiophenotypes. It does not require preseparation of the sample.[1,2] The results are reported for the total product and by carbon number (up to C21 for diesel range) and/or by boiling point distribution. A full GC-FIMS report also consists of a series of reports by carbon number in selected temperature intervals (usually 10°C intervals). The analysis is performed using an HP 5890 Series II gas chromatograph configured with an HP 5972 series mass selective detector. A semipolar RTX-5MS capillary column (30 m long × 0.25 mm internal diameter × 0.25μm film thickness) is used for separation of the peaks, and identification of the components is based on the nominal masses. The process involves the removal of an electron from a molecule by a high electric field (8–12 kV potential) through quantum mechanical tunneling. This produces the molecular ion for both paraffins and aromatics with no fragmentation.[1,2]

For the diesel components boiling below 200°C (392°F), the sample is injected into a PIONA analyzer with a prefractionator. The PIONA data reported for the fraction that boils below 200°C are combined with the GC-FIMS data for the fraction that boils above 200°C to produce reports that capture the full boiling range of the diesel fuel, discussed below. One caveat to the following discussion is the issue of the PIONA analyses for FD1A and FD2A, where isoparaffin and n-paraffin contents were underrepresented while monoaromatic content was overrepresented (see Section 7). This does not affect the data or discussions for fuels FD3A to FD9A.

Figure 6.1 shows the isoparaffin and n-paraffin contents of the nine FACE diesel fuels. The combination of PIONA and GC-FIMS is one of the few methods that distinguishes between isoparaffins and n-paraffins. The high-cetane fuels (FD5A to FD8A) show relatively high n-paraffin content (25 to 35 wt %) and lower isoparaffin content (5 to 15 wt %) compared to the low-cetane fuels (FD1A to FD4A), which have high isoparaffin content (16 to 28 wt %) and low n-paraffin content. The exception is FD6A, which shows about twice as much isoparaffin to n-paraffin content. FD9A shows about 15 wt % isoparaffins and 10 wt % n-paraffins. The monocycloparaffin, dicycloparaffin, and polycycloparaffin contents are shown in Figure 6.2. In most cases, samples have much higher monocycloparaffin content in the 10 to 15 wt % range. The exception again is FD6A, which has about equal concentrations of monocycloparaffins, dicycloparaffins, and polycycloparaffins (11, 14, and 16%). The center-point fuel, FD9A, has about 20 wt % monocycloparaffins and about 10 wt % each of dicycloparaffins and polycycloparaffins. Figure 6.3 shows the monoaromatic content of the diesel fuels broken down by alkylbenzenes, benzocycloalkanes, and benzodicycloalkanes. All fuels, except FD6A, exhibit much higher concentrations of alkylbenzenes. The low-cetane fuels (FD1A to FD4A) show much higher values of alkylbenzene concentrations (40 to 52 wt %). Fuels FD6A and FD8A, the high-T_{90}, high-cetane fuels, show very low monoaromatic content. The breakdown in diaromatic content by naphthalenes, biphenyls, naphthocycloalkanes, and fluorenes is shown in Figure 6.4. Only fuels FD7A and FD8A show significant diaromatic content. It appears that the high amounts of 1,1-diphenyl ethanes observed in the 2-D gas chromatographic mass spectrometric data (Section 4.2) appear as biphenyls in the GC-FIMS analysis. Figure 6.5 shows the total hydrocarbon type breakdown for the FACE diesel fuels.

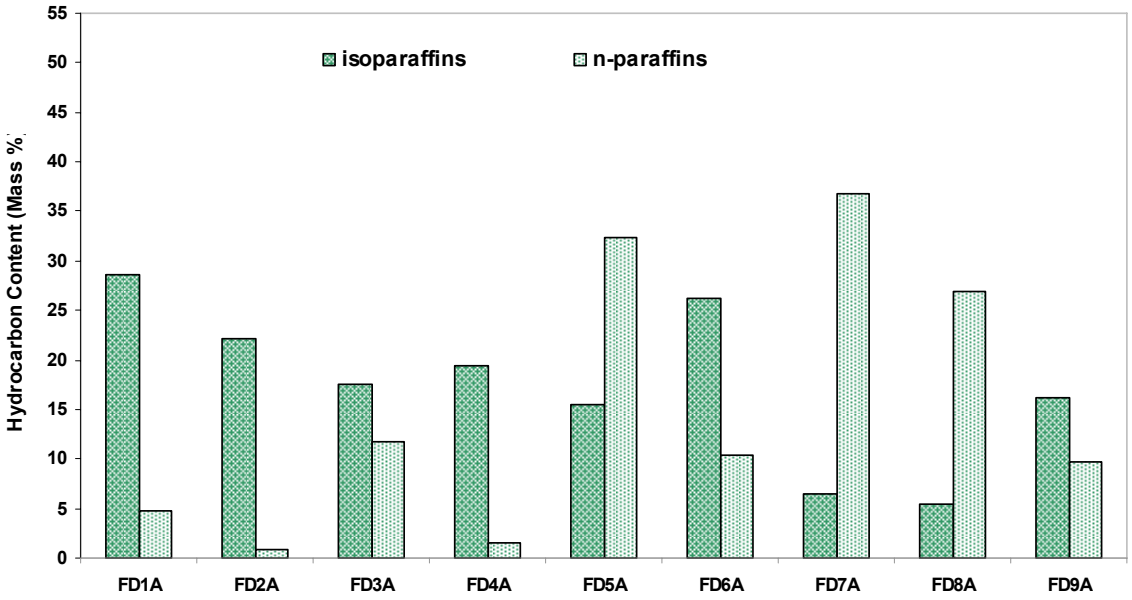

Figure 6.1. Isoparaffin and n-paraffin content in FACE diesel fuels by GC-FIMS and PIONA.

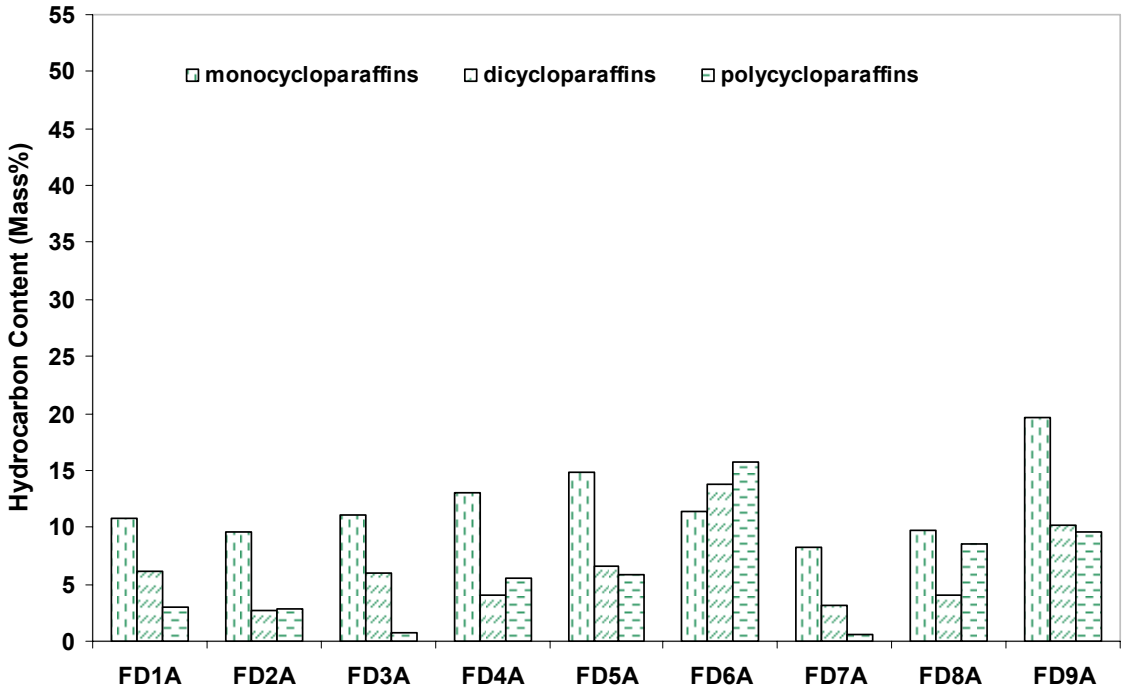

Figure 6.2. Cycloparaffin content in FACE diesel fuels by GC-FIMS and PIONA.

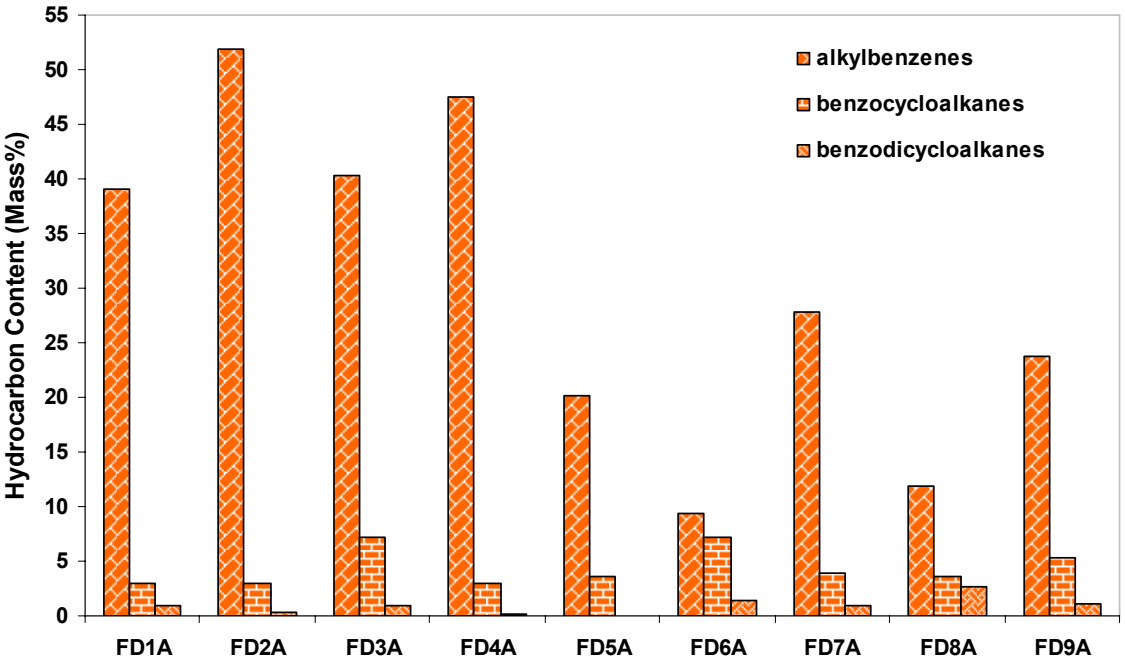

Figure 6.3. Monoaromatic content in FACE diesel fuels by GC-FIMS and PIONA.

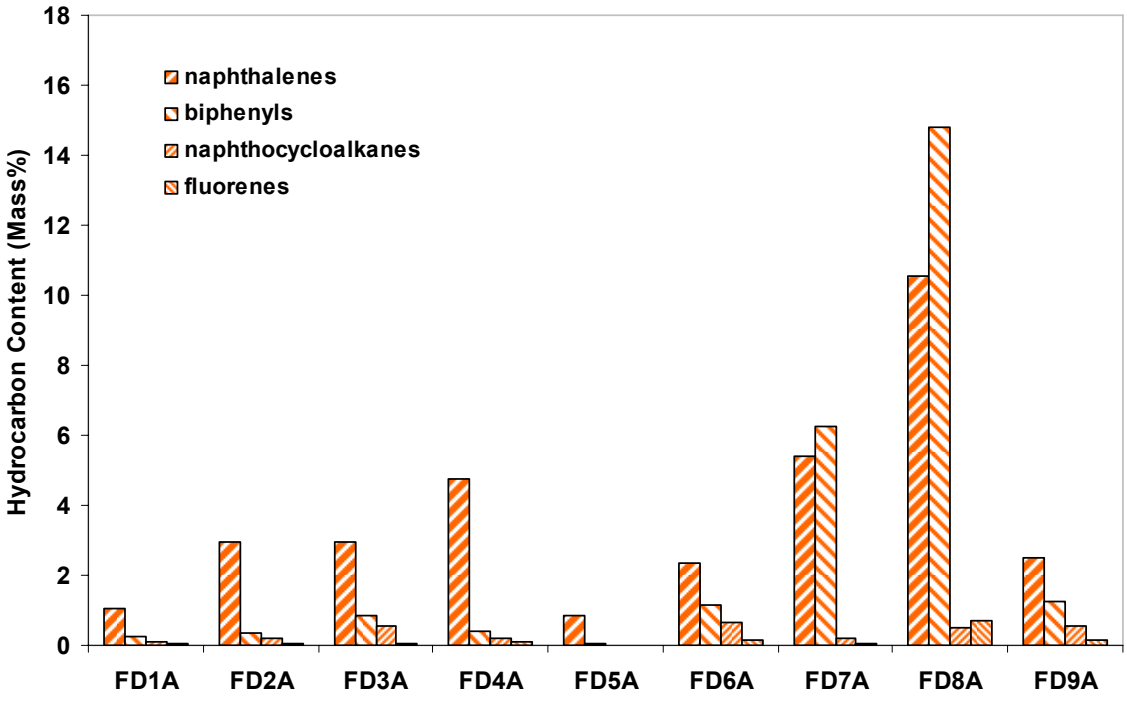

Figure 6.4. Diaromatic content in FACE diesel fuels by GC-FIMS and PIONA.

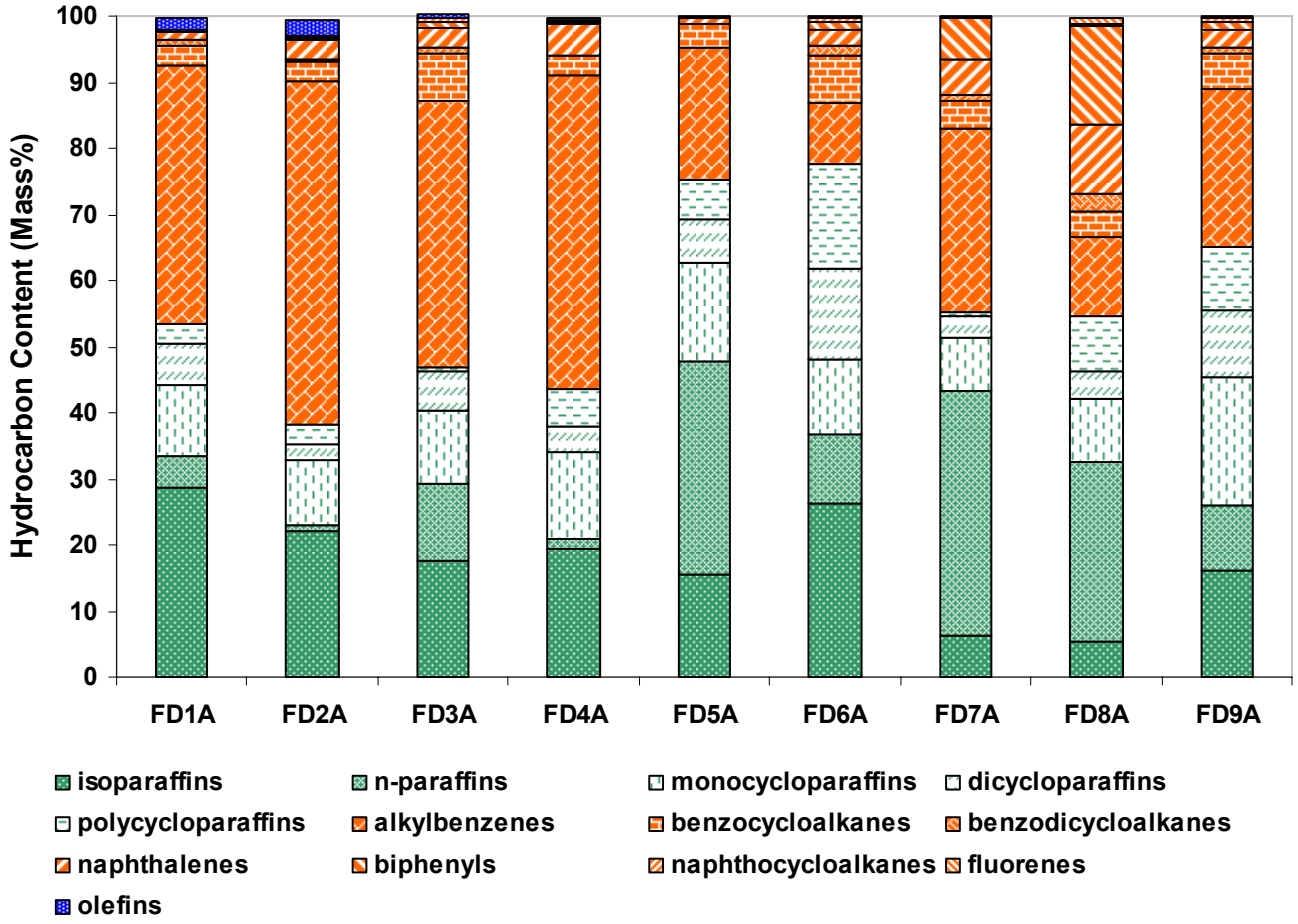

Figure 6.5. Hydrocarbon content in FACE diesel fuels by GC-FIMS and PIONA.

Figures 6.6 to 6.14 show the distribution of hydrocarbon types by carbon number for the FACE diesel fuels using the data from PIONA and GC-FIMS. The complete tables of GC-FIMS data by carbon number are given in Appendix B, Tables 1 to 9, while the PIONA data by carbon number are in Appendix C, Tables 1 to 9. The low-cetane fuels (FD1A to FD4A) all have very high contents of C_9 monoaromatics. The high-cetane fuels (FD5A to FD8A) clearly show that this is accomplished through very different hydrocarbon distributions. The high-aromatic fuels (FD3A, 4A, 7A, 8A) contain high C_9 monoaromatics (FD3A, 4A, 7A) or C_{14} monoaromatics and diaromatics (FD8A) rather than a distribution of aromatics by carbon number. It is difficult to see trends in the low-aromatic fuels (FD1A, 2A, 5A, 6A). This reflects again the problems with PIONA analysis for FD1A and FD2A. It may well be that some of the components associated as C_9 monoaromatics are actually paraffinic compounds. It is also difficult to identify trends in the differences in the low-T_{90} (FD1A, 3A, 5A, 7A) and high-T_{90} (FD2A, 4A, 6A, 8A) fuels.

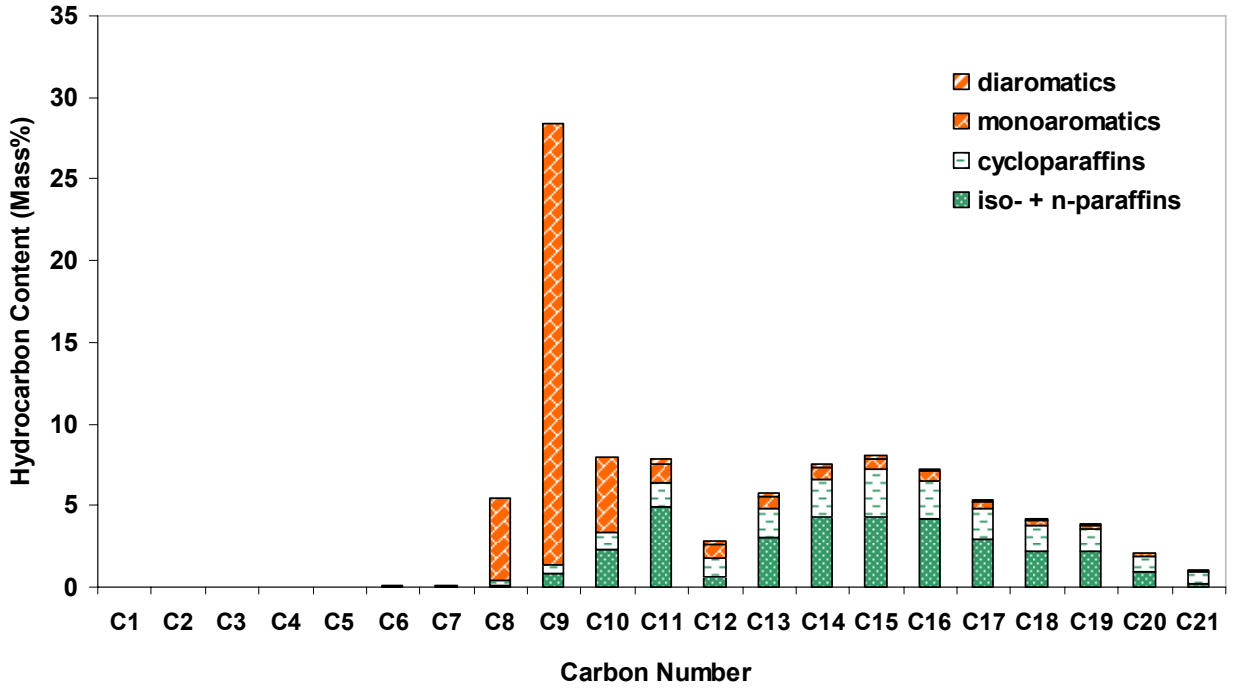

Figure 6.6. GC-FIMS and PIONA data for FD1A.

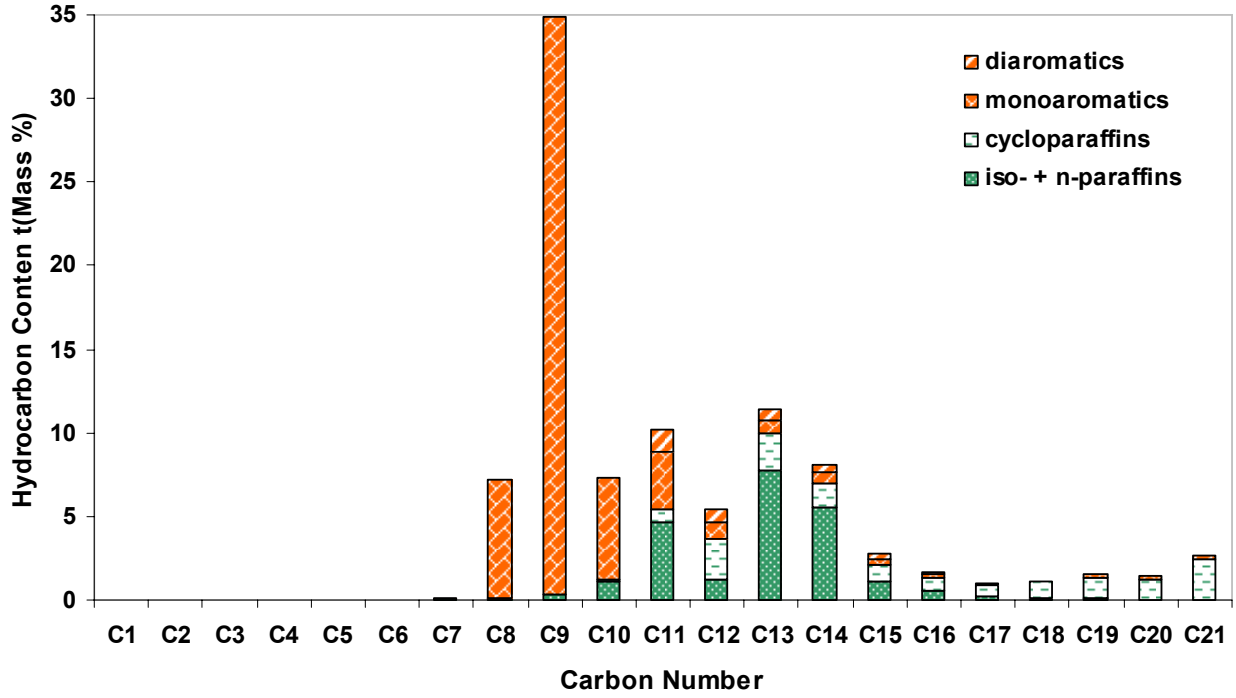

Figure 6.7. GC-FIMS and PIONA data for FD2A.

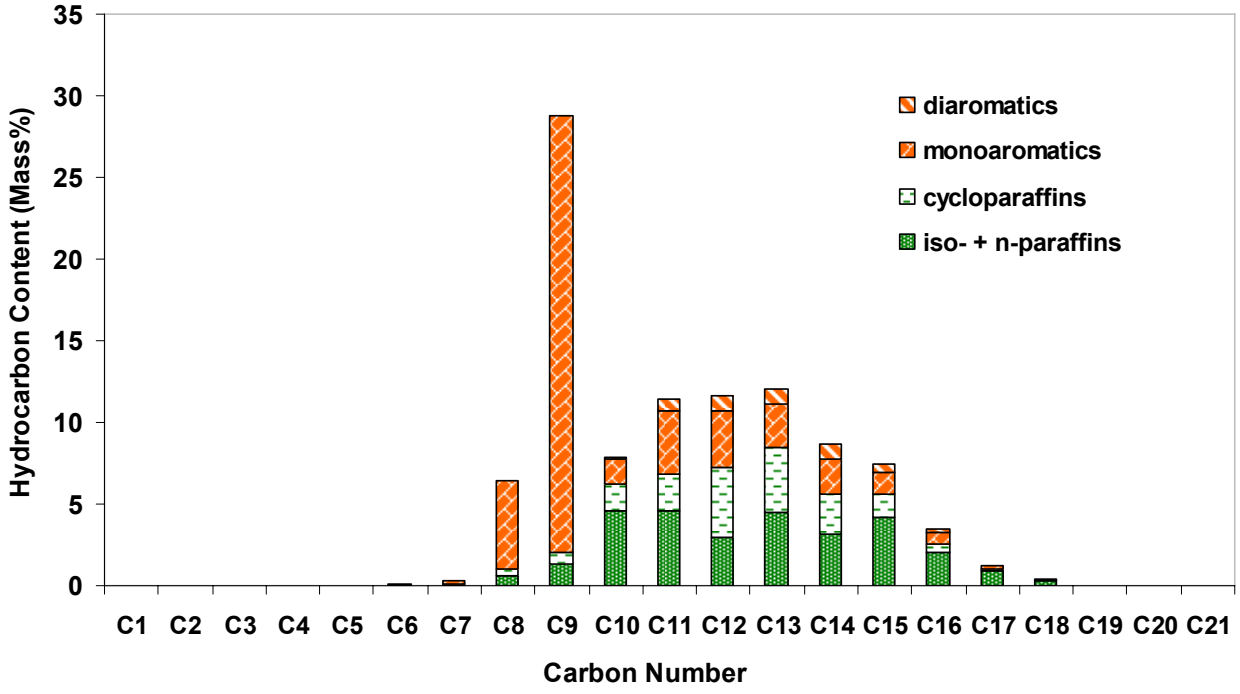

Figure 6.8. GC-FIMS and PIONA data for FD3A.

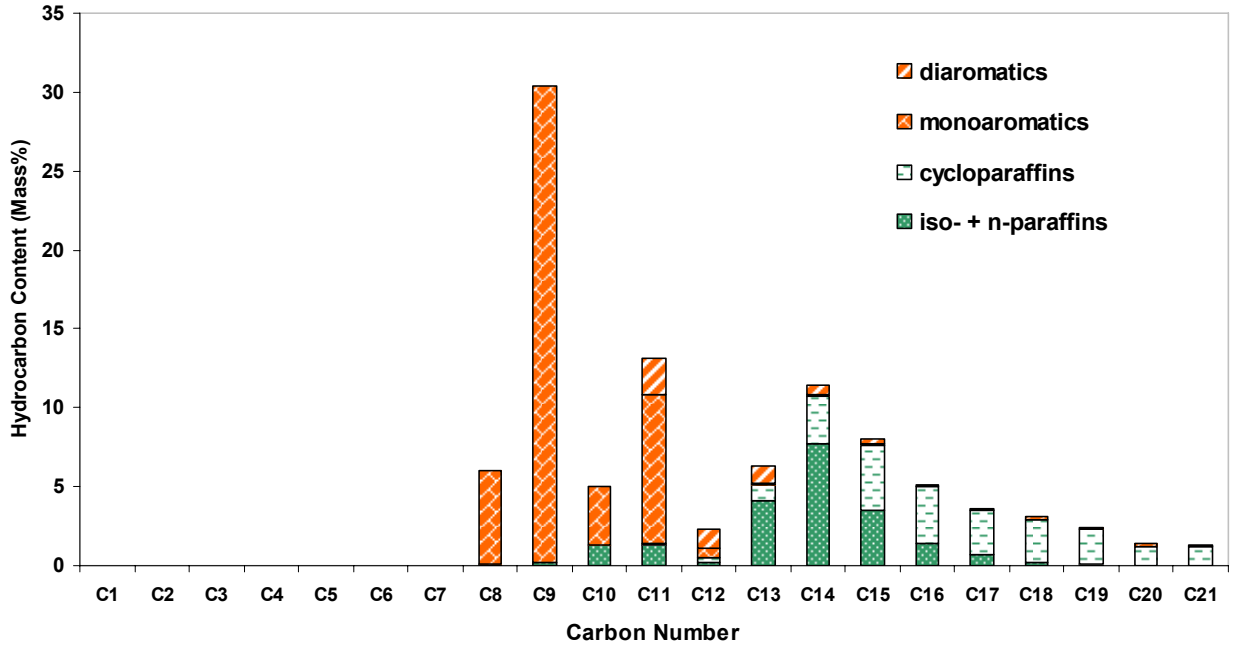

Figure 6.9. GC-FIMS and PIONA data for FD4A.

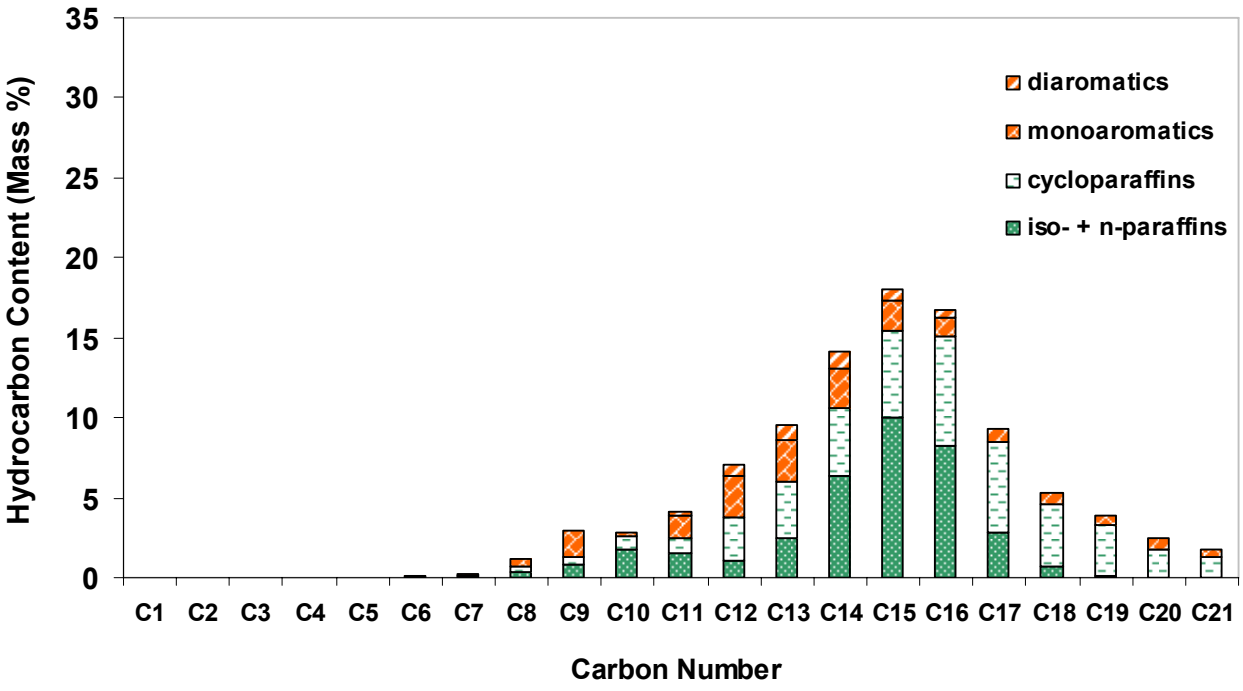

Figure 6.10. GC-FIMS and PIONA data for FD5A.

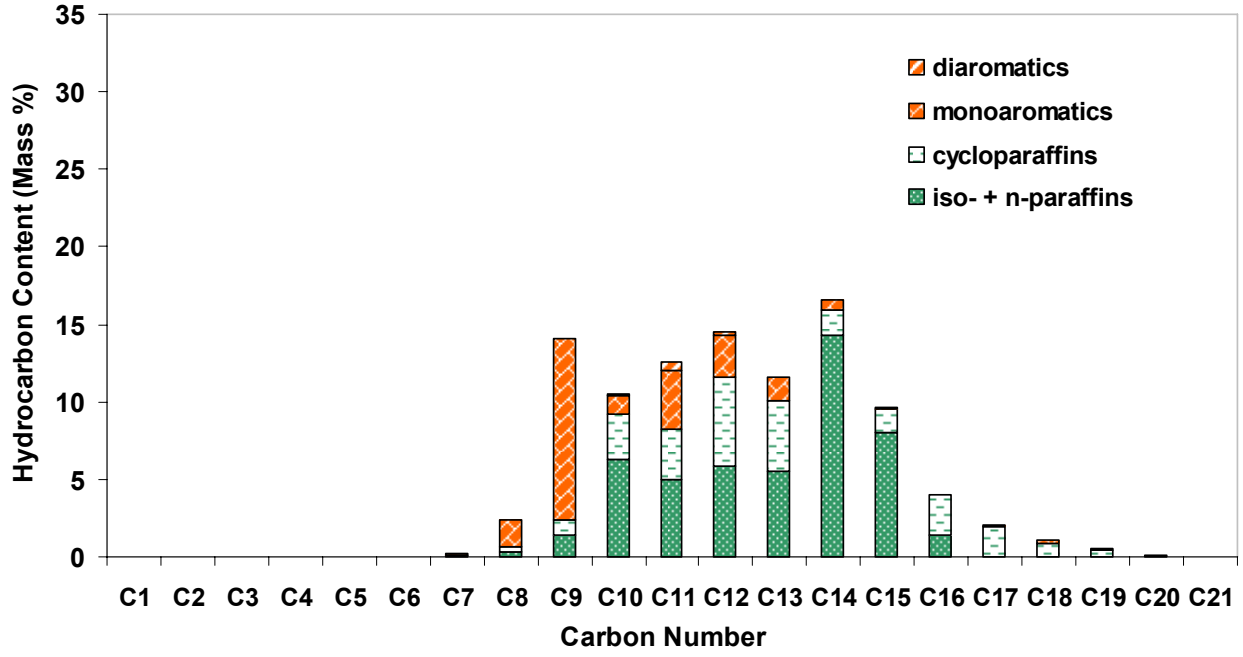

Figure 6.11. GC-FIMS and PIONA data for FD6A.

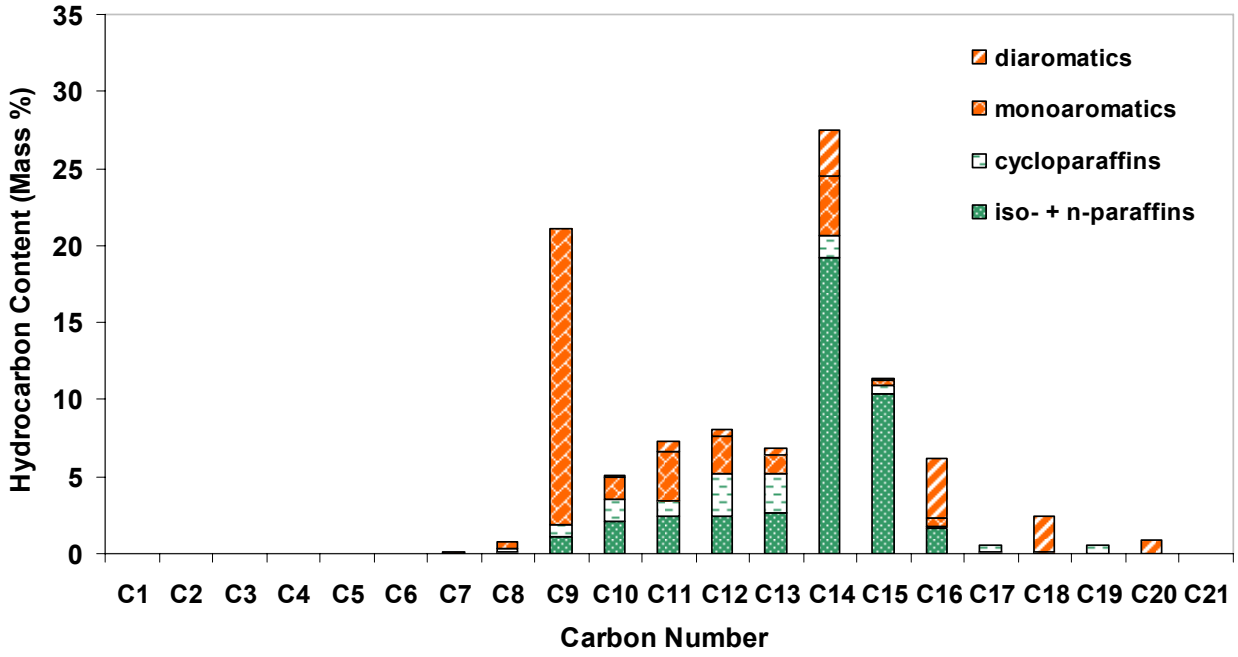

Figure 6.12. GC-FIMS and PIONA data for FD7A.

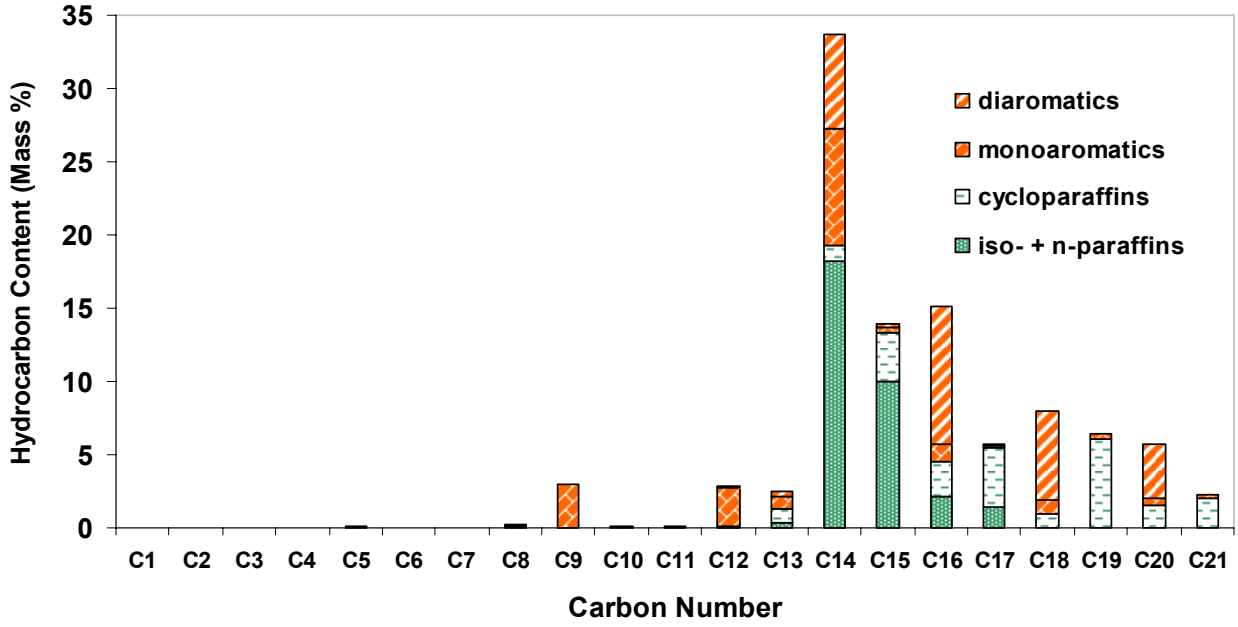

Figure 6.13. GC-FIMS and PIONA data for FD8A.

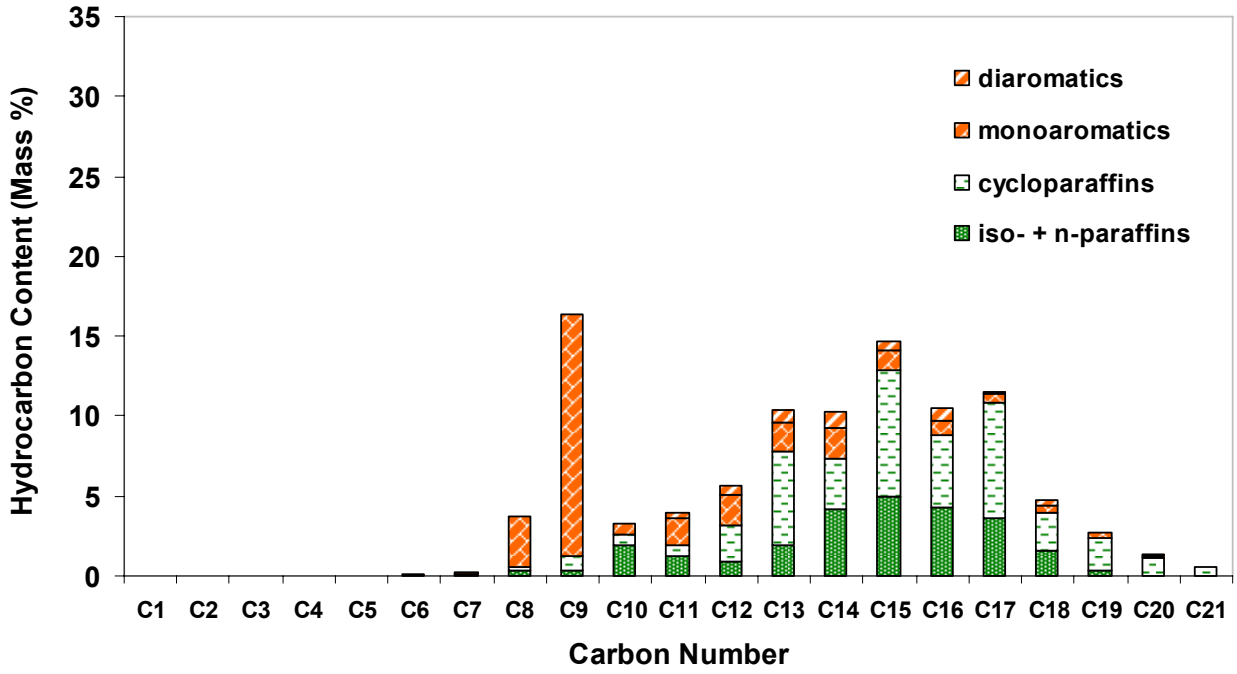

Figure 6.14. GC-FIMS and PIONA data for FD9A.

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).

7. PIONA ANALYSIS FOR HYDROCARBONS BOILING AT LESS THAN 200°C

This analysis uses a multicolumn gas chromatograph to separate petroleum samples into paraffins, isoparaffins, olefins, naphthenes, and aromatics and is described in ASTM D5443[1] and ASTM D6839[2] as a method for hydrocarbon analysis for samples which boil at less than 200°C (392°F). Distillate and diesel hydrocarbon type analyses such as ASTM D2425,[3] D2786[4] or D3239[5] are all derived for distillate liquids boiling above 200°C (392°F). Diesel fuels, however, often contain a significant amount of material boiling below this point. To obtain a composite hydrocarbon type analysis of wide boiling distillates, NCUT uses PIONA in combination with other advanced characterization methods. The instrument (Analytical Control PIONA Analyzer-Reformulizer) was modified by installing a prefractionator to vent off the distillate material that boils above 200°C. Samples must be low in sulfur (no more than 1,000 ppm). Instrument software allows for full hydrocarbon analysis that presents the PIONA data by carbon number (C_3 to C_{11}) for the following hydrocarbon types:

n-paraffins, saturated;
isoparaffins, saturated;
naphthenes, saturated;
n-paraffins, unsaturated (olefin);
isoparaffins, unsaturated (olefin);
naphthenes, unsaturated (olefin); and
aromatics.

Two assumptions were made in presenting the data: (1) cycloparaffins (naphthenes) were all monocycloparaffins and (2) aromatics were all monoaromatics, specifically alkylbenzenes. The PIONA data for the fuels are presented in Tables 1 to 9 in Appendix C. These data are used in conjunction with additional detailed hydrocarbon analyses in upcoming sections. A summary of the SOAP contents for hydrocarbons boiling below 200°C (392°F) in the FACE diesel fuels is given in Table 7.1 and Figure 7.1.

Several of the FACE diesel fuels have a series of isoparaffins and/or n-paraffins in the C_{10} to C_{12} region. The prefractionator in the PIONA gas chromatograph was designed to cut off these saturates just before normal C_{12} appeared, or at 200°C (392°F). Compounds C_{12} and above would then show in the GC-MS or GC-FIMS region. The results for FD1A and FD2A record a very high aromatic content by PIONA that upsets the final total aromatic contents in these two fuels. The original PIONA traces for samples FD1A and FD9A are shown in Figures 7.2 and 7.3. The paraffins in question are shown in the region from 55 to 65 minutes on the x-axis. In sample FD1A, there is a large peak at 65 minutes (this is not the total peak as the prefractionator cut off some of the peak) that is not present in FD9A. The presence of the large peak around C_{12} causes the aromatics to be overrepresented and the saturates underrepresented by PIONA in FD1A and FD2A. It may well be that some strange physical phenomena, because of the multicolumn and valve-switching nature of PIONA, causes some of the C_{10} and C_{11} isoparaffins and n-paraffins to actually report as monoaraomatics. None of the internal distillate standards show this problem with PIONA, so the authors are reluctant to change procedures to get these two fuels to report as designed for aromatic and saturate contents.

Table 7.1. PIONA Data for Hydrocarbons that Boil at Less Than 200°C (392°F)

Element	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
Saturates[a]	11.54	7.1	14.85	2.99	18.7	6.4	9.3	0.33	5.88
Olefins[a]	1.76	2.5	0.23	0.09	0.18	0.12	0.1	0.02	0.13
Aromatics[a]	36.37	46.22	32.42	36.19	13.62	2.29	19.76	3.11	18.42
Polars[a]	0	0	0	0	0	0	0	0	0
Sum[a]	49.67	55.82	47.5	39.27	32.5	8.81	29.16	3.46	24.43

[a]Unless indicated otherwise, data are in weight percents.

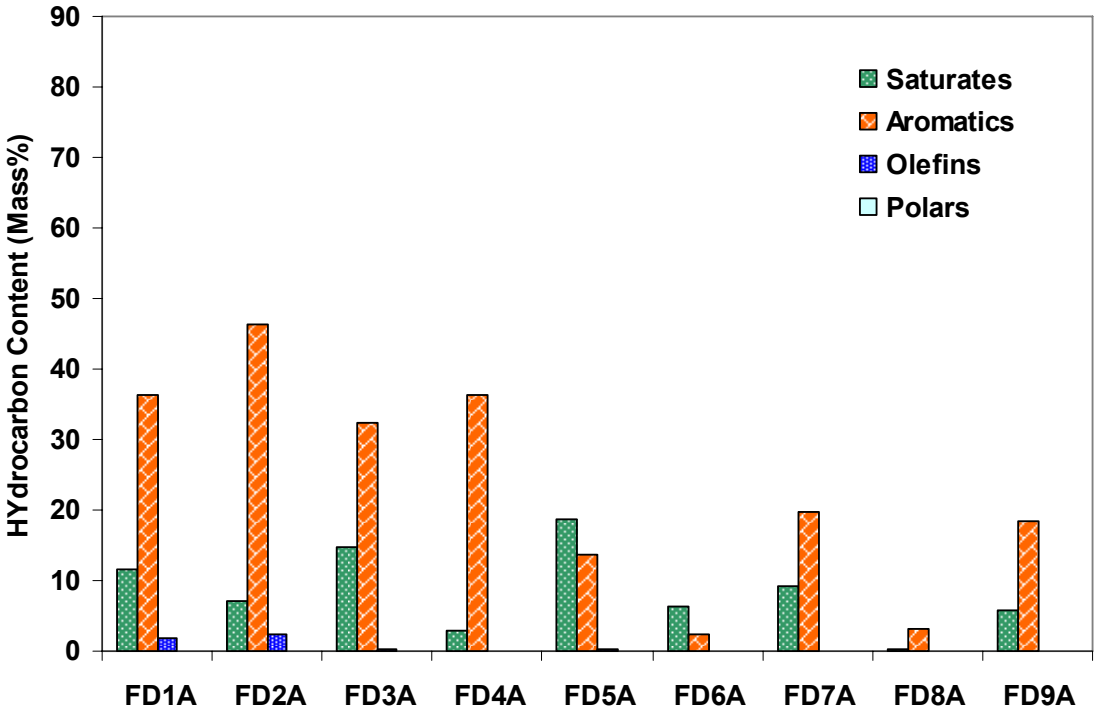

Figure 7.1. PIONA data for hydrocarbons boiling below 200°C (392°F).

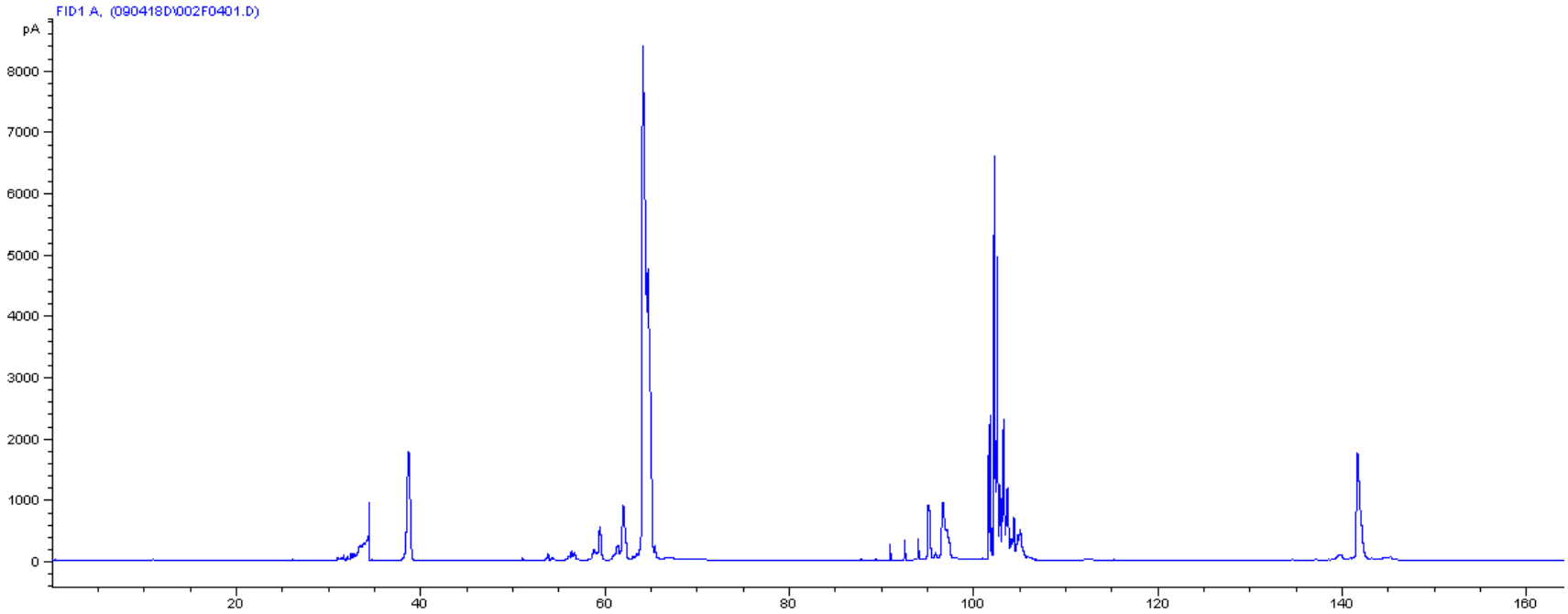

Figure 7.2. PIONA composite chromatogram for FD1A.

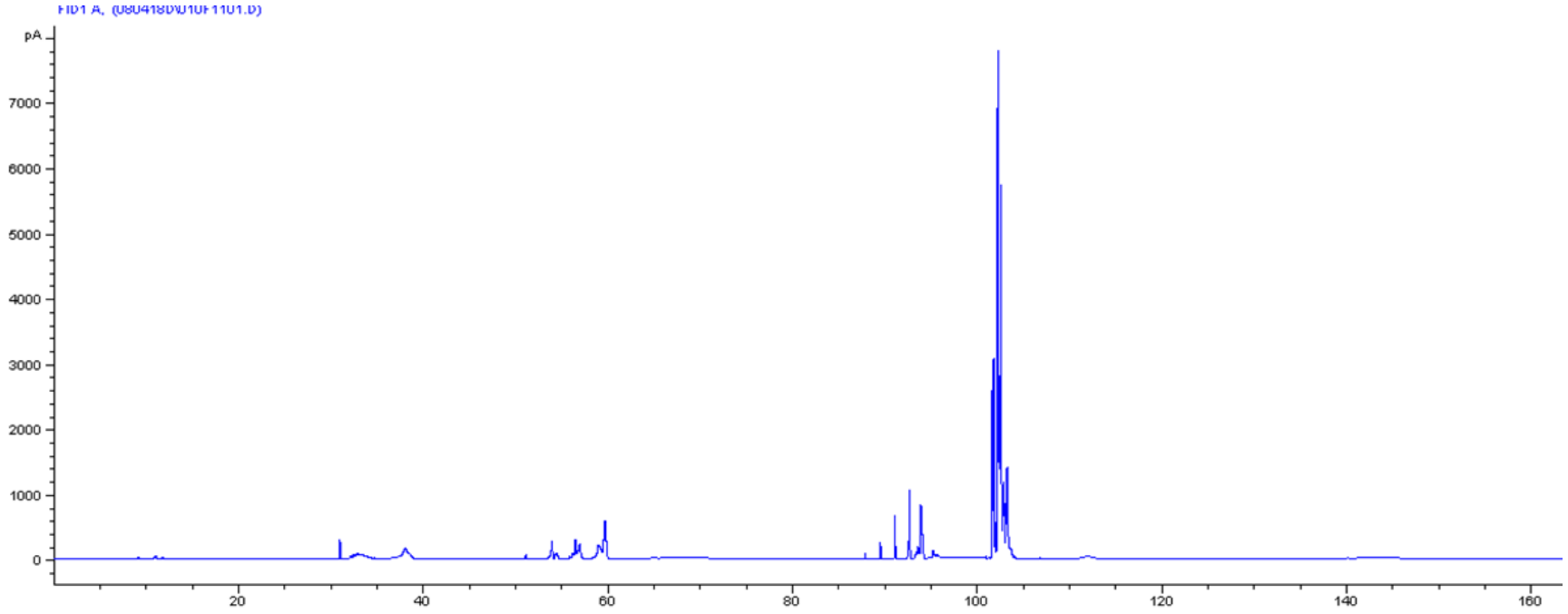

Figure 7.3 PIONA composite chromatogram for FD9A.

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, Pennsylvania, 2004).

3. ASTM International, *Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry,* ASTM D2425-04 (ASTM International, Pennsylvania, 2004).

4. 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).

5. 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).

8. SOAP-SOLID PHASE EXTRACTION ANALYSIS FOR HYDROCARBONS BOILING AT MORE THAN 200°C

Distillate hydrocarbon-type analyses by GC such as ASTM D2786[1] for saturates and D3239[2] for aromatics require separation of the distillate into saturate and aromatic fractions. Class separations by open chromatographic columns are highly time-consuming. Liquid chromatography (LC) is used extensively in characterizing petroleum distillates (ASTM D2007[3] for saturates, aromatics, and polar compounds) and diesel fuel (ASTM D2549[4] for saturates and aromatics). Typically the choice of LC method is based upon simulated distillation and/or color as the presence of a dark color in fuels normally indicates a relatively high content of polar materials. The original ASTM D2007 method calls for 280 ± 10 mL of *n*-pentane for collection of the saturates from a two-section column assembly, with attapulgus clay in the upper section and silica gel in the lower. Then, these two sections of the column assembly are disconnected to allow the lower (silica gel) to drain into a receiver. The upper (attapulgus clay) is washed with an additional 150 mL of *n*-pentane, which are then added to the drain from the lower section. After that, the lower section is placed into an extraction assembly and extracted with 200 mL of toluene. This extract is combined with the previously collected 150 mL of *n*-pentane effluent from the upper section and the drain from the lower section and considered as the aromatic fraction. The polars are collected by eluting the upper section with 250–300 mL of toluene-acetone mixture (50/50 by volume). This method renders an aromatic fraction that consists mostly of monoaromatics and diaromatics. To separate and collect the total aromatic fraction, a modified method was developed. The modified ASTM D2007 method uses 1,560 mL of a 50/50 by volume *n*-pentane/toluene mixture to elute the aromatics from the upper section instead of using 150 mL of *n*-pentane alone, as the original method requires. Polar contents measured with this modified method are smaller than they would be had they been separated by the original method. Similarly, aromatic contents are larger to reflect the presence of tri- and higher aromatics. The LC methods were verified against other separation techniques such as SFC, high-pressure LC, and hot fluorescence indicator absorption.[5] The modified ASTM D2007 method was then scaled down to use less sample and lower solvent quantities as shown in Figure 8.1.

Solid phase extraction (SPE) is an alternative that has been further developed for hydrocarbon analyses, in combination with GC, to provide saturate, aromatic, and polar content from very small amounts of sample.[6] An in-house NCUT method was developed to separate hydrocarbon samples with low polar content into saturate, olefin and aromatic fractions. This is accomplished by eluting the sample through SPE cartridges containing silica-based stationary phases using different solvents or mobile phases. The eluted fractions are concentrated to a known volume before being quantified using GC-FID (Agilent 6890). The FID's response is reasonably universal for hydrocarbons and is directly proportional to the mass flow rate of reduced carbon atoms. This quantification is determined for hydrocarbons that boil above 200°C (392°F) by starting the integration at a retention time equivalent to that of an n-paraffin that boils at 200°C. Unless the sample has a large concentration of heteroatoms, carboxylic acids, carbon dioxide, water, or other polar compounds, the integrated FID signal is proportional to the mass of the material. Saturate and aromatic fractions can be further investigated using GC-MS to identify and quantify their individual hydrocarbon components (ASTM D2786[7] for saturates, ASTM D3239[8] for aromatics). The SPE procedure greatly reduces the time required to separate hydrocarbon fractions and the amounts of solvents used in the laboratory.[9] The first SPE column contains silica (5 g) and the second 10% silver nitrate in silica (3 g, +200 mesh). Both are 14 mL SPE cartridges and are operated in sequence (i.e., one on top of the other) with 14 mL pentane solvent to capture saturates. Then, the lower silver nitrate/silica cartridge is separated from the silica column and run with 20 mL dicloromethane to capture olefins. The top SPE column is run a second time with 20 mL dicloromethane to capture aromatics. When the top silica cartridge appears colored, then methanol (20 mL) is used to capture any polar compounds. For the FACE diesel

fuels, no color appeared and no polar contents were measured. The SPE method produces SOAP analysis.

The data from PIONA and SOAP-SPE are shown in Tables 8.1 and 8.2 and Figures 8.2 and 8.3. Table 8.3 and Figure 8.4 show the sum of the two methods to give total SOAP contents. The amounts of material boiling above and below 200°C (392°F) were taken from the simulated distillation data. Samples FD4A to FD9A contained less that 1 wt % olefin content by this method. This is in contrast to the ASTM D1319[10] data, which indicated that FD4A, FD6A, and FD9A had high olefin contents. FD3A had the highest olefin content by this method at 4.2 wt %; FD2A had 2.7 wt % olefins, and FD1A had 2.1 wt % olefins by this method. Table 8.4 shows the total aromatic content measured by different methods: SOAP + PIONA, ASTM D1319, and ASTM D5186.[11] Clearly, the methods give reasonable agreement except for samples FD1A and FD2A, where the SOAP + PIONA data give a total aromatic content nearly twice that of ASTM D5186.

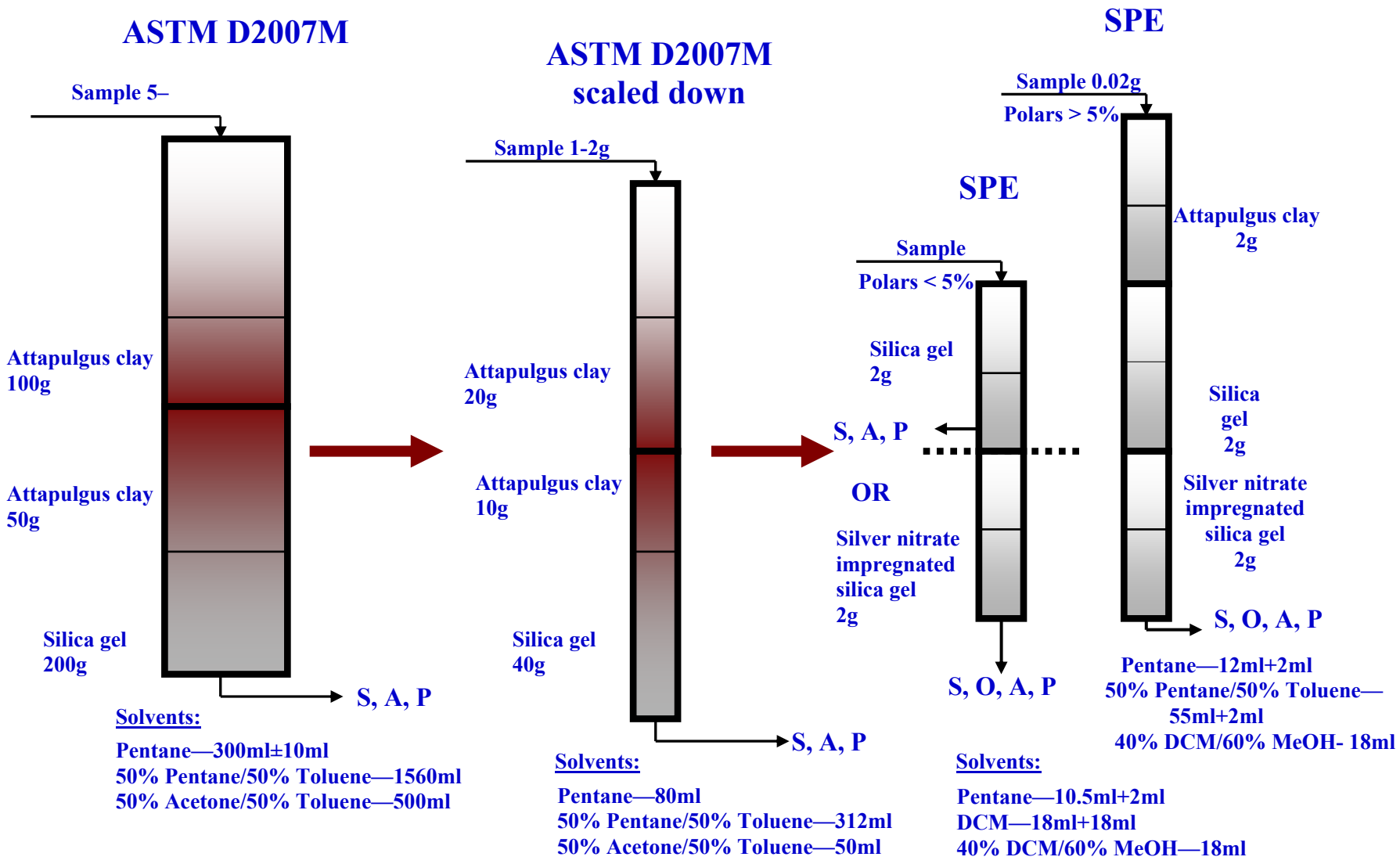

Figure 8.1. Hydrocarbon class separation by open chromatographic columns.

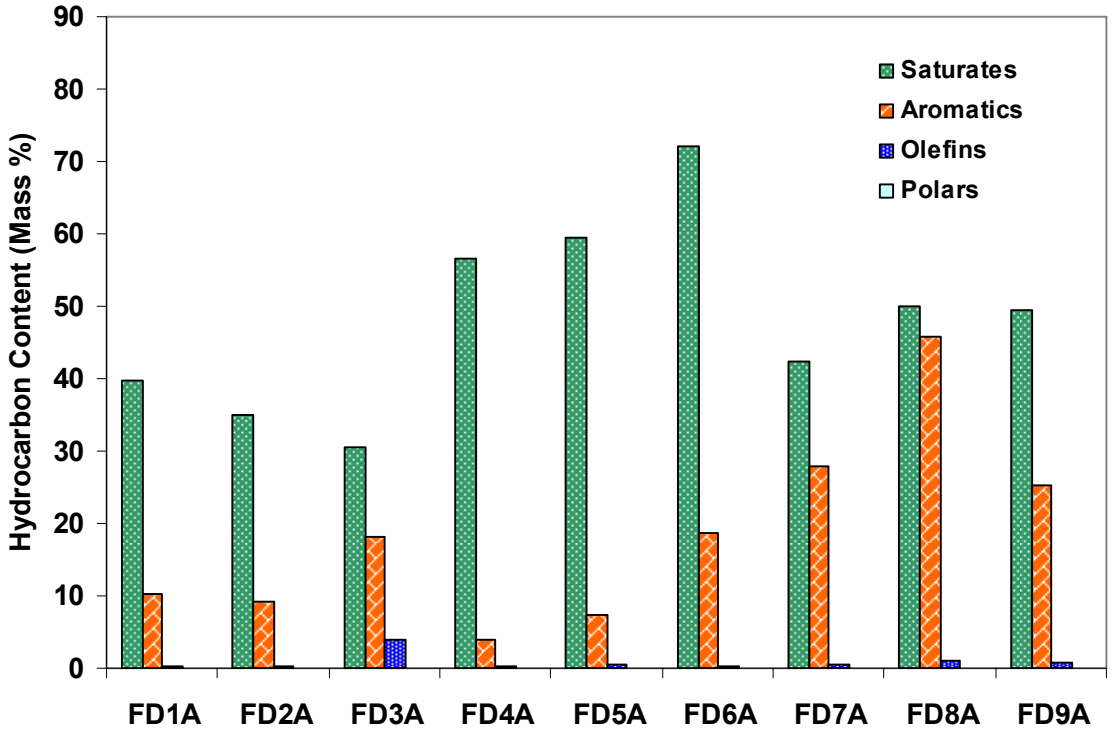

Figure 8.2. SOAP-SPE data for hydrocarbons boiling above 200ºC (392°F).

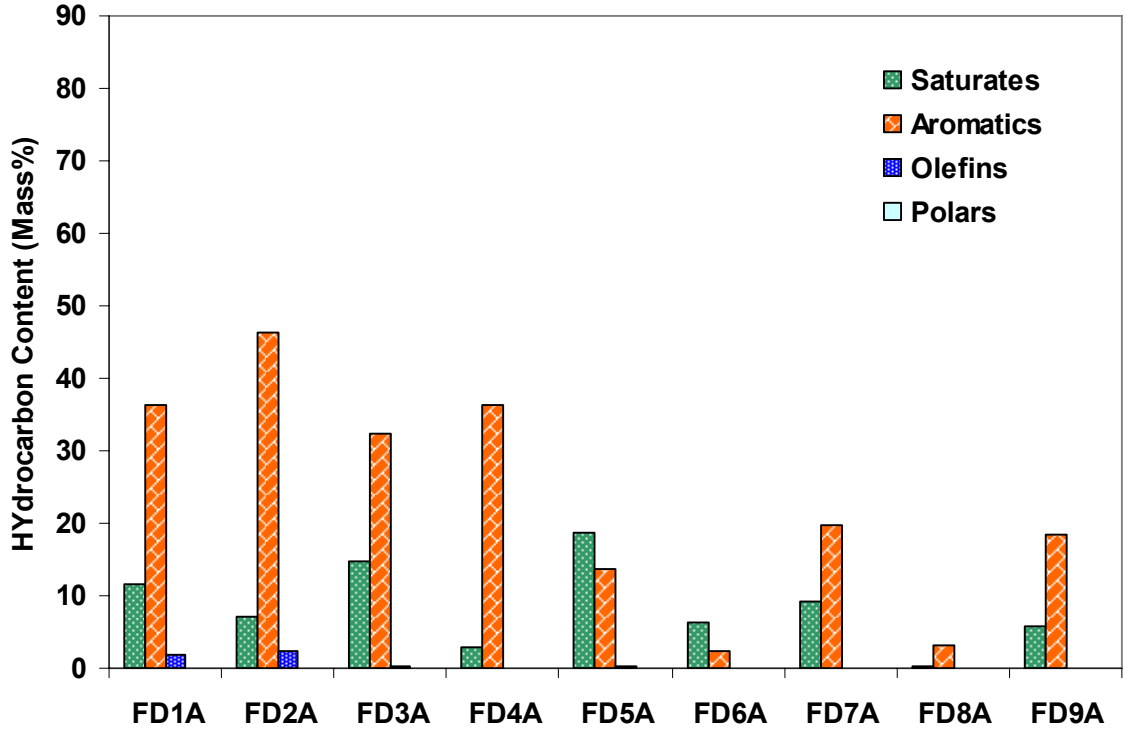

Figure 8.3. PIONA data for hydrocarbons boiling below 200ºC (392°F).

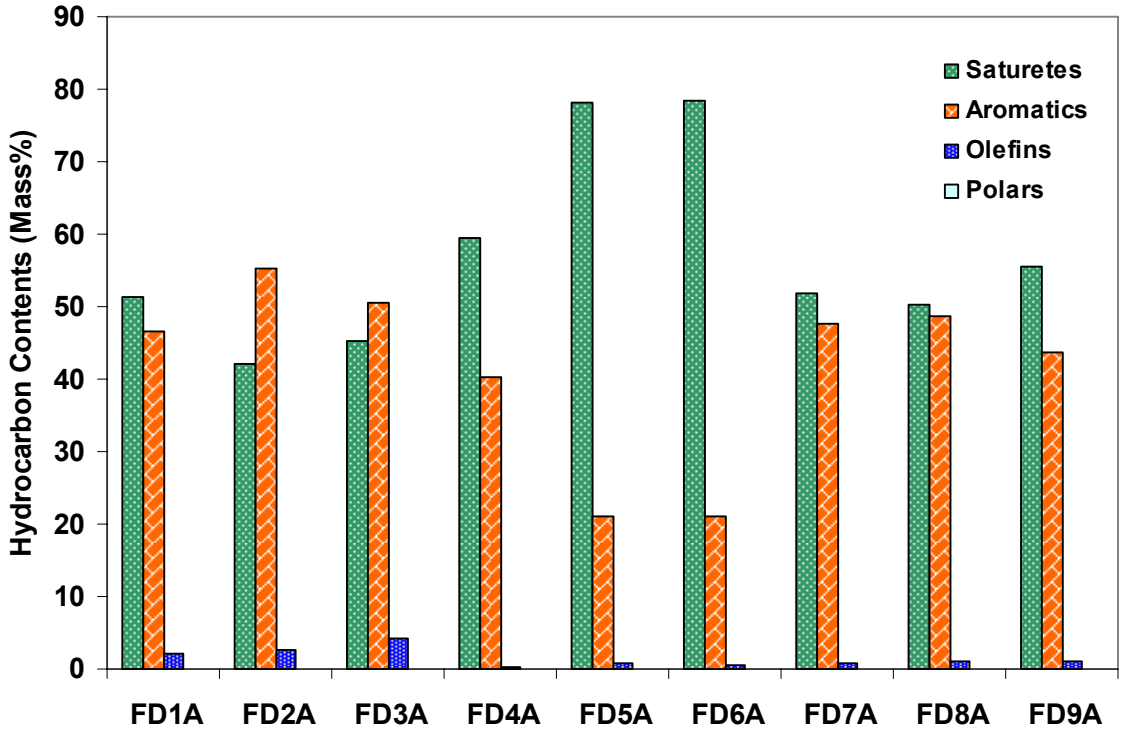

Figure 8.4. SOAP-SPE + PIONA data for FACE diesel fuels (initial to final boiling point).

Table 8.1. SOAP-SPE Data for Hydrocarbons That Boil at More Than 200°C (392°F)[a]

	Element	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SOAP-SPE	Saturates	39.7	34.9	30.4	56.5	59.5	72.1	42.5	49.9	49.6
SOAP-SPE	Olefins	0.3	0.2	4	0.3	0.5	0.3	0.6	1	0.8
SOAP-SPE	Aromatics	10.3	9.1	18.1	4	7.4	18.8	27.8	45.7	25.2
SOAP-SPE	Polars	0	0	0	0	0	0	0	0	0
	Sum	50.3	44.2	52.5	60.8	67.4	91.2	70.9	96.6	75.6

[a]Unless otherwise specified, units are weight percents.

Table 8.2. PIONA Data for Hydrocarbons That Boil at Less Than 200°C (392°F)[a]

	Element	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
PIONA	Saturates	11.54	7.1	14.85	2.99	18.7	6.4	9.3	0.33	5.88
PIONA	Olefins	1.76	2.5	0.23	0.09	0.18	0.12	0.1	0.02	0.13
PIONA	Aromatics	36.37	46.22	32.42	36.19	13.62	2.29	19.76	3.11	18.42
PIONA	Polars	0	0	0	0	0	0	0	0	0
	Sum	49.67	55.82	47.5	39.27	32.5	8.81	29.16	3.46	24.43

[a]Unless otherwise specified, units are weight percents.

Table 8.3. SOAP + PIONA Data for FACE Diesel Fuels[a]

	Element	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SOAP+PIONA	**Saturates**	51.2	42	45.3	59.5	78.2	78.5	51.8	50.2	55.5
SOAP+PIONA	**Olefins**	2.1	2.7	4.2	0.4	0.7	0.4	0.7	1.0	0.9
SOAP+PIONA	**Aromatics**	46.7	55.3	50.5	40.2	21.0	21.1	47.6	48.8	43.6
SOAP+PIONA	**Polars**	0	0	0	0	0	0	0	0	0
	Sum	100.0	100.0	100.0	100.1	99.9	100.0	100.1	100.1	100.0

[a]Unless otherwise specified, units are weight percents.

Table 8.4. Aromatic Content by Different Methods for FACE Diesel Fuels[a]

	Element	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SOAP+PIONA	**Aromatics**	46.67	55.32	50.5	40.2	21.0	21.1	47.6	48.8	43.6
ASTM D5186	**Aromatics**	26.6	23.3	50.5	40.7	22.5	21.5	46.9	44.4	37.4
ASTM D1319 avg[b]	**Aromatics**	23.5	21.0	46.9	51.8	20.7	20.4	41.6	41.9	37.3
GC-FIMS+PIONA	**Aromatics**	44.8	59.3	52.8	56.5	24.6	22.3	44.7	44.9	34.7
Target[b]	**Aromatics**	20	20	45	45	20	20	45	45	33

[a]Unless otherwise specified, units are weight percents.
[b]Volume percent.

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. 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).

4. 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).

5. Neill, W.S., et al., *Canadian Diesel Fuel Composition and Emissions—II,* Report PET-1466-99S (National Research Council Canada, Institute for Chemical Process and Environmental Technology, Ottawa, 1999).

6. 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).

7. 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, 2008).

8. 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, 2006).

9. 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).

10. ASTM International, *Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption,* ASTM D1319-08 (ASTM International, Pennsylvania, 2008).

11. ASTM International, *Standard Test Method for Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography,* ASTM D5186-03(2009) (ASTM International, Pennsylvania, 2009).

9. SOLID PHASE EXTRACTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY PLUS PIONA DATA

Samples were initially analyzed by SPE to determine the SOAP contents for hydrocarbons boiling above 200°C (392°F). Then SPE fractions were analyzed by 1-D GC-MS using ASTM D2786[1] for the saturates boiling above 200°C and ASTM D3239[2] for the aromatics boiling above 200°C. The separate GC-MS data were combined to derive total hydrocarbons boiling above 200°C, and these data were then combined with PIONA data for hydrocarbons boiling below 200°C to give the total hydrocarbon type contents for the diesel fuels (IBP to FBP). These data are provided in tabular form in Appendix D. The total contents for saturates, olefins, aromatics, and polars are given by the earlier SOAP-SPE + PIONA data.

The saturate content was determined as the sum of isoparaffins plus n-paraffins, monocycloparaffins, dicycloparaffins, and polycycloparaffins as shown in Figure 9.1. The low-cetane FACE diesel fuels (FD1A to FD4A) show the total of isoparaffins plus n-paraffins in the range from 27 to 34 wt %, with 7 to 13 wt % monocycloparaffins. These fuels have a large content of hydrocarbons boiling below 200°C (392°F)—49.7, 55.8, 47.5, and 39.3 wt % for fuels FD1A to FD4A as measured by PIONA. The high-cetane fuels, FD5A to FD8A, show total isoparaffin plus n-paraffin contents from 26 to 49 wt %, with FD5A (49 wt %) and FD7A (39 wt %) showing high contents. These two fuels are the low-T_{90}, high-cetane fuels and also show higher content of hydrocarbons boiling below 200°C by PIONA (33 and 29 wt % for FD5A and FD7A) compared to FD6A and FD8A (9 and 4 wt % boiling below 200°C).

The monoaromatic content given by alkylbenzene, benzocycloalkane, and benzodicycloalkane contents is shown in Figure 9.2. In all fuels, the monoaromatics were composed predominantly of alkylbenzenes. The low-cetane fuels show much higher alkylbenzene content (all >40 wt %) than the high-cetane fuels, which ranged from 8 to 29 wt % alkylbenzene content. The diaromatic content given by naphthalene, naphthocycloalkane, and fluorene is shown in Figure 9.3. The low-cetane fuels showed very little diaromatic content. Only FD7A and FD8A showed significant diaromatic content at 11 and 22 wt %, respectively. FD8A exhibited a very high concentration of naphthocycloalkanes (15 wt %). Previously, this fuel was identified as having high diphenylethane content, and this compound is likely being identified as a naphthocycloalkane by ASTM D3239. Figure 9.4 shows the hydrocarbon type distribution for all nine diesel fuels in one plot.

Figures 9.5 to 9.8 show the distribution of hydrocarbon types in terms of total isoparaffins and n-paraffins and total cycloparaffins, monoaromatics, and diaromatics between PIONA and SPE-GC-MS [i.e., between hydrocarbons boiling below and above 200°C (392°F)]. In all cases, the monoaromatics were found mostly in the range below 200°C, diaromatics only in the material above 200°C. Cycloparaffins and total isoparaffins plus n-paraffins were found predominantly in the material above 200°C.

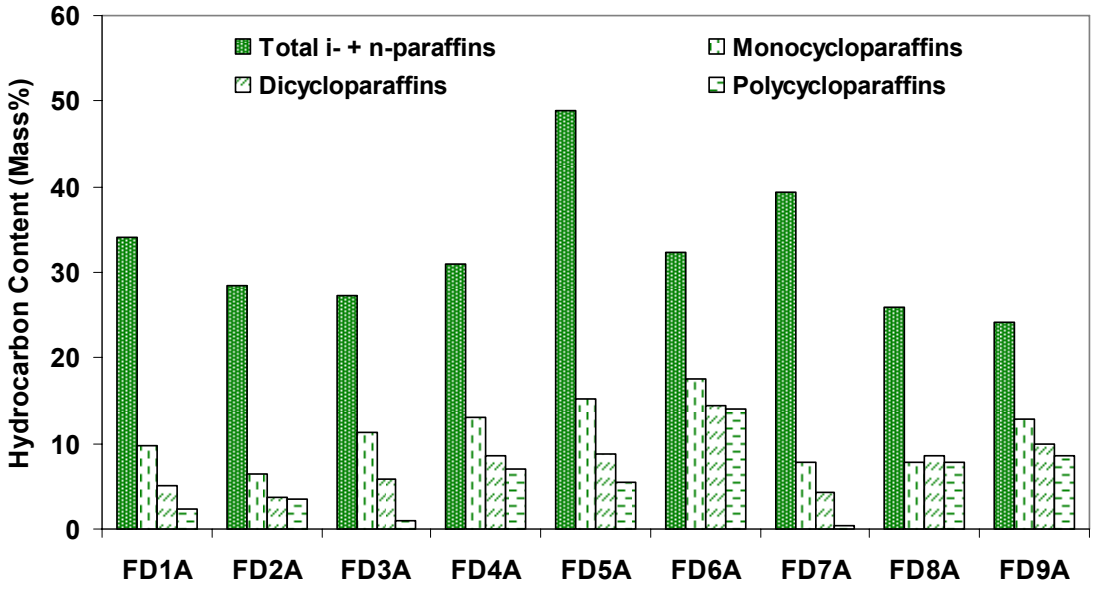

Figure 9.1. SPE-GC-MS + PIONA data for saturates in FACE diesel fuels.

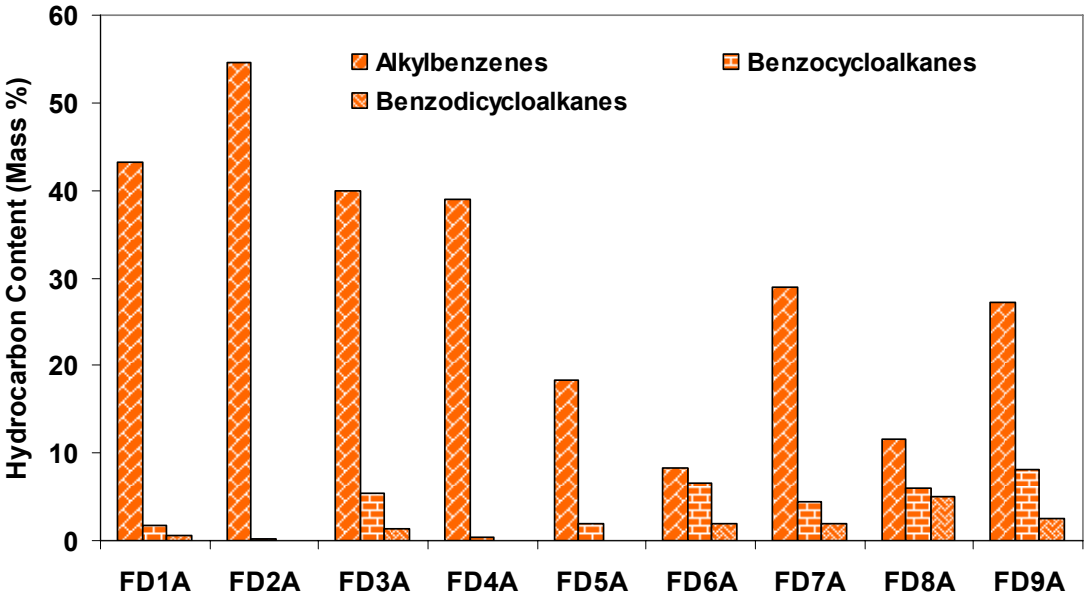

Figure 9.2. SPE-GC-MS + PIONA data for monoaromatics in FACE diesel fuels.

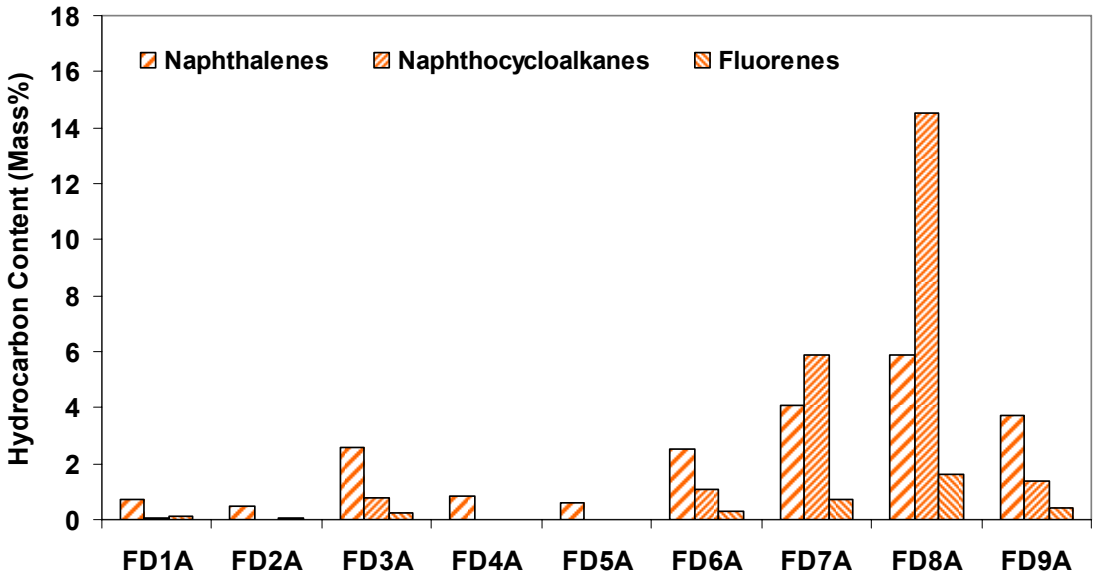

Figure 9.3. SPE-GC-MS + PIONA data for diaromatics in FACE diesel fuels.

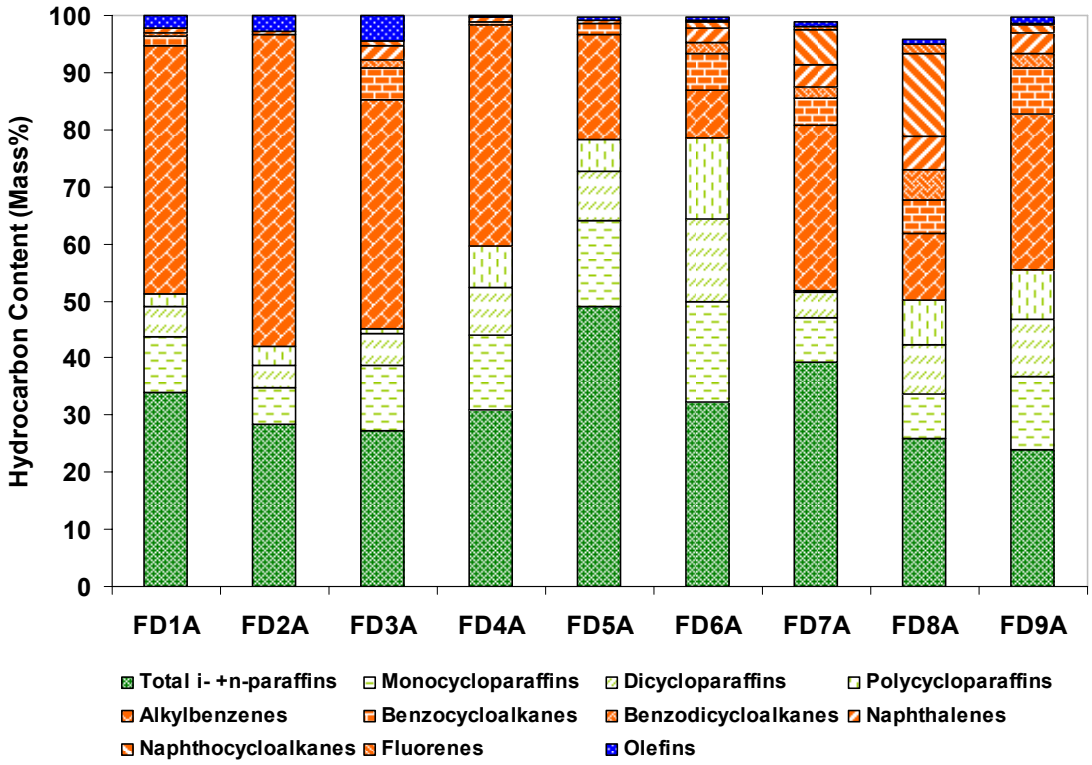

Figure 9.4. SPE-GC-MS + PIONA data for FACE diesel fuels.

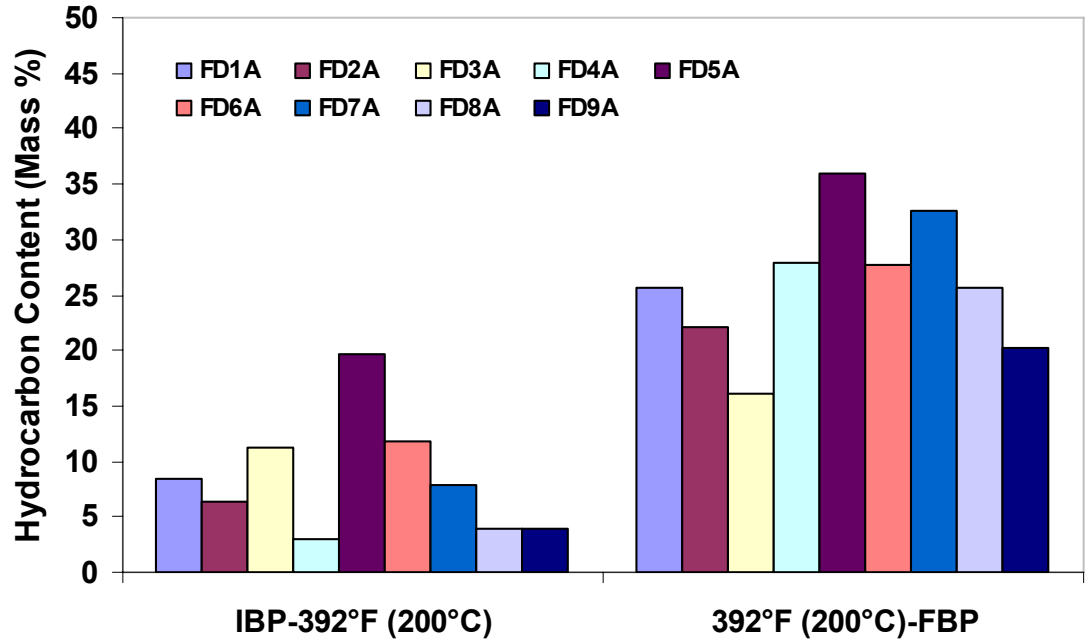

Figure 9.5. Total isoparaffin plus n-paraffin content in FACE diesel fuels by SPE-GC-MS and PIONA. (IBP = initial boiling point; FBP = final boiling point.)

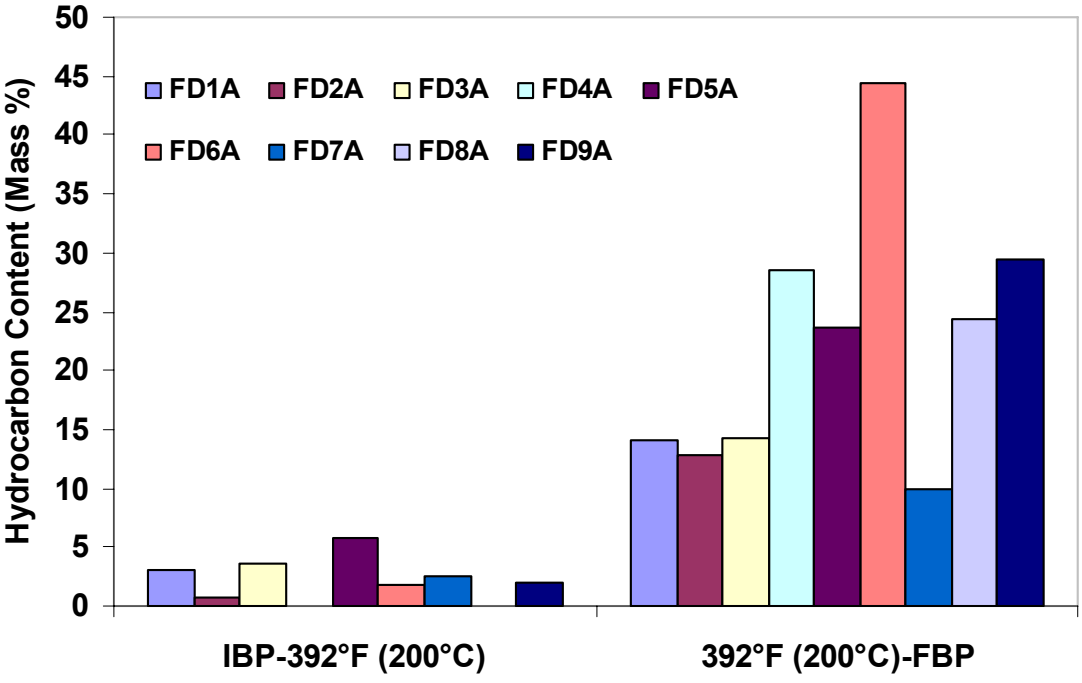

Figure 9.6. Total cycloparaffin content in FACE diesel fuels by SPE-GC-MS and PIONA. (IBP = initial boiling point; FBP = final boiling point.)

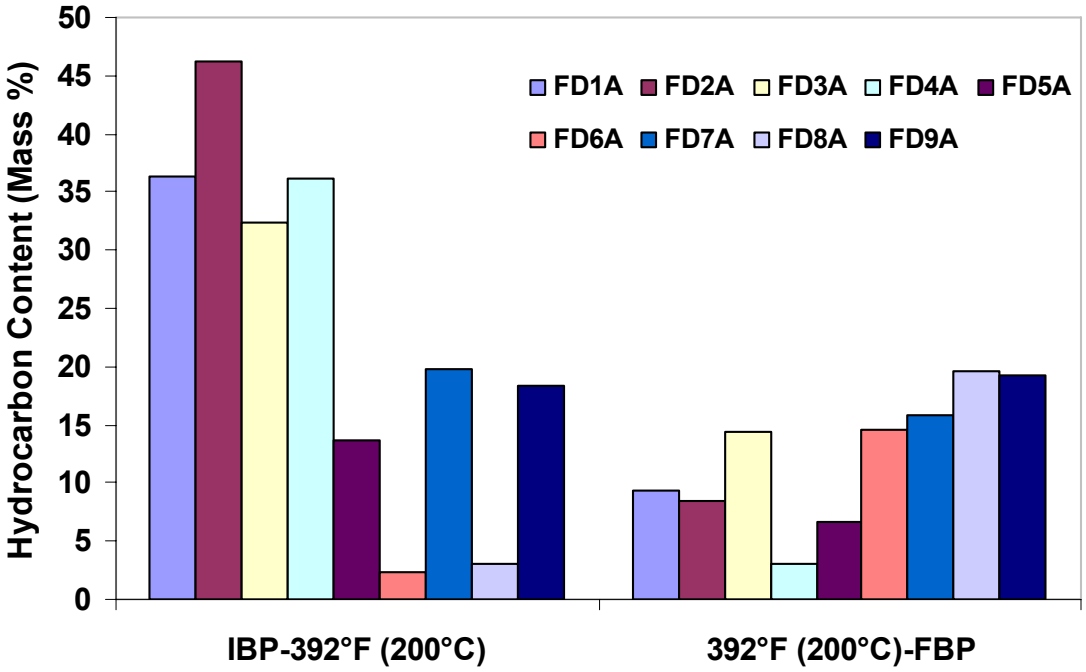

Figure 9.7. Monoaromatic content by SPE-GC-MS and PIONA. (IBP = initial boiling point; FBP = final boiling point.)

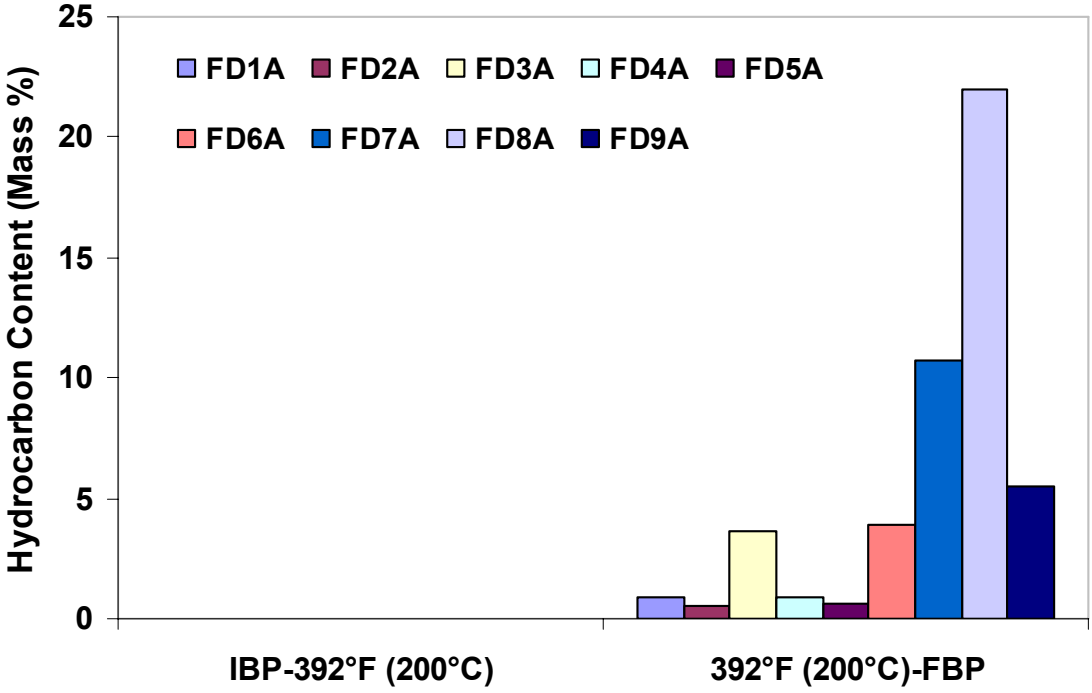

Figure 9.8. Diaromatic content by SPE-GC-MS and PIONA. (IBP = initial boiling point; FBP = final boiling point.)

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, 2008).

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, 2006).

10. DETAILED HYDROCARBON ANALYSIS PLUS GC-FIMS

Because of some of the problems experienced with PIONA analysis of some of the FACE diesel fuels, detailed hydrocarbon analysis (DHA) was also performed on the nine diesel fuel samples. DHA by ASTM D6730[1] is another standard method for naphtha fractions, like PIONA. Unlike PIONA, DHA is run on one column in a gas chromatograph, operated with a prefractionator to eliminate hydrocarbons that boil at temperatures greater than 200°C (392°F). Following standard DHA, the data were manipulated to give hydrocarbon type analyses with the data presented by carbon number (Appendix E, Tables E.1 to E.9) or by boiling point (Appendix E, Tables E.10 to E.18). Figures 10.1 to 10.9 show the DHA analyses by carbon number along with the data from PIONA by carbon number. For the most part, the data from the two methods agree reasonably well as shown in Tables E.1 to E.9 in Appendix E and Tables C.1 to C.9 in Appendix C. The differences between PIONA and DHA in FD1A and FD2A, shown in Figures 10.1 and 10.2 are not significant and still do not show the expected distribution between aromatics and saturates in these two samples. Differences between DHA and PIONA are apparent in FD6A and FD8A, Figures 10.6 and 10.8; however, the y-scale in these two figures is a different scale from the other fuels so that the differences are very small in absolute concentrations. The saturates, olefins, and aromatics contents from DHA, as shown in Table 10.1, do not differ significantly from the PIONA data reproduced in Table 10.2. Unknowns from DHA constitute from 0.3 to 3.3 mass %.

Table 10.1. DHA Data for Hydrocarbons Boiling at Less Than 200°C (392°F)[a]

Element	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
Saturates	17.25	6.91	11.02	3.42	13.60	4.92	8.07	0.40	5.38
Olefins	0.45	0.29	0.87	0.19	0.71	0.44	0.80	0.02	0.38
Aromatics	29.45	45.31	34.52	35.35	16.79	2.75	19.41	3.01	18.21
Polars	0	0	0	0	0	0	0	0	0
Unknowns	2.52	3.32	1.09	0.31	1.40	0.71	0.88	0.04	0.45
Sum	49.67	55.83	47.50	39.26	32.50	8.81	29.15	3.46	24.43

[a]Units are mass %.

Table 10.2. PIONA Data for Hydrocarbons Boiling at Less Than 200°C (392°F)[a]

Element	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
Saturates	11.54	7.10	14.85	2.99	18.7	6.40	9.30	0.33	5.88
Olefins	1.76	2.50	0.23	0.09	0.18	0.12	0.10	0.02	0.13
Aromatics	36.37	46.22	32.42	36.19	13.62	2.29	19.76	3.11	18.42
Polars	0	0	0	0	0	0	0	0	0
Sum	49.67	55.82	47.50	39.27	32.5	8.81	29.16	3.46	24.43

[a]Units are mass %.

The combined data from DHA and GC-FIMS is shown in a boiling point distribution (10°C intervals) with respect to hydrocarbon types in Figures 10.10 to 10.18. In this representation, it is clear that many of the fuels do not show a typical by-boiling-point distribution, which is shown by FD6A only. As for the SPE GC-MS + PIONA and other methods, the amounts of material boiling above and below 200°C (392°F) was derived from the simulated distillation ASTM D2887[2] data. Fuels FD1A and FD2A are clearly seen to be skewed by low boiling point hydrocarbons in Figures 10.10 and 10.11. The highest concentrations of hydrocarbon types are in the range from 190 to 210°C (374 to 410°F), which adds to the difficulty of using analytical methods for regions above and below 200°C (392°F). The low T_{90} fuels did not exhibit one large spike in the boiling point distribution that corresponds with the large C_9 aromatic content as was shown in the GC-FIMS + PIONA results. Instead, FD1A and FD2A had large aromatic contents in the 180 to 200°C (356 to 392°F) range, while FD3A and FD4A showed large aromatic contents in the 160 to 180°C (320 to 356°F). In the high T_{90} fuels FD5A to FD8A, Figures 10.14 to 10.17, it is clear that a large component of hydrocarbons boiling in the 250 to 260°C (482 to 500°F) boiling range was added to FD5A, FD7A, and FD8A. When considered along with the GC-FIMS + PIONA data, this particular material can be seen to be primarily a C_{14} n-paraffin. The GC-FIMS data by boiling point are given in tabular form in Appendix E Tables E.19 to E.27. The combination of hydrocarbon types by carbon number from GC-FIMS + PIONA and by boiling point by DHA + GC-FIMS along with 2D GC data provides a great deal of detail on the hydrocarbon composition of these diesel fuels.

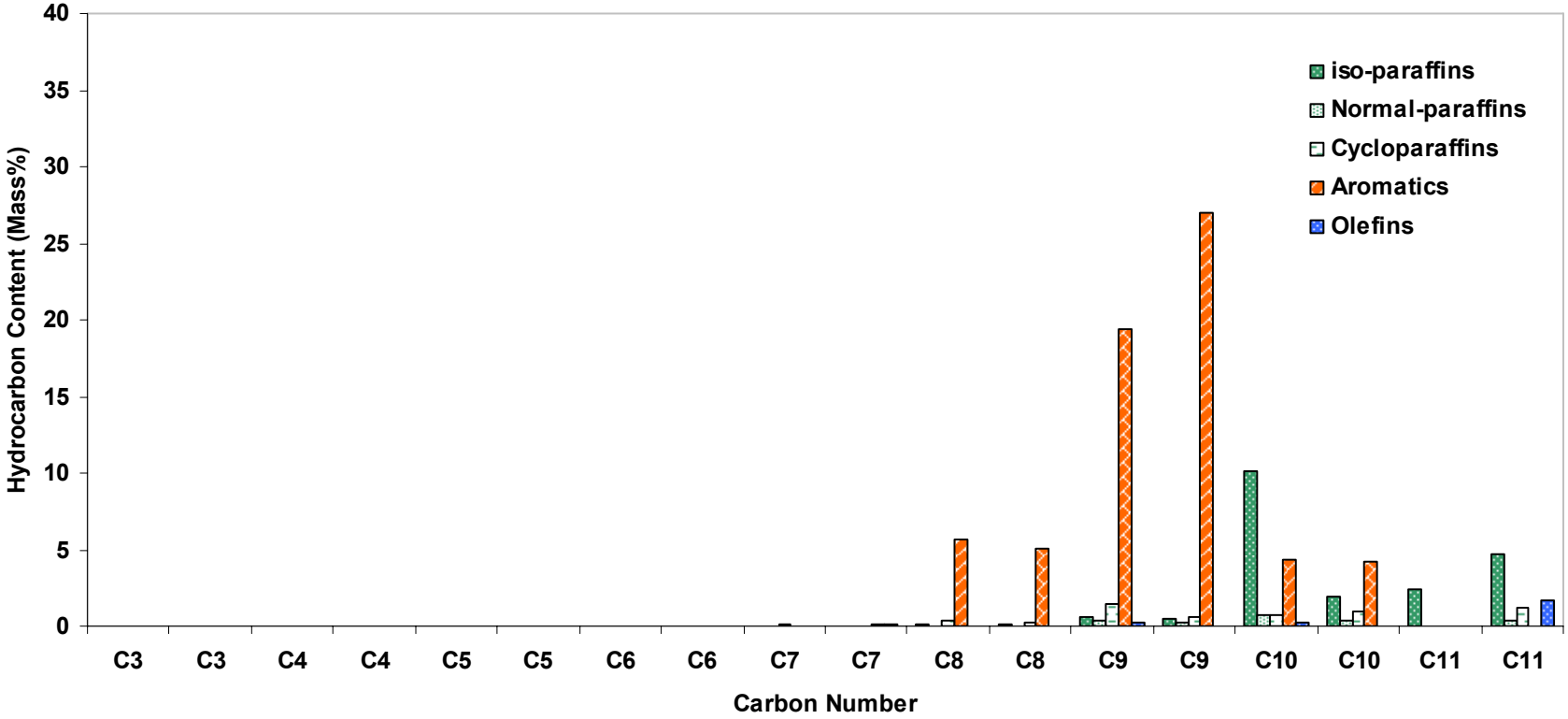

Figure 10.1. DHA and PIONA data for FD1A.

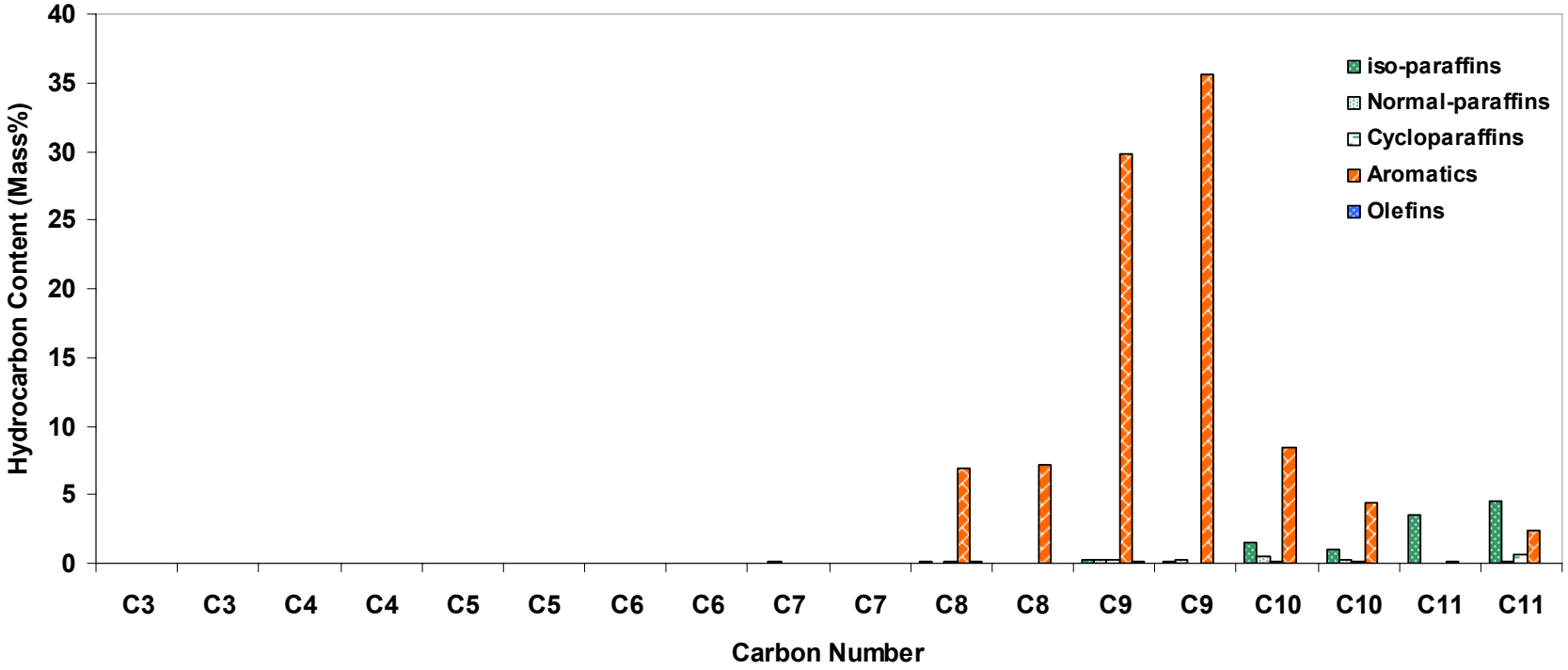

Figure 10.2. DHA and PIONA data for FD2A.

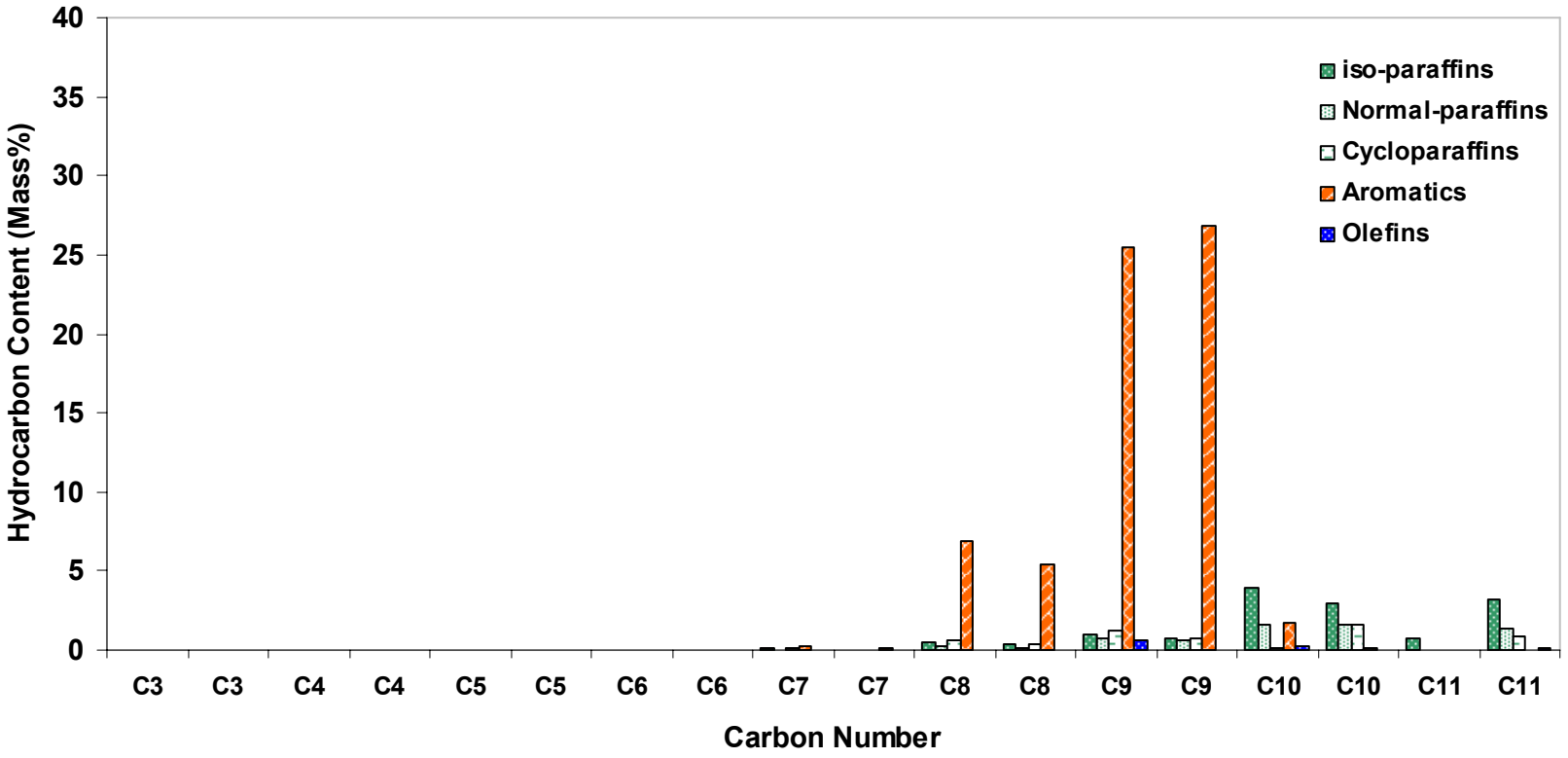

Figure 10.3. DHA and PIONA data for FD3A.

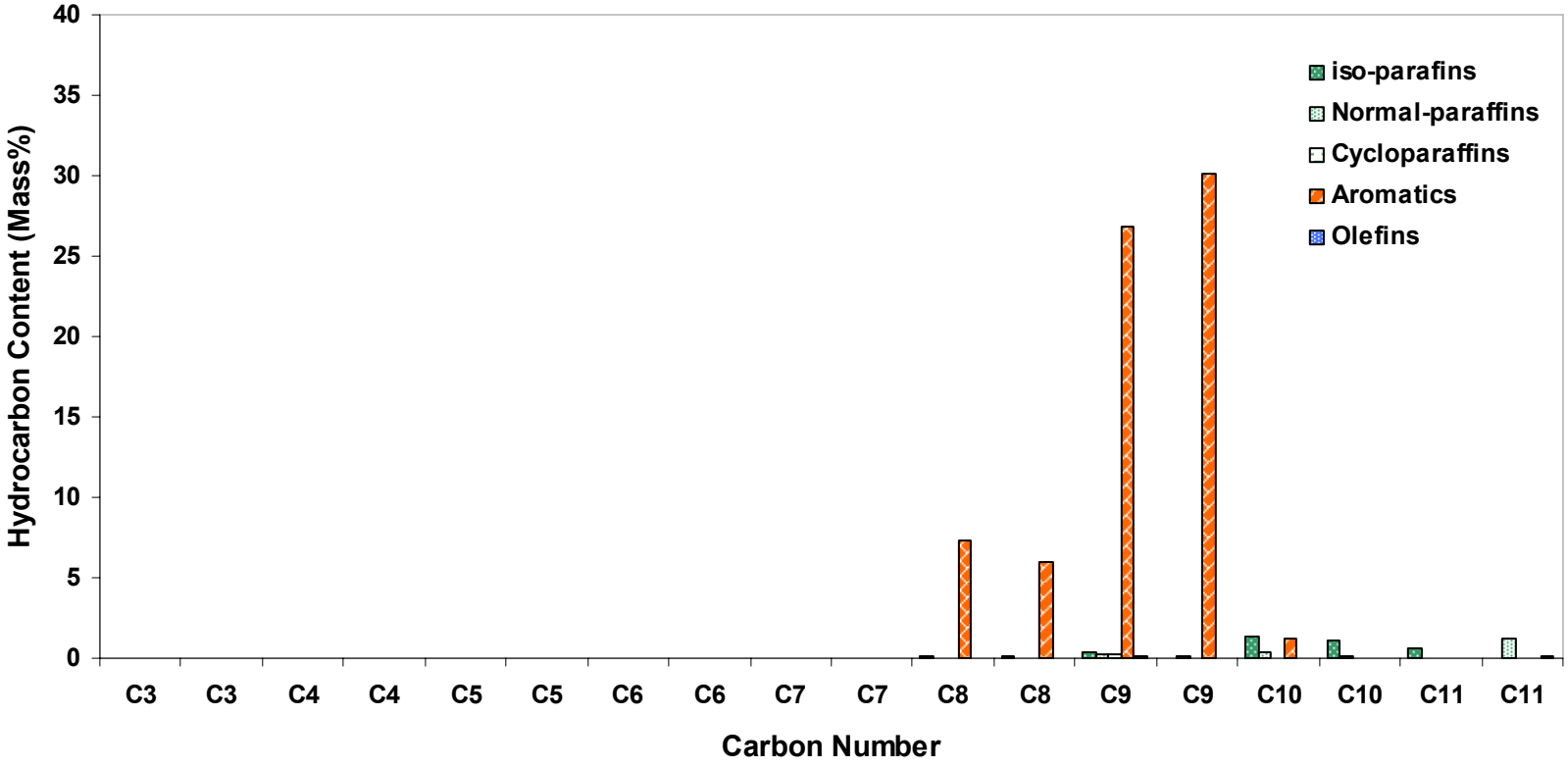

Figure 10.4. DHA and PIONA data for FD4A.

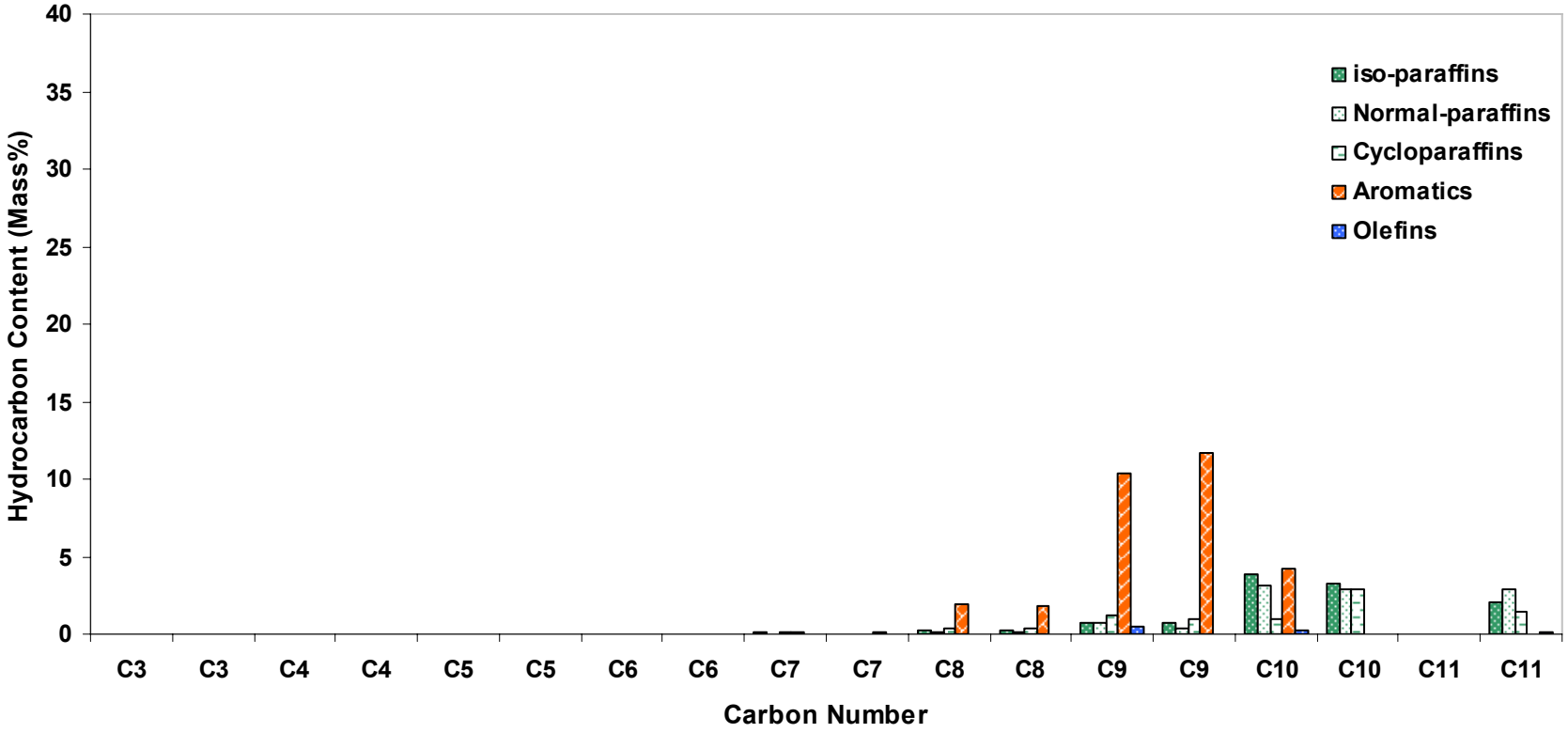

Figure 10.5. DHA and PIONA data for FD5A.

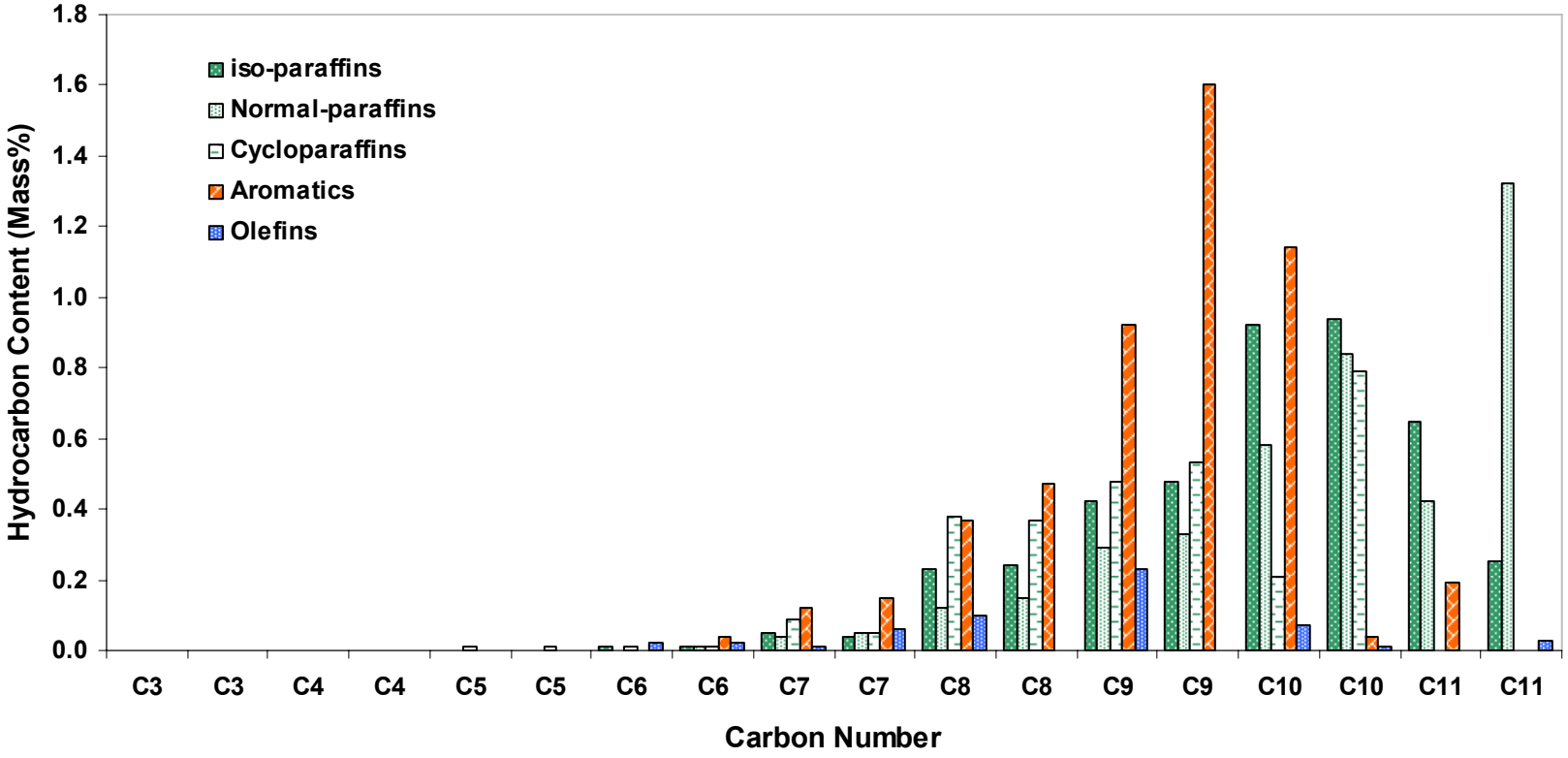

Figure 10.6. DHA and PIONA data for FD6A.

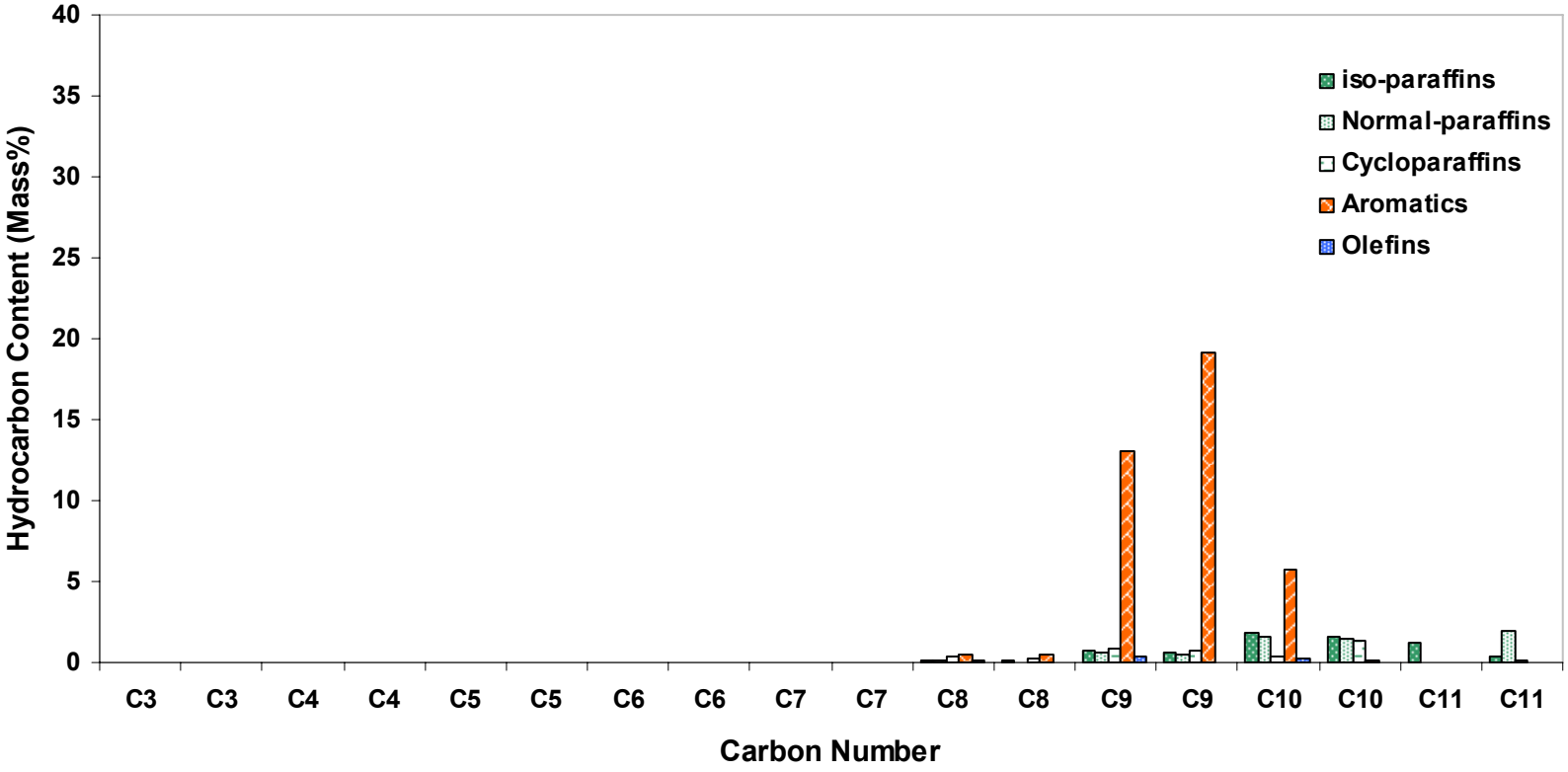

Figure 10.7. DHA and PIONA data for FD7A.

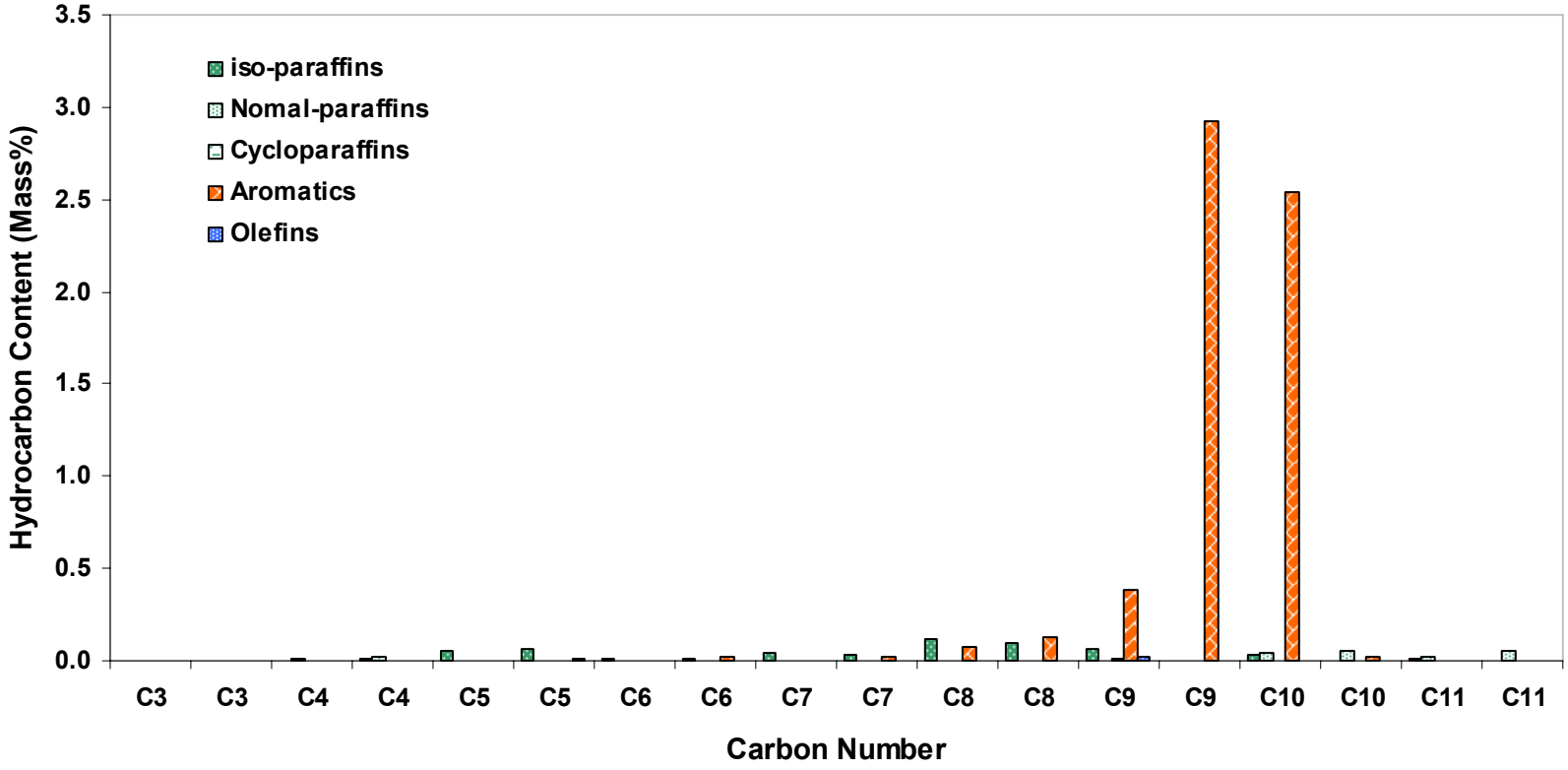

Figure 10.8. DHA and PIONA data for FD8A.

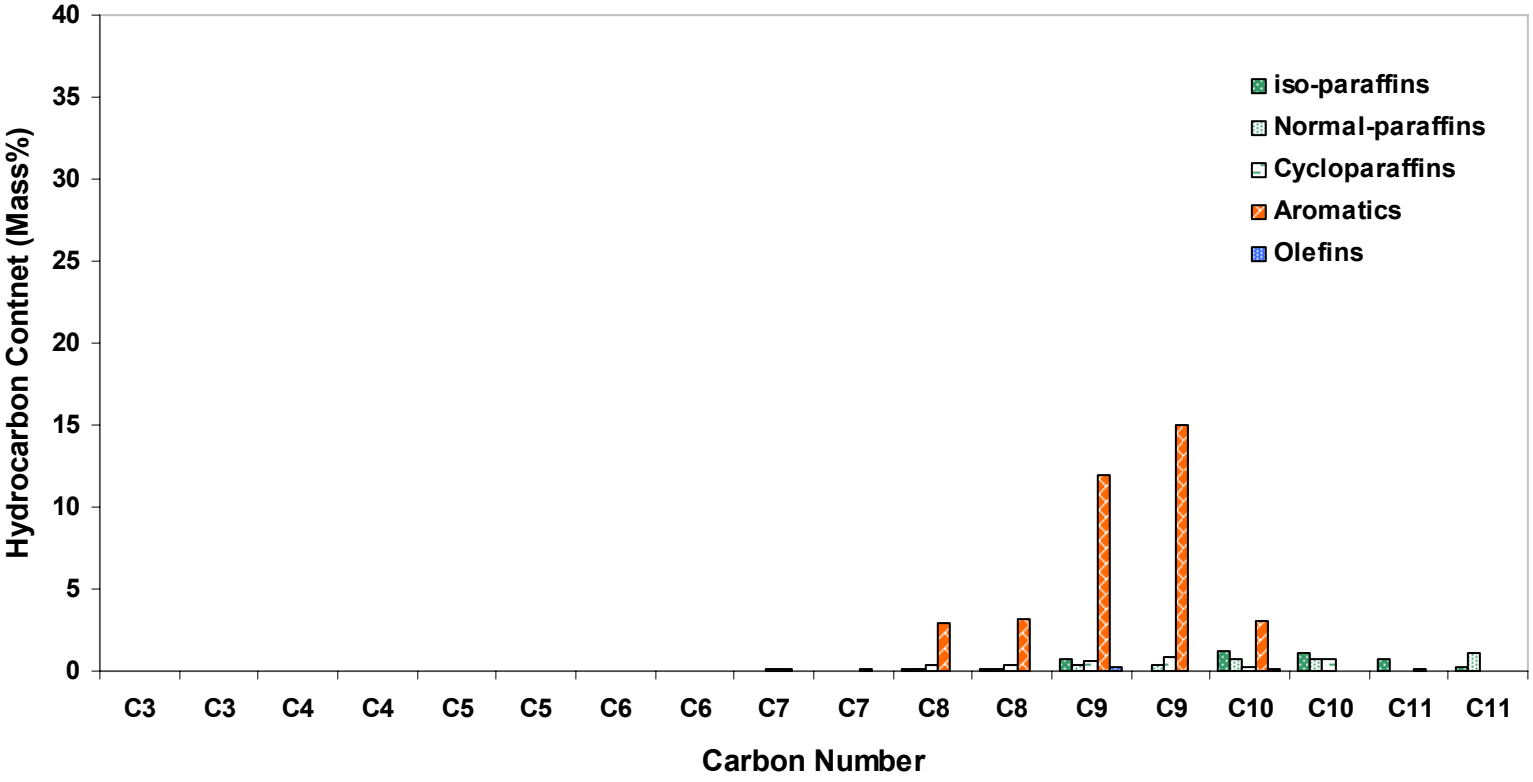

Figure 10.9. DHA and PIONA data for FD9A.

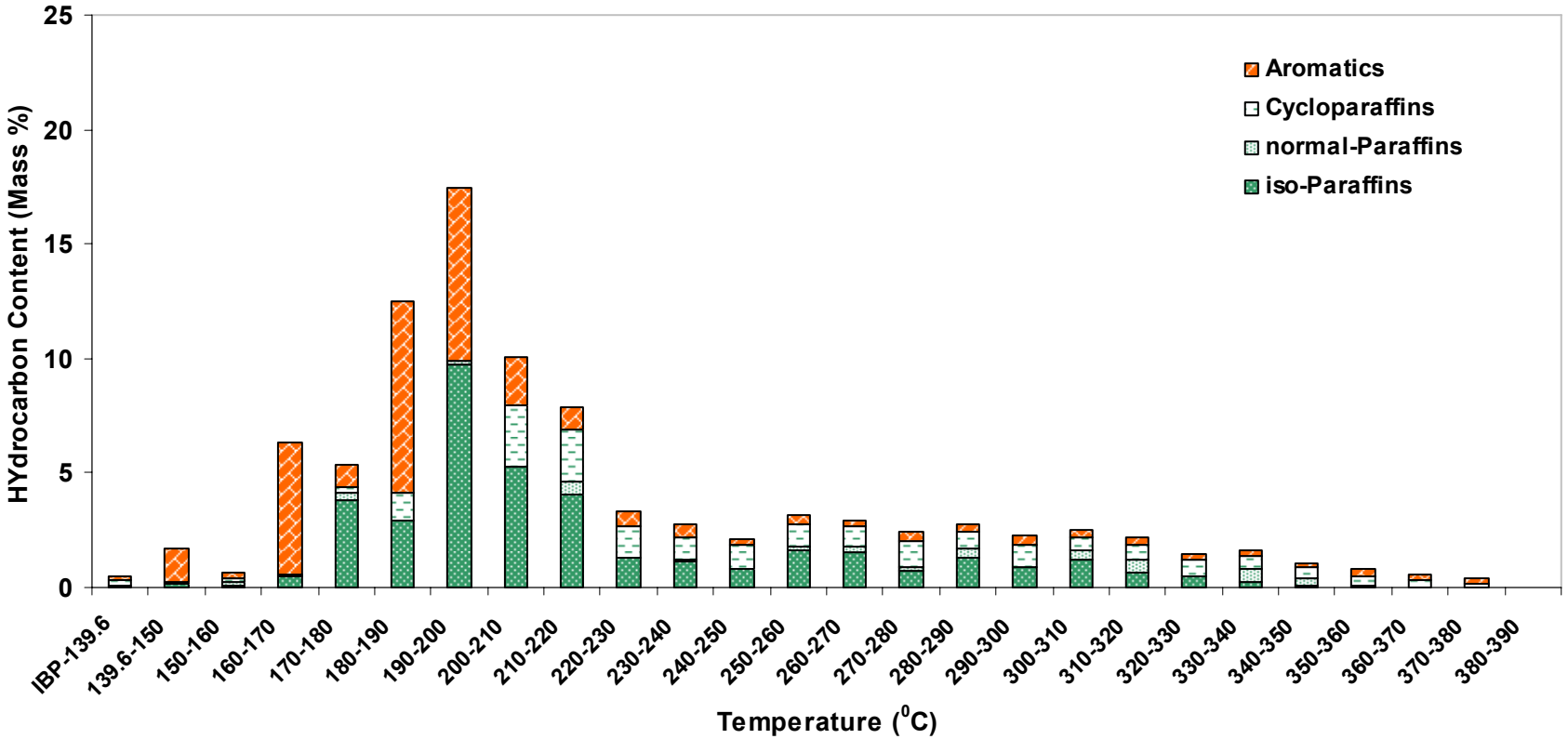

Figure 10.10. DHA and GC-FIMS Data for FD1A. (IBP = initial boiling point.)

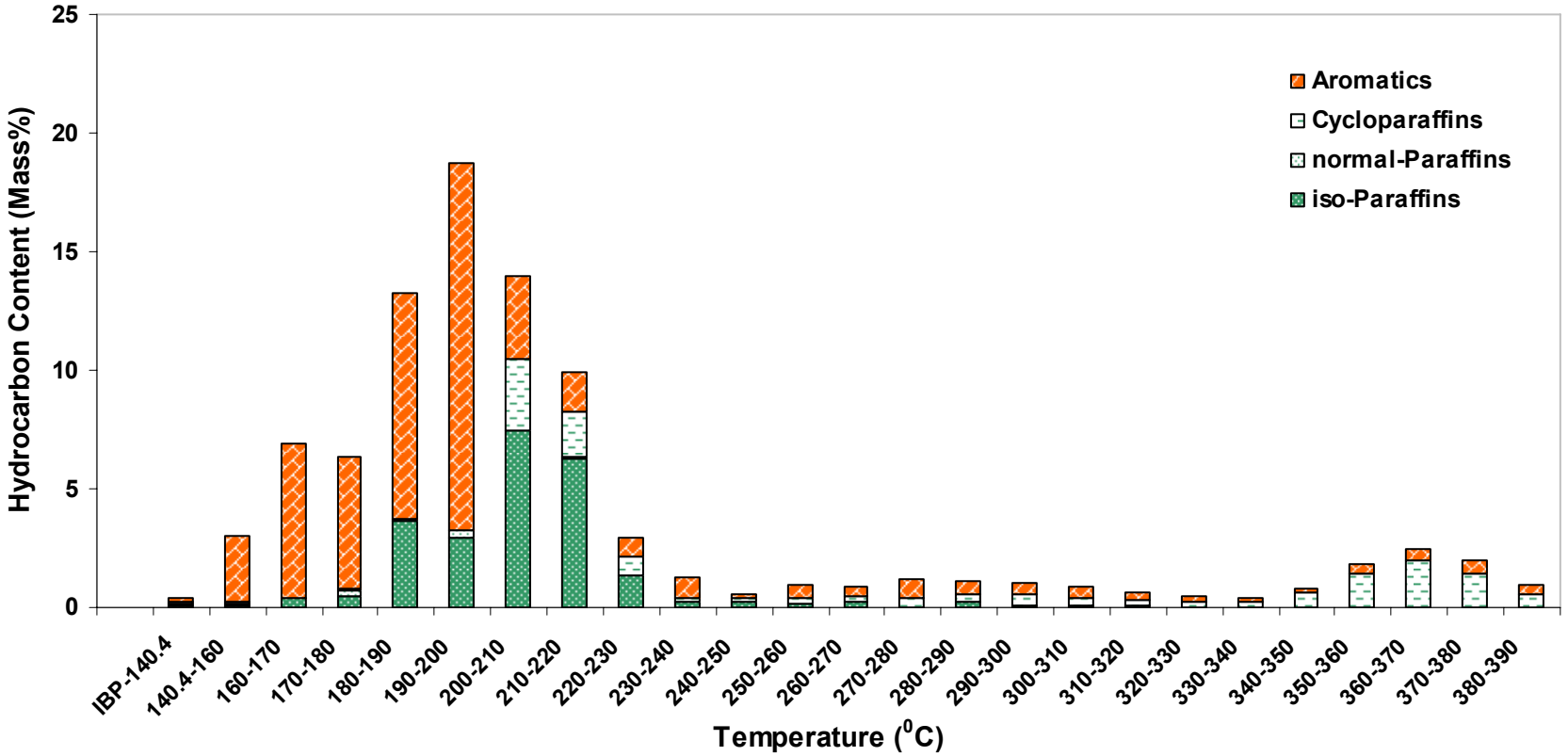

Figure 10.11. DHA and GC-FIMS data for FD2A. (IBP = initial boiling point.)

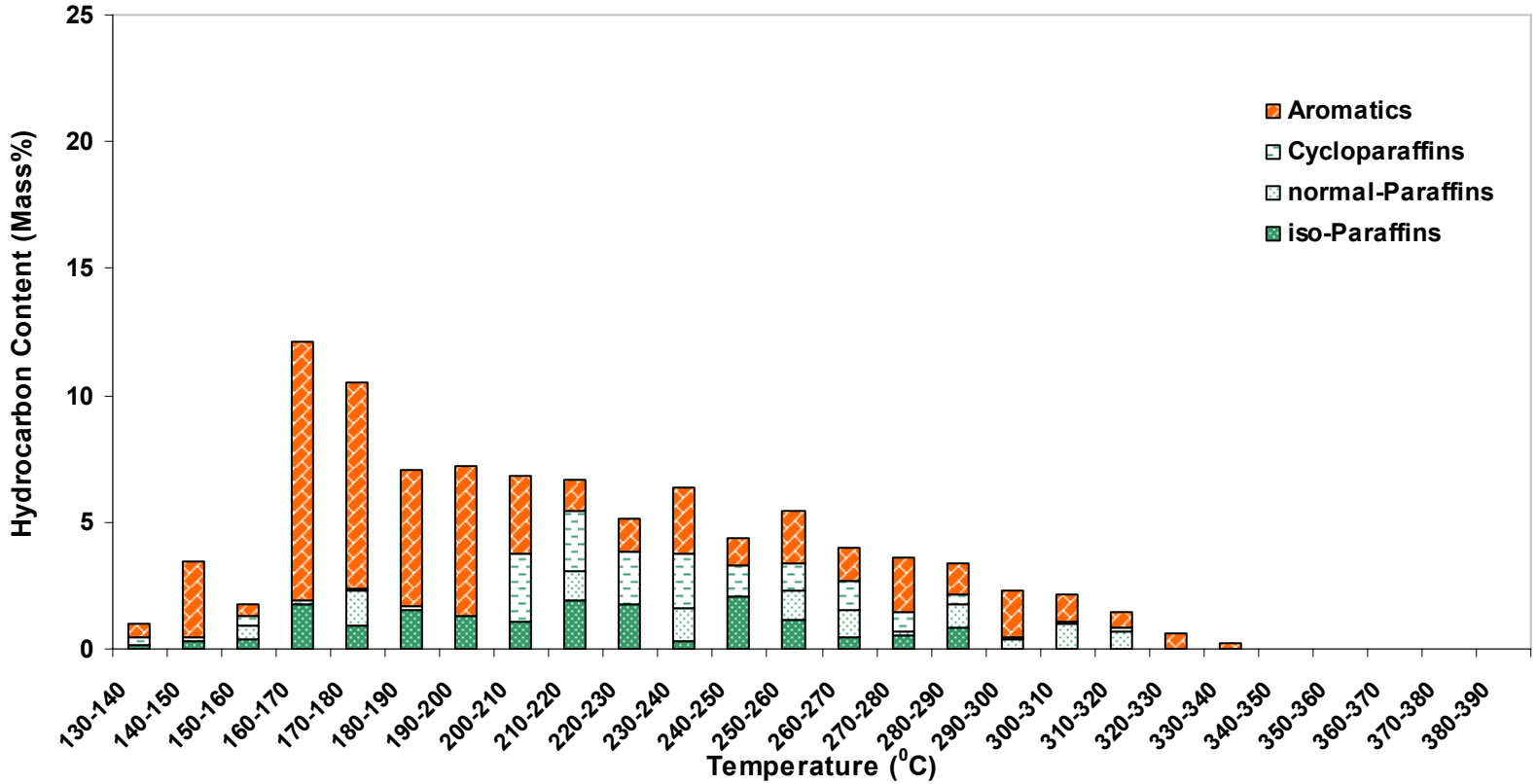

Figure 10.12. DHA and GC-FIMS Data for FD3A. (IBP = initial boiling point.)

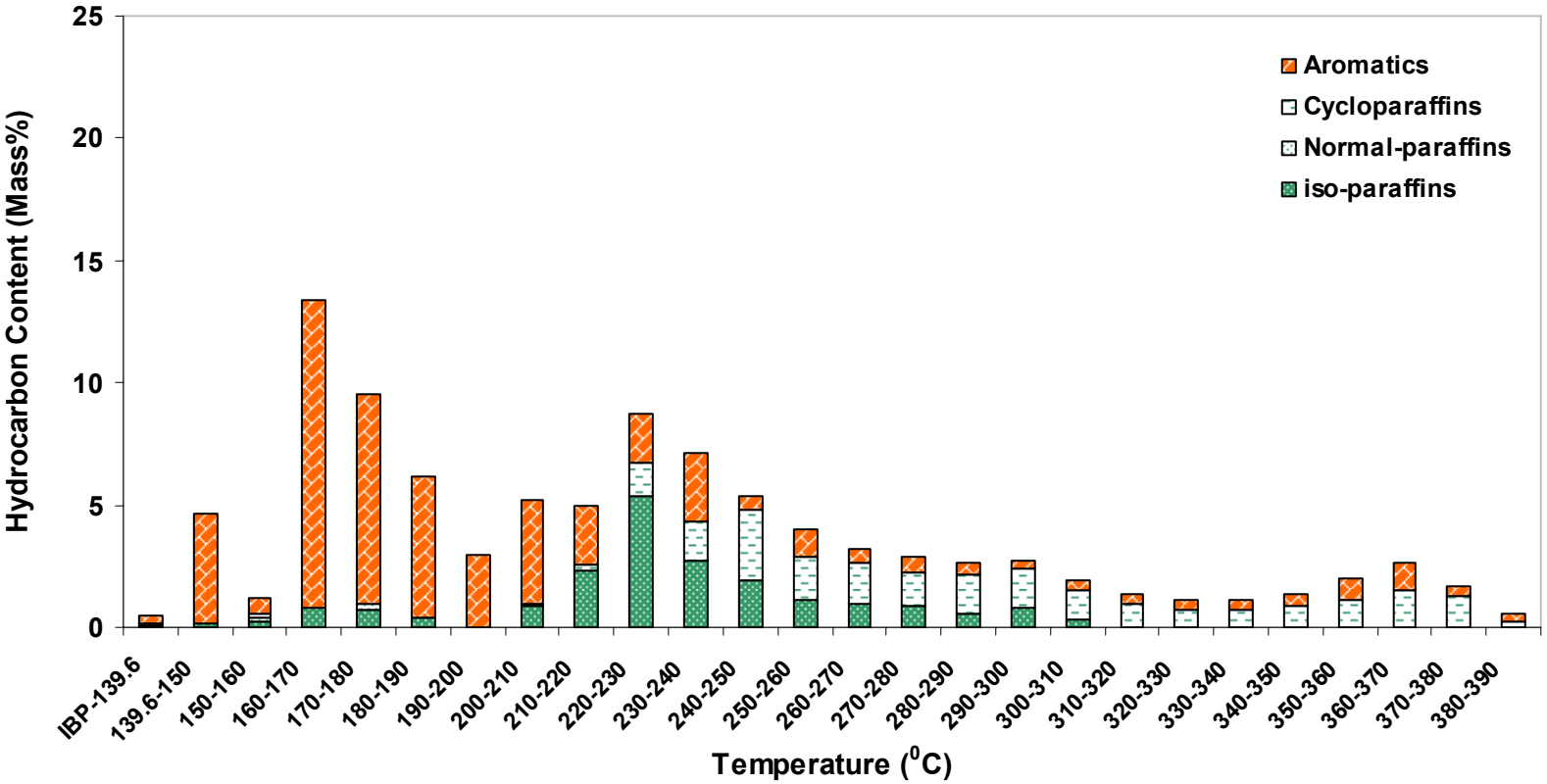

Figure 10.13. DHA and GC-FIMS Data for FD4A. (IBP = initial boiling point.)

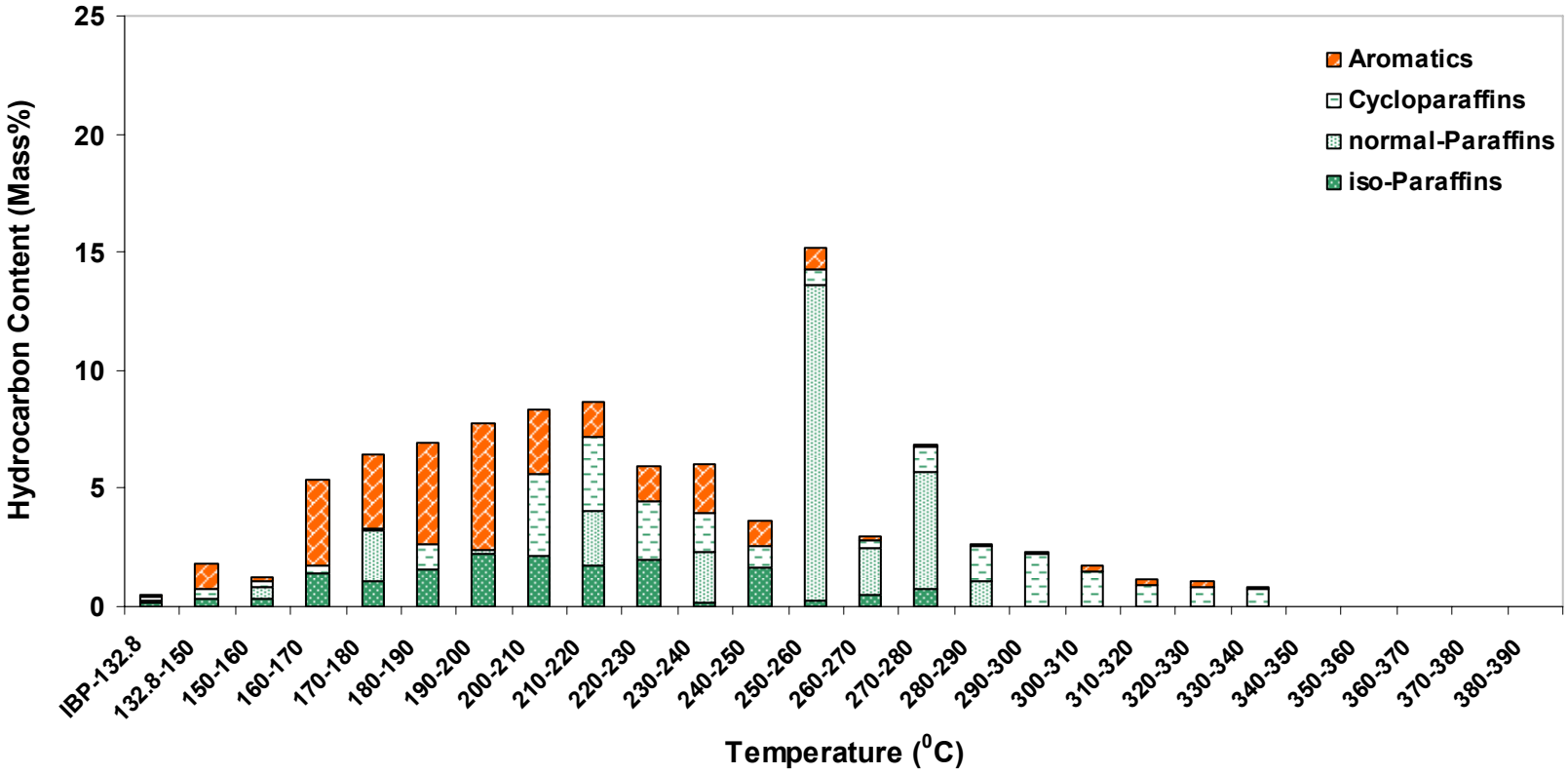

Figure 10.14. DHA and GC-FIMS Data for FD5A. (IBP = initial boiling point.)

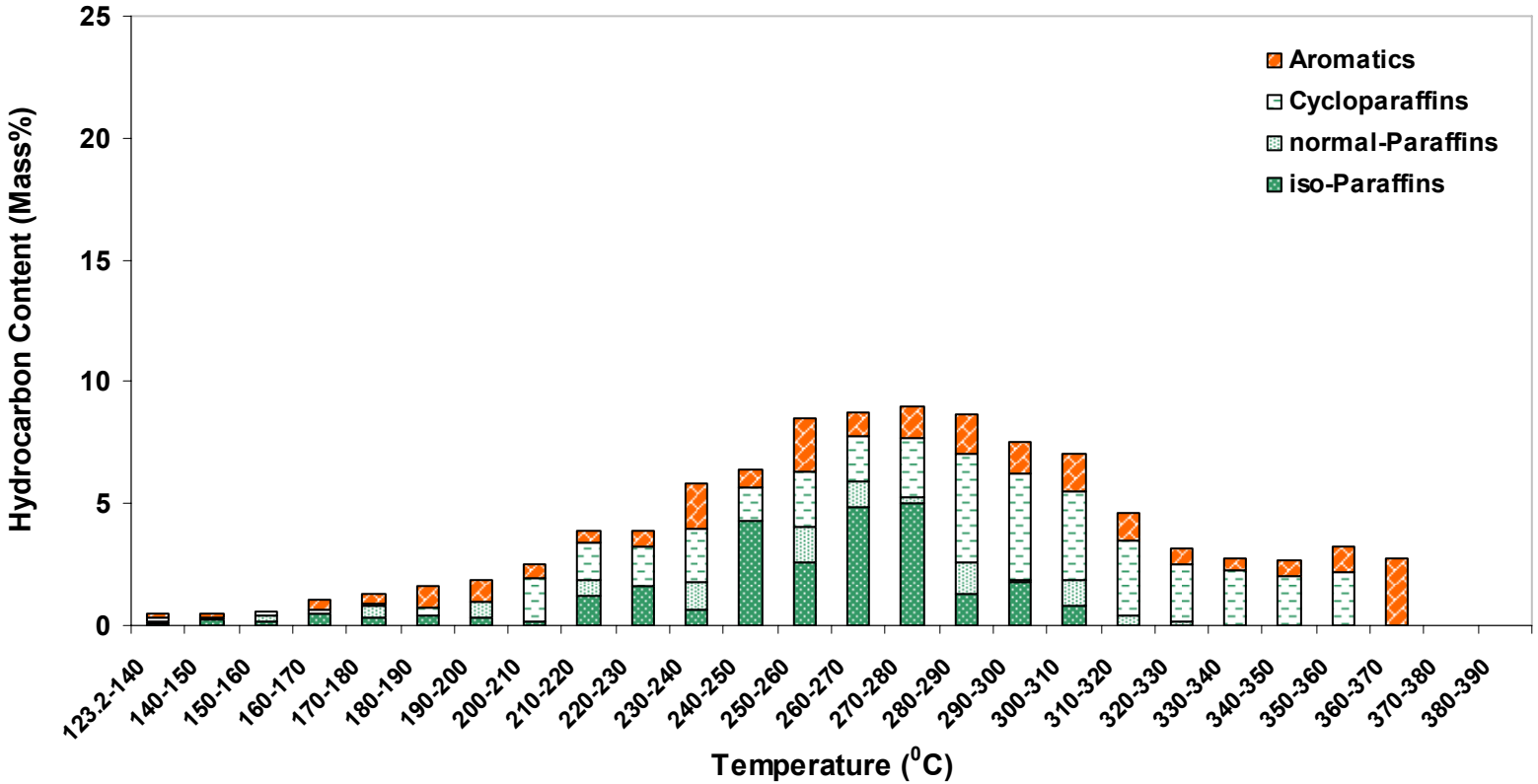

Figure 10.15. DHA and GC-FIMS Data for FD6A. (IBP = initial boiling point.)

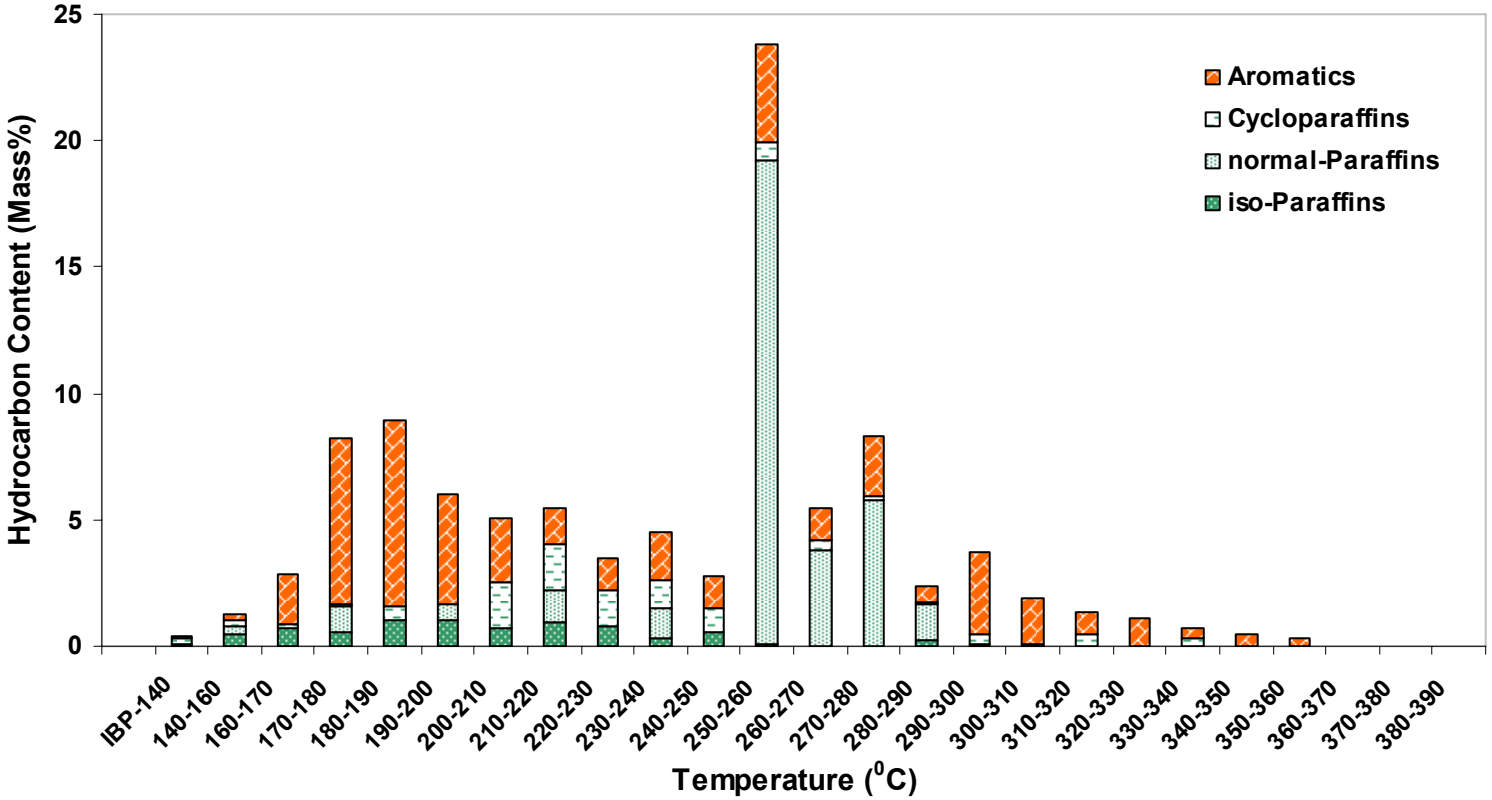

Figure 10.16. DHA and GC-FIMS Data for FD7A. (IBP = initial boiling point.)

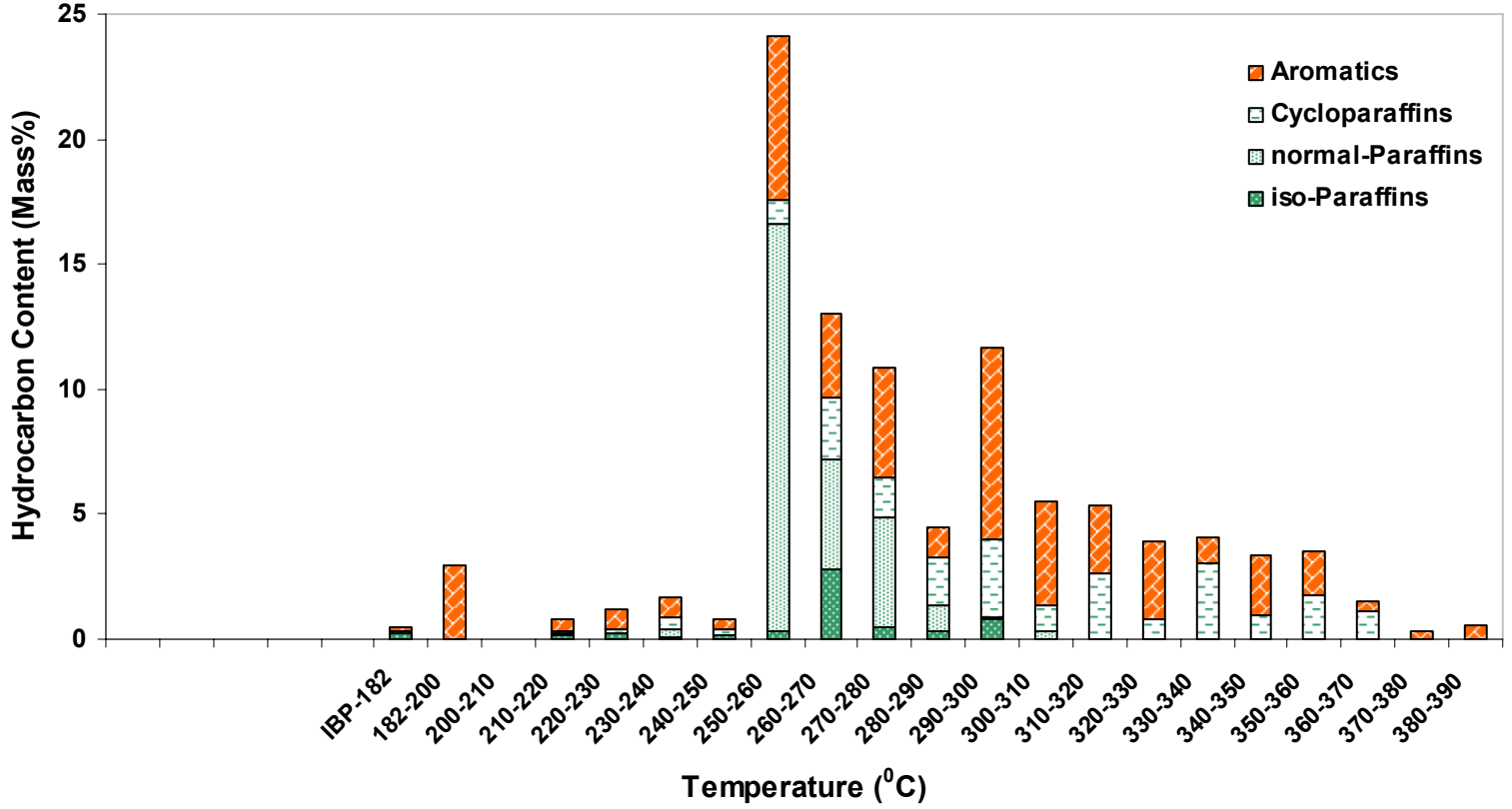

Figure 10.17. DHA and GC-FIMS Data for FD8A. (IBP = initial boiling point.)

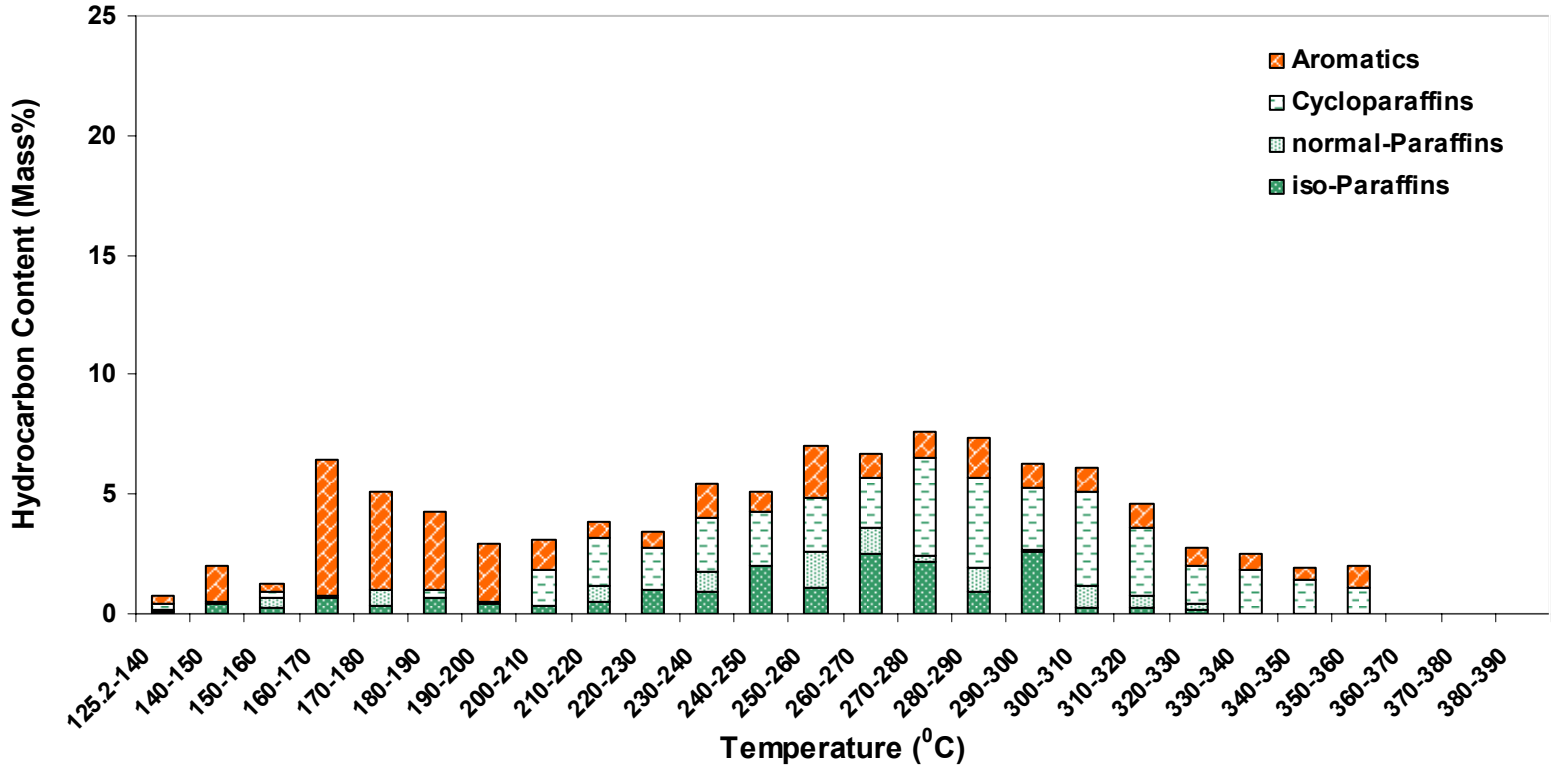

Figure 10.18. DHA and GC-FIMS Data for FD9A. (IBP = initial boiling point.)

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 D6730-01(2006)e1 (ASTM International, Pennsylvania, 2001).

2. ASTM International, *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography,* ASTM D2887-08 (ASTM International, Pennsylvania, 2008).

11. NUCLEAR MAGNETIC RESONANCE OF FACE DIESEL FUELS

11.1 INTRODUCTION

Nuclear magnetic resonance (NMR) analytical techniques are universally applied in experimental chemistry to establish and verify the structure of organic molecules. A variety of methods have been developed to determine statistical distributions of structures.[1] Hydrogen-1 NMR spectroscopy has been used to characterize fuels for more than four decades, and ^{13}C NMR analyses gained wide use starting in the '80s.[2] NMR analyses are particularly valuable for fuels characterization because of the speed of acquiring a spectrum (minutes to a few hours), the high degree of resolution of structure categories, and the ease of measurement of the magnitude of contribution of various structural categories found in the fuel mixture. Consequently, NMR analysis is particularly promising as a rapid method for prediction of fuel performance properties. In this section we present detailed NMR data for the FACE fuels and an analysis of the data showing structural categories (carbon types) and populations (carbon content). These structure categories and their contents potentially provide key support of significant importance to prediction of engine and component performance and key predictive capability for combustion and related studies.

NMR analysis provides very specific structural information regarding hydrocarbon mixtures that can be related to both physical and chemical properties of the fuel. Because ^{1}H and ^{13}C NMR can quantitatively resolve specific carbon types [e.g., α-methyl (CH_3), and β-, γ-, δ-, and ε-methylenes (CH_2) of linear paraffins, as well as methine (CH) and quaternary (C) groups], NMR techniques can quickly and conveniently identify the number of hydrogen atoms attached to each carbon and can readily quantify important structural groups such as aromatic, cycloparaffinic, normal paraffinic structure and branch paraffinic groups. The data can be readily adapted to additive functional group correlations. Carbon-13 NMR structural data can be used to reveal detailed structural categories of interest such as the positions that methyl groups occupy on branched paraffins and the chain lengths of longer branches. NMR methods can identify protons residing directly on a carbon atom (single bond correlation) or several bonds away (multibond correlations), allowing molecular connectivity (e.g., of alkyl groups to aromatic carbon) to be determined. Spectral editing methods can present carbon data by category (e.g., only methyl groups, only methylene groups, or only methine groups).[3–7] Molecular parameters derived from NMR data have been used in published and proprietary algorithms[8] that provide populations of structure groups in a fuel mixture and use that structural group information to predict performance properties based on various molecular descriptors. In the literature these descriptors have been correlated to cetane[9] and octane[10] numbers. Quantitative structure-property relationships (QSPR) have been developed for fuels,[11] and ^{13}C NMR has been applied to the determination of jet and diesel fuel properties.[12] Neural networks have been used to correlate properties with complex data sets for coal and petroleum conversion and octane number of gasoline using ^{1}H NMR data.

A somewhat more satisfying approach is to identify structural groups responsible for observed properties and to correlate properties with the abundance of those groups according to the principle of group additivity, similar to the Benson methods for thermochemical kinetics.[13] Thus NMR analysis, which reports the relative molar abundance of carbon types, is well-positioned to correlate the composite reactivity of organic groups with the statistical weight of the groups in question, yielding QSPR. However, the existing correlations may only be valid for the range of chemistries used to establish the correlation. Although NMR analysis of the FACE fuels is focused on distillate (diesel-like) fuel, as mentioned above, NMR analysis has been successfully applied to jet fuel and gasoline.

The data in this section are presented in a manner that has been adopted by Pacific Northwest National Laboratory (PNNL) and CanmetENERGY, specific to their clients' requirements, and have not been optimized for combustion research. However, the NMR format of molecular structural descriptors can assist in identifying any influence molecular structure has on low-temperature combustion.

The hypothetical structure of Figure 11.1 illustrates the spectroscopic separation of eight classes of structure type in a single molecule with predicted parts-per-million chemical shifts shown in blue:

1. alkyl-substituted aromatic(135.6 ppm),
2. protonated aromatic (128.8 ppm),
3. terminal long alkane methyl (14.1 ppm),
4. methyl of pendant ethyl (10.8 ppm),
5. methine CH (41.1 ppm),
6. methyl on aromatic ring (21.3 ppm),
7. β-methylene of long chain (23.0 ppm), and
8. γ-methylene of long alkane (29.6 ppm).

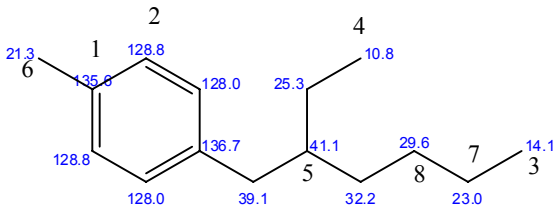

Figure 11.1. Typical diesel molecule structure.

By careful analysis of chemical shifts of methyl groups, the population of n-paraffins, isoparaffins, and alkane branching structures can be deduced (see Appendix F). Average alkane chain lengths, end groups of chains, average aromatic ring cluster sizes, the degree of substitution of aromatic rings, and other parameters can be determined. Because combustion properties and other engine/injection performance measures depend on group contributions to average molecular structure, NMR analysis can provide a structure-based technique with which to correlate properties. In the remainder of this section, we provide details and a discussion of measured NMR spectral distributions observed for the nine FACE fuels and examples of component molecules that contribute to the observed data.

11.2 EXPERIMENTAL

11.2.1 PNNL Nuclear Magnetic Resonance Method

Quantitative ^{13}C NMR and ^{1}H NMR spectra were acquired at 499.67 and 125.65 MHz, respectively, using a 45° observe pulse; acquisition and delay times of 3 and 5 seconds, respectively, with ^{1}H Waltz decoupling off 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. These conditions lead to an average integral error of about ±2 % (in carbon aromaticity). Carbon-13 spectra

are referenced to internal $CDCl_3$ (77.24 ppm), tetramethylsilane (0 ppm), or the α-carbon of linear long chain saturated hydrocarbons (14.16 ppm). Samples consisted of 0.15–0.2 mL of fuel diluted to 1.0 mL in $CDCl_3$ in 5 mm outer diameter NMR tubes. Spectra resulted from 400–1,600 scans.

Quantitative ^1H spectra were acquired at 499.67 MHz using 30° observe pulses and 11-second recycle times. Samples consisted of about 50 mg of fuel sample diluted to 1.0 mL in $CDCl_3$. 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 $CDCl_3$ (7.23 ppm). Spectra resulted from 100 scans.

11.2.2 CanmetENERGY Nuclear Magnetic Resonance Method

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

The quantitative carbon spectra were acquired using an acquisition time of 1.0 second and a sweep width of 36,003.6 Hz. A flip angle of 26.0° (3.3 µs) and a relaxation delay of 15 seconds were 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 1,600 scans. Line broadening of 3 Hz was used to improve the signal-to-noise ratio of the spectra. The spectra were referenced to the deuterochloroform being set to 77 ppm.

The quantitative proton spectra were acquired using an acquisition time of 3.0 seconds and a sweep width of 20,000 Hz. A flip angle of 29.6° (3.0 µs) and a relaxation delay of 4 seconds were used. The spectra were the result of 128 scans. Line broadening of 0.33 Hz was used to improve the signal-to-noise ratio of the spectra. The spectra were referenced to the deuterochloroform being set to 7.24 ppm. Carbon type analyses were performed using proton and carbon NMR spectra and elemental analysis results using a procedure based on that described by Japanwala et al.[14]

11.3 RESULTS

In Tables 11.1 and 11.2, integrated values over the continuous chemical shift range are presented for ^1H and ^{13}C data. The subregions chosen to quantify specific structural groups are considered applicable by the authors, but no standard format has been established for distillate fuel analysis. Several of the chemical shift assignments contain structural groups that normally are either not found in hydrotreated fuels (e.g., ketone, aldehydic, phenolic carbon) or found in low concentrations (olefinic carbon). Tables 11.1 and 11.2 are typical of assignments used in either distillate fuel analysis or crude oil.[15] See Appendix F for further definition of structure categories.

Table 11.3 presents the results of detailed processing of 1-D ^1H and ^{13}C NMR data. Complete processing of the spectroscopic data to allow the structure categories to be quantified requires detailed application of a variety of bonding relationships and approximations. Appendix G illustrates structural definitions which correspond to Table 11.3.

Table 11.1. Integrated ^{1}H NMR Spectra (PNNL data) for FACE Fuels

Label	Structure Definition	Chemical Shift	FD-1A	FD-2A	FD-3A	FD-4A	FD-5A	FD-6A	FD-7A	FD-8A	FD-9A
HA1	polyaromatic H	7.4-10.7	0.2	0.2	0.5	0.3	0.1	0.4	0.4	0	0.7
HA2	monoaromatic H	7.4-6.2	3.9	3.6	8.6	7.3	3.4	2.6	8.6	10	5.6
HO1	olefinic CH	5.1-6.2	0	0	0.1	0	0	0	0	0	0
HO2	olefinic CH2	4.8-5.1	0	0	0	0	0	0	0	0	0
HO3	olefinic CH2	4.3-4.8	0	0	0	0	0	0	0	0	0
HP1	α-to-aromatic CH2	2.4-4.3	2.4	1.7	5.6	2.7	2	2.8	5	5.9	4.2
HP2	α-to-aromatic CH3	2.0-2.4	5.7	5.8	12.2	11.8	4.7	2.8	8.4	1	7.8
HP3	paraffinic CH2	1.09-2.0	36.4	33.8	43.8	36.4	57.9	56.9	55.3	60.6	51.7
HP4	paraffinic CH3	0.5-1.09	51.4	55	29.1	41.5	31.9	34.5	22.3	22.5	30.1

Table 11.2. Integrated ^{13}C NMR Spectra (PNNL data) for FACE Fuels

Label	Structure Definition	Chemical Shift	FD-1A	FD-2A	FD-3A	FD-4A	FD-5A	FD-6A	FD-7A	FD-8A	FD-9A
CA1	Oxygenated carbon (ketone, carboxylate)	190 - 170	0	0	0	0	0	0.08	0	0	0
CA2	Quaternary aromatic	155 - 129	8.31	8.72	18.34	14.73	6.14	5.31	13.33	9.14	13
CA3	Aromatic C-H	129 - 120	7.87	8.26	15.41	13.15	6.78	6.04	17.32	20.05	11.51
CA4	Olefinic CH	115 - 113	0.01	0.07	0	0	0	0	0.02	0	0.06
CA5	Olefinic CH2	113 - 100	0	0.02	0.08	0	0	0	0	0	0.29
CP1	Paraffinic CH	55 - 45	1.77	1.34	0.75	1.47	2.25	2.77	1.06	1.64	1.93
CP2	Paraffinic CH * CH2	45 - 32.7	20.67	19.79	13.56	18.63	17.95	24.78	10.31	14.36	18.91
CP3	Chain γ-CH2 β-to-aromatic CH2; chain δ-CH2 α-to-aromatic naphthenes	32.7 - 30	8.53	8.25	4.83	7.56	10.76	10.44	8.18	6.65	5.96
CP4	Aromatic-attached ethyl CH2	30.8 - 28.5	14.1	14.18	11.81	11.7	22.02	17.79	21.76	21.15	14.47
CP5	Cycloparaffin CH2	28.5 - 25	8.83	8.72	5.9	6.9	6.08	8.37	3.79	6.2	7.37
CP6	Chain β-CH2, α to aromatic or isobutyl CH3	25 - 21.9	8.79	8.91	7.7	5.91	10.49	9.28	8.27	7.15	8.1
CP7	α-to-ring CH3	21.9 - 17.6	11.3	11.28	11.49	12.2	7.2	7.35	7	4.43	9.67
CP8	Aromatic-attached ethyl CH3	17.6 - 14.7	3.81	3.99	2.54	2.98	1.45	0.95	2.41	3.25	1.71
CP9	Chain α-CH3	14.7 - 12.3	4.1	4.22	5.42	3.28	7.64	5.62	6.41	5.18	5.33
CP10	Branched-chain CH3	12.3 - 5	1.92	2.27	2.16	1.49	1.25	1.23	0.13	0.81	1.71

Table 11.3. Combined ^{1}H and ^{13}C NMR Analysis of Structure Categories Using CanmetENERGY-NCUT Data

Structural Definition	FD-1A	FD-2A	FD-3A	FD-4A	FD-5A	FD-6A	FD-7A	FD-8A	FD-9A
Aromatic carbon (Mole % C)	18.17	19.08	32.90	26.79	18.68	12.97	29.38	27.49	22.57
Ar carbon cluster size	7	6	9	6	11	8	8	7	7
Cy carbon cluster size	7	7	8	8	8	8	7	7	11
Alpha to aromatic cycloparaffin (Mole % C)	0.00	0.00	1.34	0.00	0.32	0.00	0.99	0.87	0.78
Chain ends (Mole % C)	9.22	9.92	10.19	10.66	12.61	13.28	9.61	8.88	11.59
Chain midsection (Mole % C)	6.37	5.37	5.87	3.67	14.83	8.97	15.26	14.49	7.38
Average chain length	5.0	4.5	4.4	3.6	6.4	4.9	7.4	7.6	4.8
Chain Ends	Fraction	Fraction	Fraction	Fraction	Fraction	Fraction	Fraction	Fraction	Fraction
Aromatic	0.3	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2
Olefin	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cycloparaffin	0.3	0.4	0.3	0.5	0.2	0.3	0.3	0.2	0.3
Branched Paraffin	0.3	0.2	0.2	0.2	0.3	0.3	0.1	0.2	0.3
Paraffin Terminal Methyl	0.2	0.1	0.3	0.1	0.4	0.2	0.5	0.4	0.2
Sulphidic Sulphur	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Carbon Type	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C
Aromatic	18.17	19.08	32.90	26.79	18.68	12.97	29.38	27.49	22.57
Cycloparaffinic	33.34	32.89	21.52	27.11	18.40	25.72	18.89	22.01	24.51
Branched Paraffin	14.65	14.48	11.87	13.62	16.93	22.32	5.17	7.39	17.16
Paraffin Chain (C1+)	33.70	33.28	33.52	32.28	45.73	38.80	46.27	42.85	35.65
Olefin	0.14	0.27	0.19	0.20	0.27	0.19	0.29	0.26	0.11
C=O*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
* C=O was not measured									
Carbon Type	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C	Mole % C
C=O*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic and Olefin									
Aromatic NS (C+CH)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aromatic Bridge C	0.25	0.01	4.60	(0.00)	3.99	1.12	2.39	1.96	1.12
Aromatic Alkyl Subst. C	9.01	9.53	11.03	12.21	5.06	5.03	9.76	5.85	8.83
Aromatic CH	8.91	9.55	17.26	14.58	9.62	6.82	17.22	19.67	12.61
Methyl-Aromatic	4.11	4.36	6.05	7.79	2.02	1.65	4.99	0.30	4.47
Ethyl-Aromatic	4.96	5.41	3.86	4.50	2.11	1.42	4.65	5.87	2.73
Propyl-Aromatic	0.22	0.10	0.24	0.29	0.14	0.00	0.00	0.03	0.12
Diphenyl Methane CH2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Olefin CH	0.12	0.20	0.15	0.16	0.21	0.15	0.22	0.21	0.10
Olefin CH2	0.01	0.03	0.02	0.02	0.02	0.02	0.03	0.02	0.01
Olefin CH2(=C)	0.01	0.04	0.02	0.02	0.03	0.02	0.04	0.04	0.00
Cycloparaffin and Paraffin									
Cycloparaffin Bridge CH	1.30	2.06	1.76	2.47	1.41	2.96	1.24	1.03	4.92
Cycloparaffin Alkyl Subst. CH	3.40	4.63	3.99	5.26	2.98	5.84	3.50	4.89	4.08
Cycloparaffin CH2	28.63	26.16	15.75	19.36	13.98	16.90	14.10	16.05	15.52
Cycloparaffin C(=CH2)	0.01	0.04	0.02	0.02	0.03	0.02	0.04	0.04	0.00
Methyl-Cycloparaffin	0.30	0.10	0.00	0.00	0.00	1.78	0.91	2.72	0.00
Ethyl-Cycloparaffin	1.01	0.81	0.93	0.64	1.03	1.15	0.21	0.23	0.79
Paraffin Chain	11.30	8.77	13.00	6.22	30.36	18.06	28.92	25.77	15.16
Branched Paraffin									
Methyl-Branched Chain	13.26	12.19	10.00	10.17	16.89	21.30	5.17	7.39	15.30
Ethyl-Branched Chain	0.74	0.91	0.83	1.17	0.04	0.71	0.00	0.00	0.41
+Butyl-Branched Chain	0.64	1.38	1.04	2.28	0.00	0.32	0.00	0.00	1.45
Chain Attachments									
a to Sulphides	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ab to Aromatic Rings	4.70	4.86	3.27	4.15	3.22	5.34	2.93	3.48	4.37
a to Olefin	0.12	0.20	0.15	0.16	0.21	0.15	0.22	0.21	0.10
a to Cycloparaffin Rings	2.59	4.12	3.52	4.94	2.47	3.48	2.48	2.06	3.68
ab to Branch Points	4.39	4.54	2.50	3.60	4.17	5.76	0.96	2.18	4.24
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

11.4 DISCUSSION

Because the NMR techniques and integration ranges with associated algorithms may vary among analysts and in many cases are considered proprietary, it is not possible to make a direct and complete comparison of NMR data among the laboratories. However, a good assessment can be based on the aromaticity defined by both laboratories. Table 11.4 shows the calculated carbon aromaticity of the nine FACE fuels, showing good agreement within an average of ±2.2% and a maximum discrepancy of 5% for FD5A.

Table 11.4. Comparison of PNNL and NCUT Fuel Carbon Aromaticity

	Aromatic Carbon (%)	
FACE Fuel	PNNL	NCUT
FD1A	17.3	18.2
FD2A	17.1	19.1
FD3A	33.1	32.9
FD4A	28.1	26.8
FD5A	13.1	18.6
FD6A	11.9	13.0
FD7A	32.7	29.4
FD8A	30.7	27.5
FD9A	25.1	22.6

It needs to be restated that NMR analysis differs from more traditional fuel analysis by quantifying carbons in specific structures and not molecules. Therefore, direct comparison of NMR data with the results of traditional analyses (e.g., GC) is not possible without converting the NMR data to molecules with appropriate mathematical relationships. What is important is the fact that NMR quantifies the carbon bonds in the diesel fuel sample. As combustion depends upon the breaking of carbon bonds, it is highly likely that the relative contents of different types of carbon bonds will have a direct influence on specific aspects of the combustion process.

The analysis provided by PNNL is based on integration ranges found in the literature for diesel fuels. PNNL has reviewed the integration regions and, based on current NMR assignment tools, made some changes in definitions that are more consistent with the most probable structures for these samples. Certain attributes of the NMR results are highlighted as parameters which may be important for correlation to combustion characteristics. This includes the methyl and methylene groups using ^{1}H NMR as well as the methyl, ethyl, propyl, and butyl branches from ^{13}C NMR.

Because paraffinic structures can significantly influence combustion, the ^{1}H NMR regions (HP3 and HP4) in Table 11.1 are displayed in Figures 11.2 and 11.3 to highlight the differences among the FACE fuels.

Figure 11.2 quantifies the paraffinic carbon structures by dividing the CH_3 and CH_2 in Table 11.1 by the respective number of hydrogens. The higher the CH_3 : CH_2 ratio, the greater the branching of the paraffinic structures, which is associated with lower CNs. The lower CH_3 : CH_2 ratios for FACE fuels FD3A and FD4A, as compared to FD1A and FD2A, would be consistent with maintaining a similar CN with a higher aromatic content.

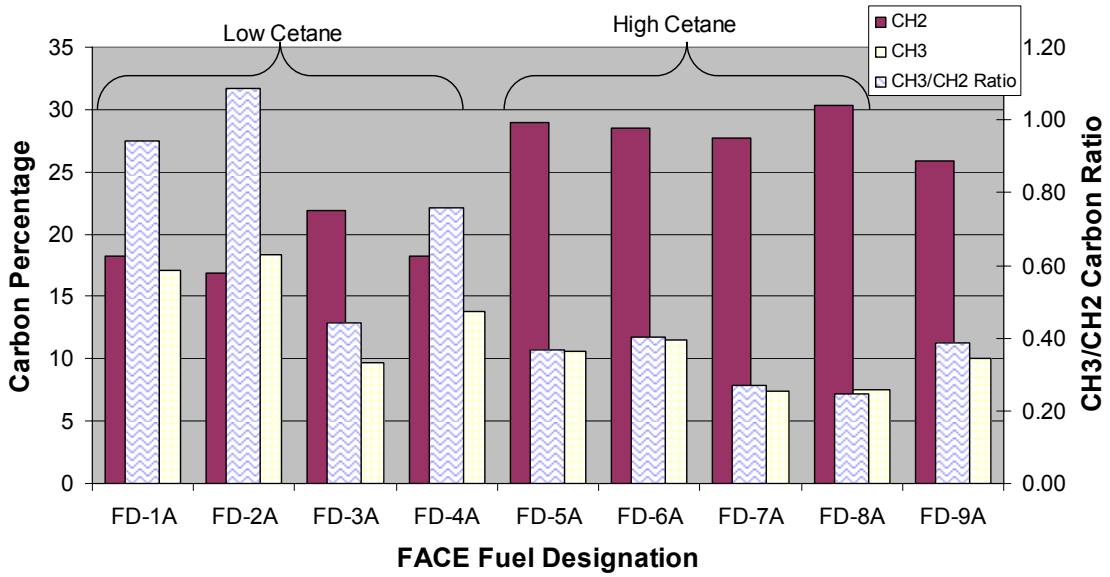

Figure 11.2. Quantification of CH_3 and CH_2 carbons based on ^1H NMR data.

The ^{13}C NMR data (Table 11.2) provide detailed information regarding the exact position of the carbon atoms in the paraffinic structure. By combining both ^1H and ^{13}C NMR, more specific structural information can be obtained. For example, NMR carbon type analysis data can be used to draw representative molecules where the parameters used for the fit include

- contents of aromatic, cycloparaffinic, branched paraffinic, and paraffinic carbon;
- aromatic and cycloparaffinic cluster sizes;
- chain segment lengths; and
- mole fraction of chain ends.

As an example, Figure 11.3 compares the aromatic carbons and alkyl substitutions using Table 11.2 ^{13}C data:

- aromatic carbons, Caro = $CA_2 + CA_3$, and
- CH_3 alkyl aromatic substitutions, CH_3aro = CP7 + CP8.

The higher CH_3 : Caro ratios (e.g., FD1A and FD2A) are consistent with higher percentage of methyl substitutions versus longer alkyl chain substitutions. The low CH_3 : Caro ratios for FD7A and FD8A are consistent with the extremely high diaromatic concentration in both samples. The Caro trends well with the aromatic content in the fuels.

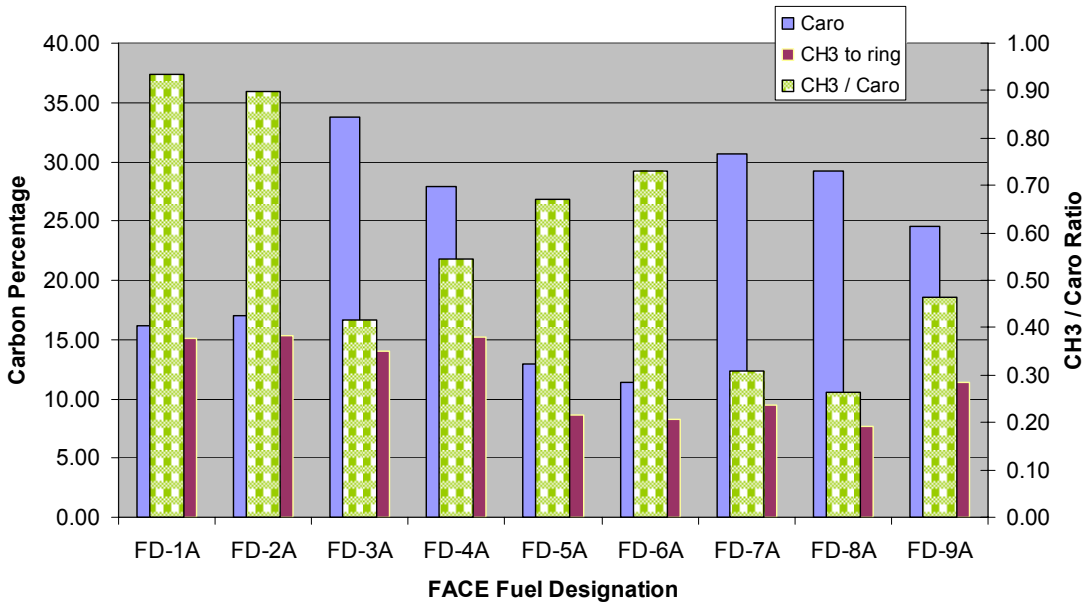

Figure 11.3. Quantification of aromatic and alkyl CH_3 carbons.

11.5 DETAILED ANALYSIS OF FD3A, FD8A, AND FD9A

Table 11.5 outlines the key characteristics of these fuels and is provided as a reference for the following discussions.

Table 11.5. FACE Fuel Matrix

Fuel	Aromatic	Cetane	T_{90}
FD3A	High	Low	Low
FD8A	High	High	High
FD9A	Center	Center	Center

Table 11.6 gives a detailed structural breakdown of the ^{13}C NMR analysis providing methylene (CH_2) position from the end methyl and separating methyls as terminal or from pendant (branching) groups. These assignments are based on theoretical and experimental data on single components. Illustrations of the linear paraffin and terminal and pendant alkyl molecular structures are given in Appendix H.

Table 11.6. ^{13}C NMR Analysis of FACE Fuels FD3A, FD8A, and FD9A

CODE	Chemical Shift	Definition	FD-3A	FD-8A	FD-9A
A	190-170	ketone and carboxylate	0	0	0
B	170-129	quaternary and oxygenated aromatic	18.34	9.14	13
C	129-115.5	aromatic C-H	15.41	20.05	11.51
D	115.5-113.5	olefinic CH_2	0	0	0.06
E	113.5-100	olefinic CH_2	0.08	0	0.29
F	70-45	paraffin CH	0.75	1.64	1.93
G	45-32.7	paraffin CH, CH_2	13.56	14.36	18.91
H	32.7-30.8	chain γ-CH_2, β-to aromatic CH_2	4.83	6.65	5.96
I	30.8-28.5	chain δ-CH_2, α-to-aromatic naphthenes, aromatic-attached ethyl CH2	11.81	21.15	14.47
J	28.5-25	cycloparaffin CH_2	5.9	6.2	7.37
K	25-21.9	chain β-CH_2, α to aromatic or isobutyl CH_2	7.7	7.15	8.1
L	21.9-17.7	α-to-ring CH_3	11.49	4.43	9.67
M	17.6-14.7	aromatic-attached ethyl CH_3	2.54	3.25	1.71
N	14.7-12.3	chain α CH_3	5.42	5.18	5.33
O	12.3-0	branched chain CH_3	2.16	0.81	1.71
		Total	**100**	**100**	**100**
α	14	α CH3 of linear alkane	2.22	4.02	2.49
β	22.7	β CH2 of linear alkane	2.12	4.02	2.85
γ	32	γ CH2 of linear alkane	2.12	3.87	2.39
δ	29.5	δ CH2 of linear alkane	2.24	3.75	2.3
ε	29.8	ε CH2 and greater, linear alkane	4.26	12.02	6.26
tMe	22.5	terminal methyl of alkane	0.83	0.54	1.63
tEt	11.3	terminal ethyl of alkane	0.61	0.27	0.68
tPr	14.3	terminal propyl of alkane	0.57	0.23	2.49
tBu	23.1	terminal butyl of alkane	0.28	0.23	0.15
pMe	19.6	pendant methyl of alkane	2.2	0.93	2.17
pEt	10.8	pendant ethyl of alkane	0.21	0.04	0.19
pPr	14.4	pendant propyl of alkane	0.25	0	0.15
pBu	23.2	pendant butyl of alkane	0.13	0.08	0.43

Comparison of CanmetENERGY and PNNL measurements in Table 11.7 shows excellent overall agreement has been achieved between the two laboratories. A comparison of three parameter groups for FACE fuels FD3A, FD8A, and FD9A are shown. Discrepancies are less than about 2% for carbon types for the independently run samples.

Table 11.7. Comparison of NCUT and PNNL Measurements

FACE Fuel	Linear Paraffin (Mole % C)		Aromatic C-H (Mole % C)		Aromatic C (Mole % C)	
	NCUT	PNNL	NCUT	PNNL	NCUT	PNNL
FD9A	15.2	16.3	12.6	11.5	22.6	24.5
FD8A	25.8	27.7	19.7	20.0	27.5	29.2
FD3A	13.0	13.0	17.3	15.0	32.9	33.8

Figures 11.4 and 11.5 are examples of how detailed NMR data from Table 11.6 and structural relationships illustrated in Appendix G can be used to quantify structural information. Figure 11.4 is derived from the pendant carbons (i.e., pMe, pEt, pPr, and pBu) and then multiplied by the respective number of pendant carbons in the pendant group. The total paraffinic carbons are defined as α through ε CH_2 carbons. The low branching ratio is typical of high cetane fuels. Figure 11.5 quantifies the branch types in these fuels.

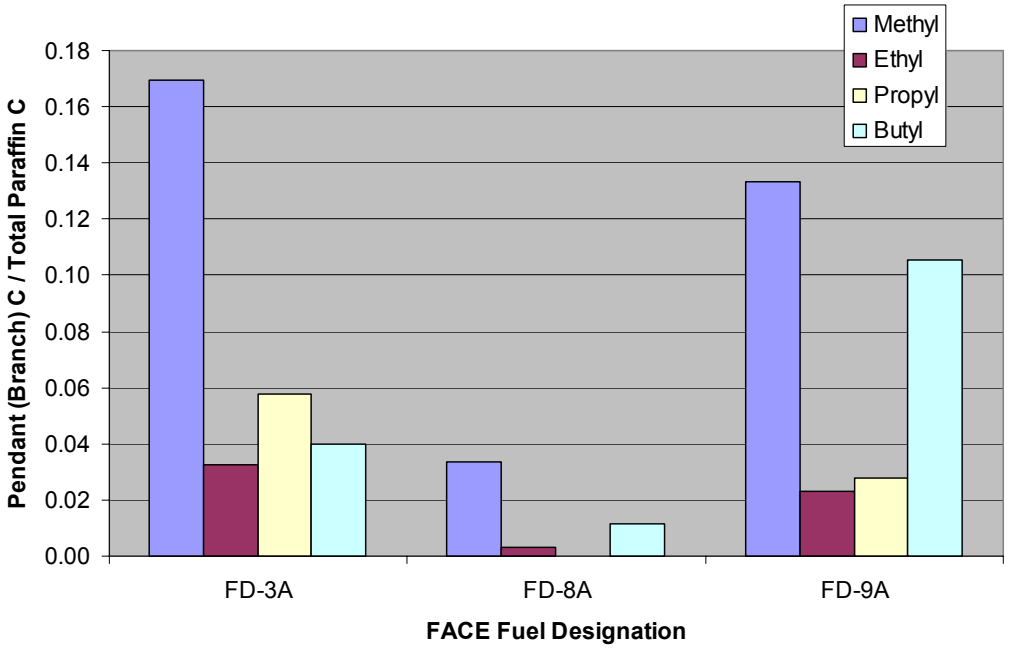

Figure 11.4. Ratio of branch carbons to paraffinic CH_2 carbons.

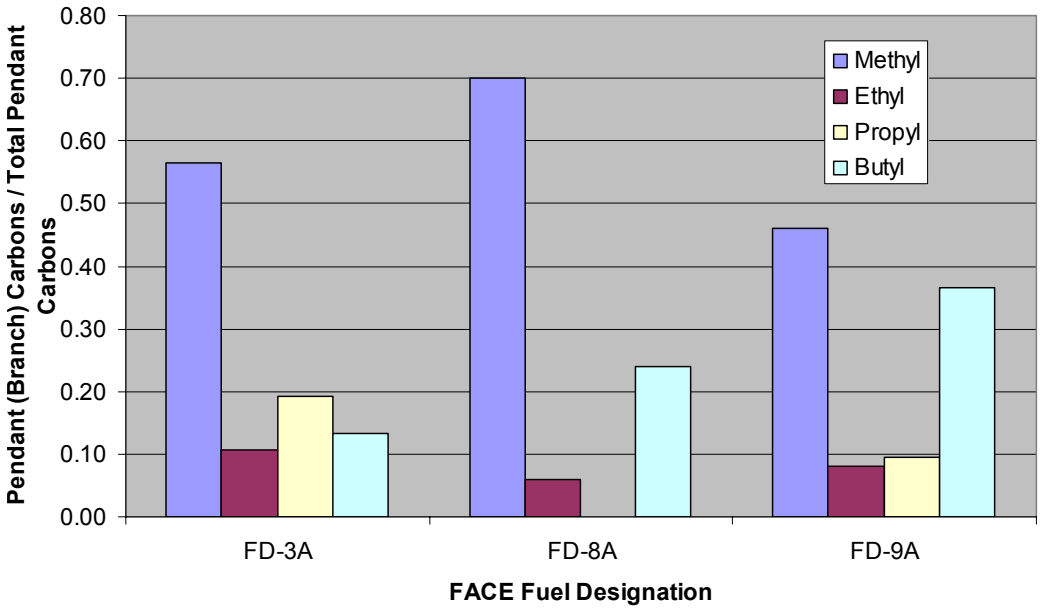

Figure 11.5. Distribution of structural branches.

Figure 11.6 shows the content (mole percent) of carbon assigned to branched species in the three diesel fuels using the CanmetENERGY NMR method. This method does not currently assign propyl-branch species.

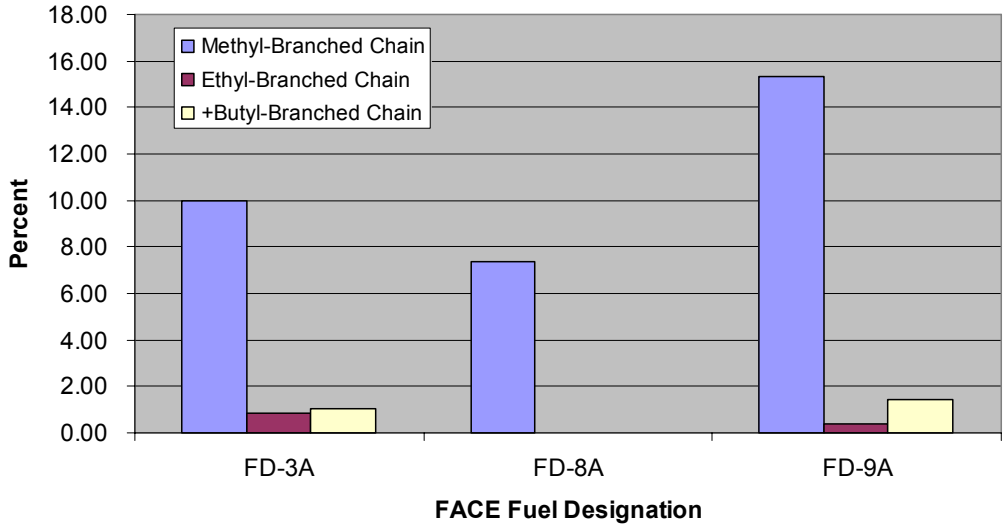

Figure 11.6. Quantification of branch chains.

11.6 FACE FUEL SURROGATE FUEL RECONSTRUCTION

Mixtures of molecules were constructed to fit the CanmetENERGY NMR and GC-FIMS results for FACE surrogate fuels FD3A, FD8A, and FD9A. The structures and fits are shown in Figures 11.7–11.9. For each mixture, two aromatic molecules (weighted 50% each of the aromatic hydrocarbon class) and one each of cycloparaffinic, branched paraffinic, and paraffinic species were chosen and are shown at the bottom of each figure. The molecular type, measured by GC, and the carbon types, measured by NMR, for each molecule used to fit FACE surrogate fuel FD3A are indicated in Figure 11.7.

The carbon number for each type of hydrocarbon was chosen as an average of the size of the species determined by GC-FIMS. The top table in Figures 11.7–11.9 gives the carbon number (C#) chosen for each class of hydrocarbon and the relative content (mole fraction) of the hydrocarbon types in the "best fit" mixtures for fitting either the NMR data (NMR fit) or GC-FIMS data (GC fit). Ideally the NMR and GC best fits should indicate the same contents of each hydrocarbon class. Of the three fuels modeled, FACE surrogate fuel 9 came closest to meeting this ideal. In the side-by-side middle tables, the NMR carbon content (mole percent) and GC molecular content (weight percent) results of the measured, NMR fit, and GC fit results are given. The NMR fit results in each table are the NMR and GC data calculated using the mole fraction of each hydrocarbon class obtained as the best fit for the NMR data. Correspondingly, the GC fit results in each table are the NMR and GC data calculated using the mole fraction of each hydrocarbon class obtained as the best fit for the GC data. The remaining two tables give the results of the NMR and GC fits to additional NMR-determined parameters including "chain end type" contents, ring cluster sizes, and chain lengths.

Molecule Type	C#	Molecular Content (mole fraction)	
		NMR Fit	GC Fit
Aromatic	12	0.53	0.58
Cycloparaffinic	13	0.28	0.17
Branched Paraffinic	15	0.18	0.15
Chain Paraffinic (C1+)	14	0.01	0.10
Olefinic	-	-	-
C=O*	-	-	-
Total		1.00	1.00

Carbon Type	Carbon Content (mole %)		
	Measured	NMR Fit	GC Fit
Aromatic	32.9	33.0	36.2
Cycloparaffinic	21.5	21.8	13.3
Branched Paraffinic	11.9	11.8	11.5
Chain Paraffinic (C1+)	33.5	33.4	39.1
Olefinic	0.2	-	-
C=O*	0.0	-	-
Total	100.0	100.0	100.0

Molecule Type	Molecular Content (weight %)		
	Measured	NMR Fit	GC Fit
Aromatic	52.8	48.2	52.9
Cycloparaffinic	17.8	28.8	17.5
Branched Paraffinic	17.5	21.8	18.2
Chain Paraffinic (C1+)	11.7	1.1	11.4
Olefinic	-	-	-
C=O*	-	-	-
Total	99.8	100.0	100.0

Chain End Type	Content (mole fraction) (±0.1)		
	Measured	NMR Fit	GC Fit
Aromatic	0.2	0.3	0.3
Olefinic	0.0	0.0	0.0
Cycloparaffinic	0.3	0.1	0.1
Branched Paraffinic	0.2	0.4	0.4
Paraffinic CH3	0.3	0.2	0.3
Sulphidic S	-	-	-
COOH	-	-	-
Total*	1.0	1.0	1.0

* Variance from 1.0 due to round-off error

Parameter	Measured	NMR Fit	GC Fit
Ar Cluster size (#carbons)	9	8	8
Cy Cluster size (#carbons)	8	10	10
Chain length	4.4	3.8	4.6

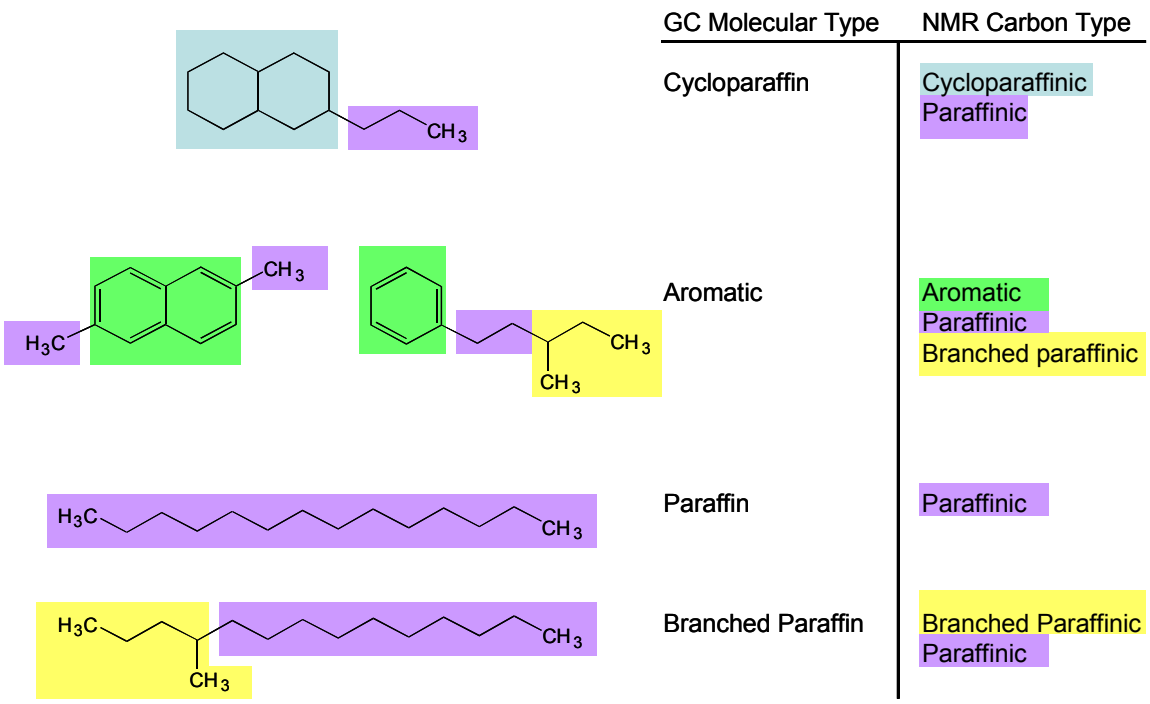

Figure 11.7. Molecular reconstruction of FD3A.

Molecule Type	C#	Molecular Content (mole fraction)	
		NMR Fit	GC Fit
Aromatic	14	0.50	0.47
Cycloparaffinic	17	0.33	0.20
Branched Paraffinic	15	0.09	0.05
Chain Paraffinic (C1+)	14	0.08	0.28
Olefinic	-	-	-
C=O*	-	-	-
Total		1.00	1.00

Carbon Type	Carbon Content (mole %)		
	Measured	NMR Fit	GC Fit
Aromatic	27.5	26.5	25.7
Cycloparaffinic	22.0	21.9	13.7
Branched Paraffinic	7.4	7.4	6.2
Chain Paraffinic (C1+)	42.8	44.2	54.5
Olefinic	0.3	-	-
C=O*	0.0	-	-
Total	100.0	100.0	100.0

Molecule Type	Molecular Content (weight %)		
	Measured	NMR Fit	GC Fit
Aromatic	44.9	45.3	43.7
Cycloparaffinic	22.3	37.8	23.5
Branched Paraffinic	5.7	9.3	5.3
Chain Paraffinic (C1+)	27.0	7.7	27.6
Olefinic	-	-	-
C=O*	-	-	-
Total	99.9	100.0	100.0

Chain End Type	Content (mole fraction) (±0.1)		
	Measured	NMR Fit	GC Fit
Aromatic	0.2	0.3	0.2
Olefinic	0.0	0.0	0.0
Cycloparaffinic	0.2	0.2	0.1
Branched Paraffinic	0.2	0.3	0.3
Paraffinic CH3	0.4	0.3	0.4
Sulphidic S	-	-	-
COOH	-	-	-
Total*	1.0	1.0	1.0

* Variance from 1.0 due to round-off error

Parameter	Measured	NMR Fit	GC Fit
Ar Cluster size (#carbons)	7	8	8
Cy Cluster size (#carbons)	7	10	10
Chain length	7.6	6.3	7.7

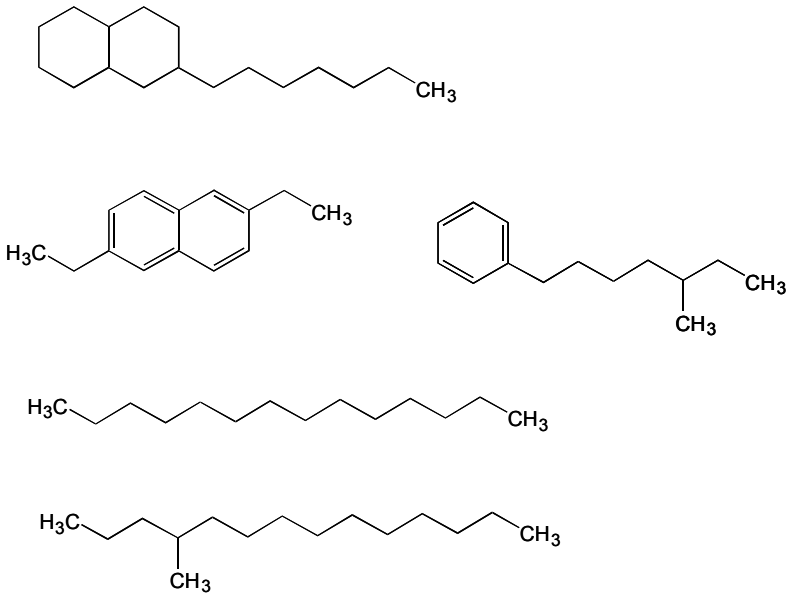

Figure 11.8. Molecular reconstruction of FD8A.

Molecule Type	C#	Molecular Content (mole fraction)	
		NMR Fit	GC Fit
Aromatic	13	0.41	0.39
Cycloparaffinic	15	0.36	0.37
Branched Paraffinic	16	0.17	0.15
Chain Paraffinic (C1+)	15	0.06	0.09
Olefinic	-	-	-
C=O*	-	-	-
Total		1.00	1.00

Carbon Type	Carbon Content (mole %)		
	Measured	NMR Fit	GC Fit
Aromatic	22.6	22.9	21.7
Cycloparaffinic	24.5	25.1	25.7
Branched Paraffinic	17.2	16.6	16.0
Chain Paraffinic (C1+)	35.6	35.5	36.6
Olefinic	0.1	-	-
C=O*	0.0	-	-
Total	100.0	100.0	100.0

Molecule Type	Molecular Content (weight %)		
	Measured	NMR Fit	GC Fit
Aromatic	34.7	36.0	34.2
Cycloparaffinic	39.3	38.0	39.0
Branched Paraffinic	16.2	19.5	17.2
Chain Paraffinic (C1+)	9.6	6.5	9.7
Olefinic	-	-	-
C=O*	-	-	-
Total	99.9	100.0	100.0

Chain End Type	Content (mole fraction) (±0.1)		
	Measured	NMR Fit	GC Fit
Aromatic	0.2	0.2	0.2
Olefinic	0.0	0.0	0.0
Cycloparaffinic	0.3	0.2	0.2
Branched Paraffinic	0.3	0.5	0.5
Paraffinic CH3	0.2	0.1	0.2
Sulphidic S	-	-	-
COOH	-	-	-
Total*	1.0	1.0	1.0

* Variance from 1.0 due to round-off error

Parameter	Measured	NMR Fit	GC Fit
Ar Cluster size (#carbons)	7	8	8
Cy Cluster size (#carbons)	11	10	10
Chain length	4.8	4.4	4.5

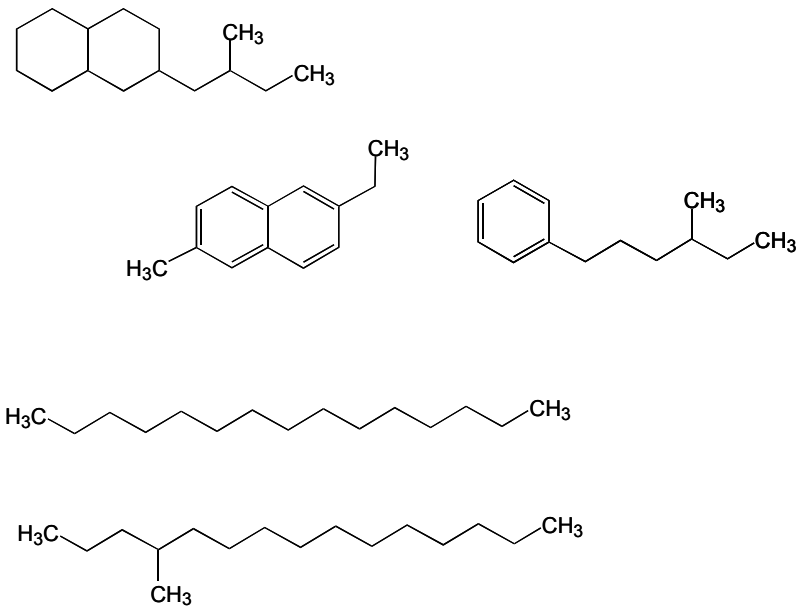

Figure 11.9. Molecular reconstruction of FD9A.

11.7 FUTURE WORK

In summary, fuel chemistry can provide many routes to meet bulk properties. NMR analysis can provide additional insight into structural detail, which can influence combustion and emissions. The collaboration with CanmetENERGY on the Unconventional Hydrocarbon Fuel Program will continue to refine relationships to define molecular structure from NMR data and explore property correlation methods (e.g., QSPRs) for fuels derived from unconventional hydrocarbon resources.

11.8 REFERENCES

1. Petrakis, L.; and Allen, D., "NMR for Liquid Fossil Fuels," Analytical Spectroscopy Library, Vol. 1 (Elsevier, New York, 1987).

2. Meusinger, R., and Moros, R., *Fuel,* **80**, 613–621 (2001).

3. Sarpal, A.S. et al., *Fuel,* **76**, 931–937 (1997).

4. Cookson, D.J., and Smith, B.E., *Org. Magn. Reson*., **16**, 111–116 (1981).

5. Cookson, D.J., and Smith, B.E., *Fuel,* **62**, 34–38 (1983).

6. Barron, P.F., et al., *Fuel,* **63**, 1276–1280 (1984).

7. Sarpal, A.S., et al., *Fuel,* **75**(4), 483–490 (1996).

8. Edwards, J.C., and Kim, J., "RCC Feedstream Analysis by ^{1}H and ^{13}C NMR: Multivariate Prediction of Chemical and Physical Properties," presented at the 236th ACS National Meeting, Philadelphia, Pennsylvania, August 17–21, 2008, (http://www.process-nmr.com/).

9. DeFries, T. H., Indtriz, D., and Kastrup, R.., *Ind. Eng. Chem. Res.,* **26**, 188 (1987).

10. Brekke, T., Kvalheim, O.M., and Sletten, E., *Anal Chim Acta,* **23**, 123 (1989).

11. Meusinger, R., and Moros, R., *Fuel,* **80**, 613–621 (2001).

12. Cookson, et al., *Fuel,* **74**, 70–78 (1995).

13. Benson, S.W., *Thermochemical Kinetics; Methods for the Estimation of Thermochemical Data and Rate Parameters,* 2nd Edition (John Wiley, New York, 1976).

14. Japanwala, S., et al., *Energy & Fuels,* **16**, 477–484 (2002).

15. Rahmani, S.; McCaffrey, W.C.; Dettman, H.D.; and Gray, M.R., *Energy & Fuels,* 2003, 17, 1048–1056.

12. COMPARISON OF THE ADVANCED CHARACTERIZATION AND ASTM TEST RESULTS

As seen in the previous sections, advanced characterization techniques provide the opportunity for much more detailed information on chemical composition than the standard ASTM tests. One important question is consistency of the various advanced methods with the standard ASTM-type composition methods. This section focuses on those comparisons.

Although the standard ASTM methods do not provide as much detailed composition information as the advanced techniques, one common denominator for all of the methods is a breakdown into the broad hydrocarbon classes of saturates (n-paraffins + isoparaffins + cycloparaffins), aromatics, and olefins/others. For the advanced characterization techniques, this involves a summing up of all of the peaks for a given chemical class and is impacted by correct peak assignment and quantification.

Comparisons of the results for the various standard ASTM and advanced characterization methods are plotted in Figures 12.1–12.9 for FACE fuels FD1A–FD9A. As SFC only measures aromatics content, only that component is included for this method. For the FIA method, a range of values around the average of the aromatics content are shown, corresponding to the results obtained from three to five different analyses obtained at three different laboratories.

For all nine fuels, the aromatics + saturates total was greater than 95%. For all fuels, the MS method (ASTM D2425*) provided the lowest value of aromatics and the highest value of saturates. Among the advanced characterization techniques, in general, the NCUT PIONA GC-MS and PIONA FIMS methods tended to give the lowest aromatic and highest saturate values while the ORNL 2-D GC-MS method tended to give the highest aromatic and lowest saturate values. Two exceptions are the PIONA FIMS and PIONA GC-MS results for FD1A and FD2A. As mentioned in a previous section, the fuel is separated into two fractions for those techniques and unfortunately for these two fuels, a large peak near the split point was not captured completely. It should be noted that the PIONA GC-MS and PIONA FIMS results are reported as mass percent, while the 2-D GC-MS and 2-D GC-FID results are reported as peak area percent. In general, the PIONA GC-MS and PIONA FIMS values were not too different from each other and were fairly close to the aromatic values from the SFC technique, which are also reported as mass percent. The SFC technique is believed to be the most accurate of the ASTM techniques used here for aromatics levels.

The relatively good agreement also of the 2-D GC-MS and 2-D GC-FID values is remarkable considering that response factors have not been applied to convert from peak area percent to mass percent, and these advanced analytical characterization techniques are still under development with additional work to be done on peak assignment and quantification.

*ASTM International, *Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry,* ASTM D2425-04 (ASTM International, Pennsylvania, 2004).

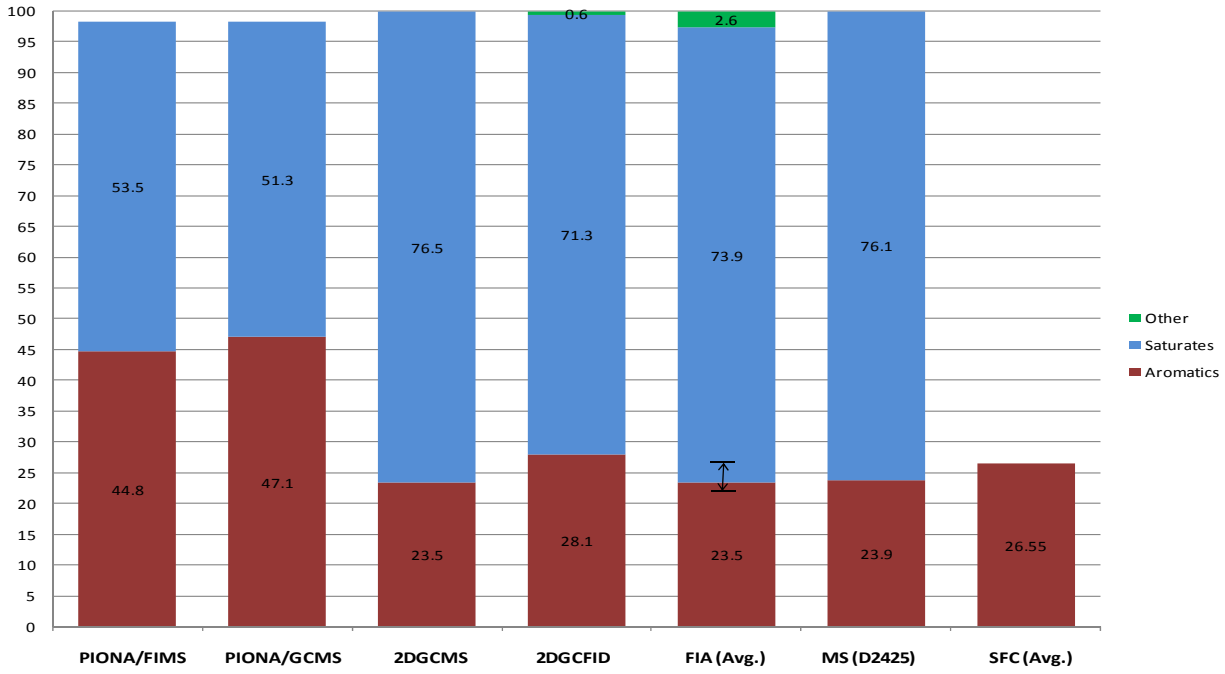

Figure 12.1. Comparison of results for FD1A.

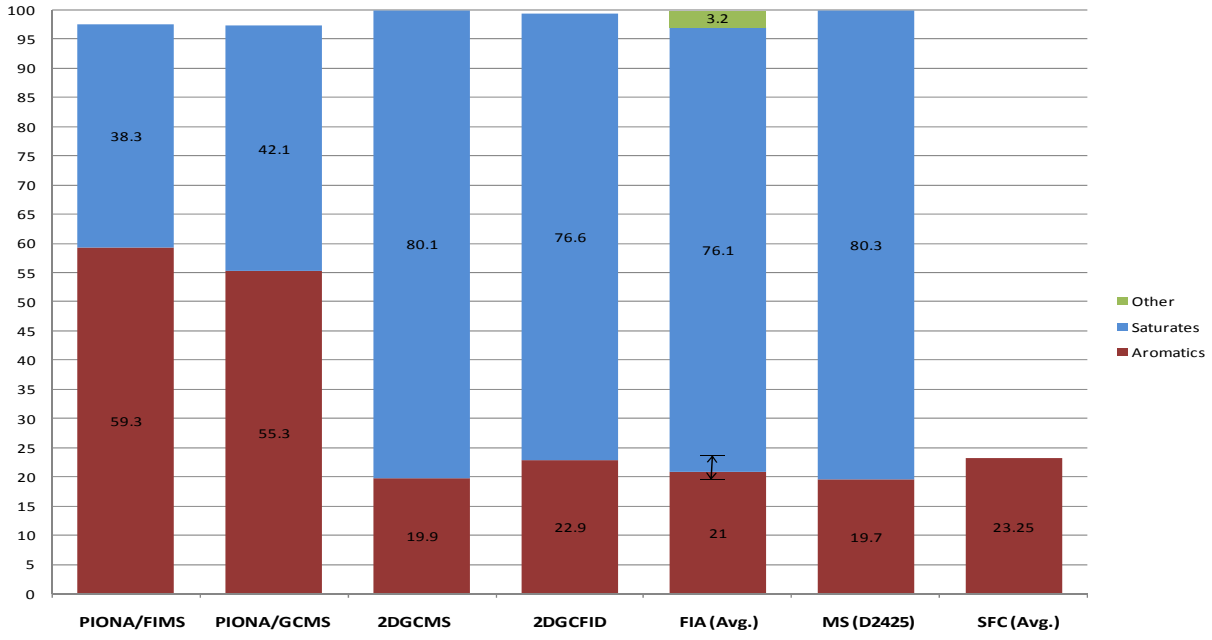

Figure 12.2. Comparison of results for FD2A.

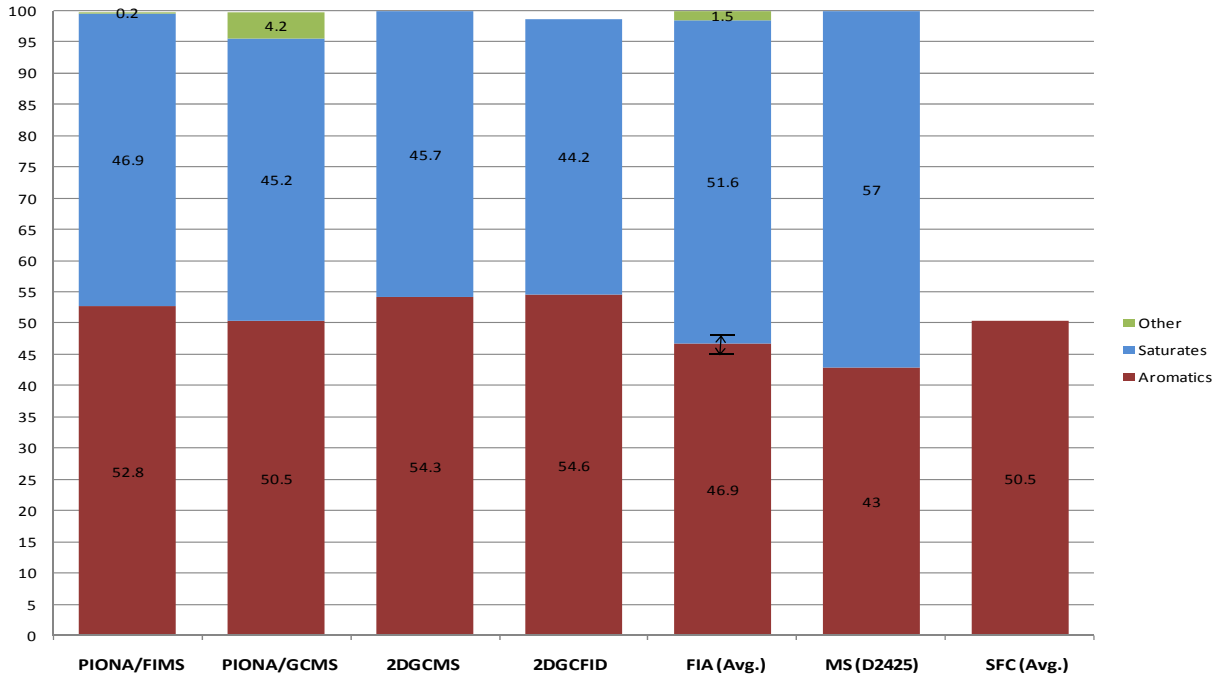

Figure 12.3. Comparison of results for FD3A.

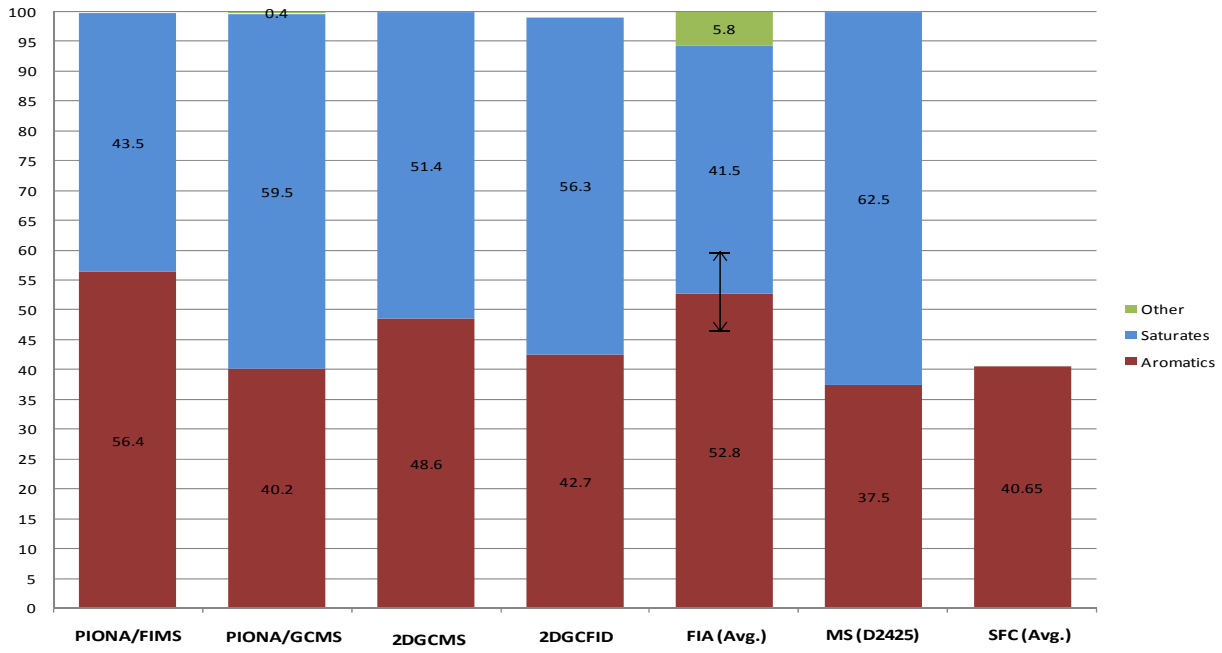

Figure 12.4. Comparison of results for FD4A.

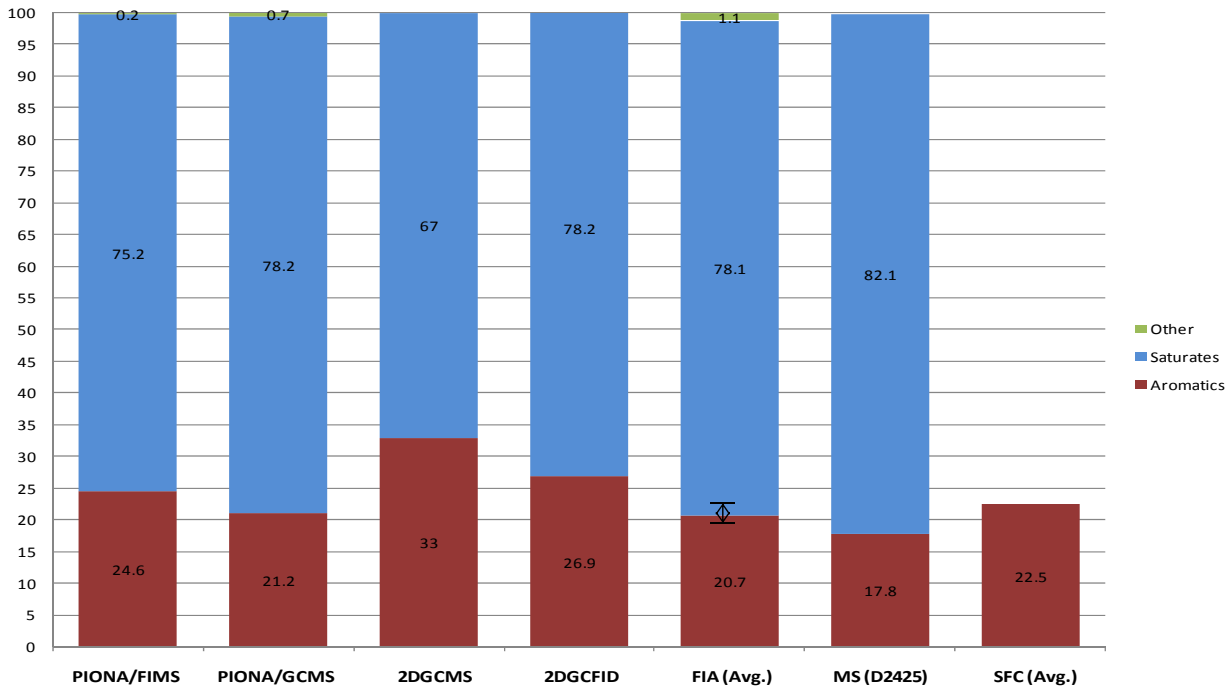

Figure 12.5. Comparison of results for FD5A.

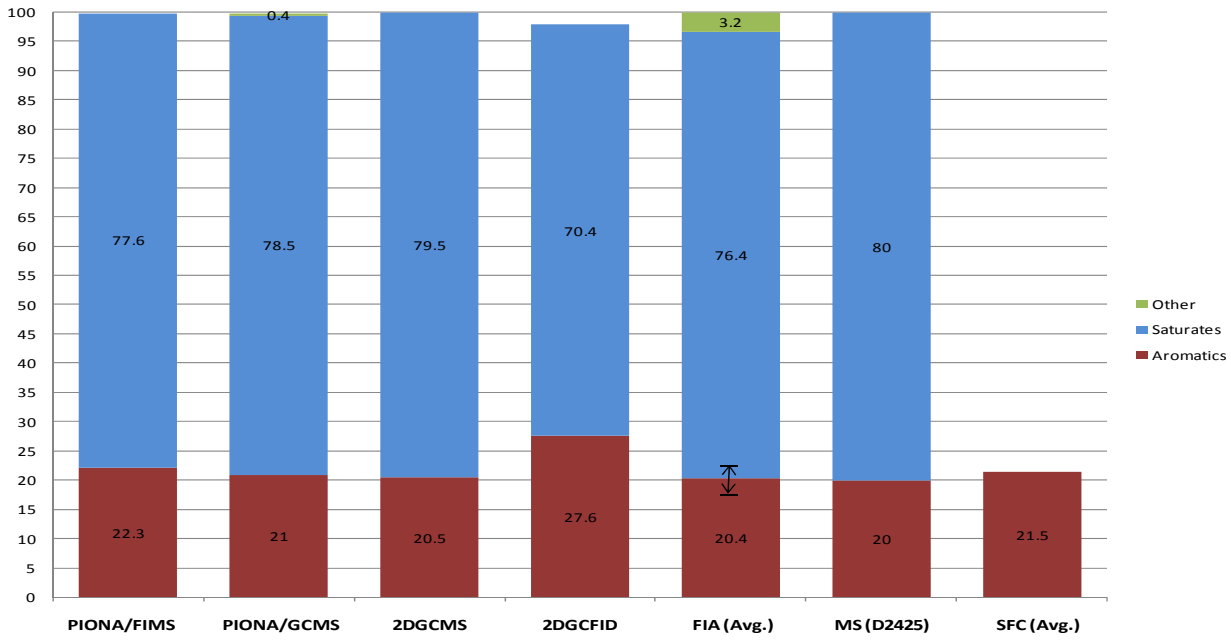

Figure 12.6. Comparison of results for FD6A.

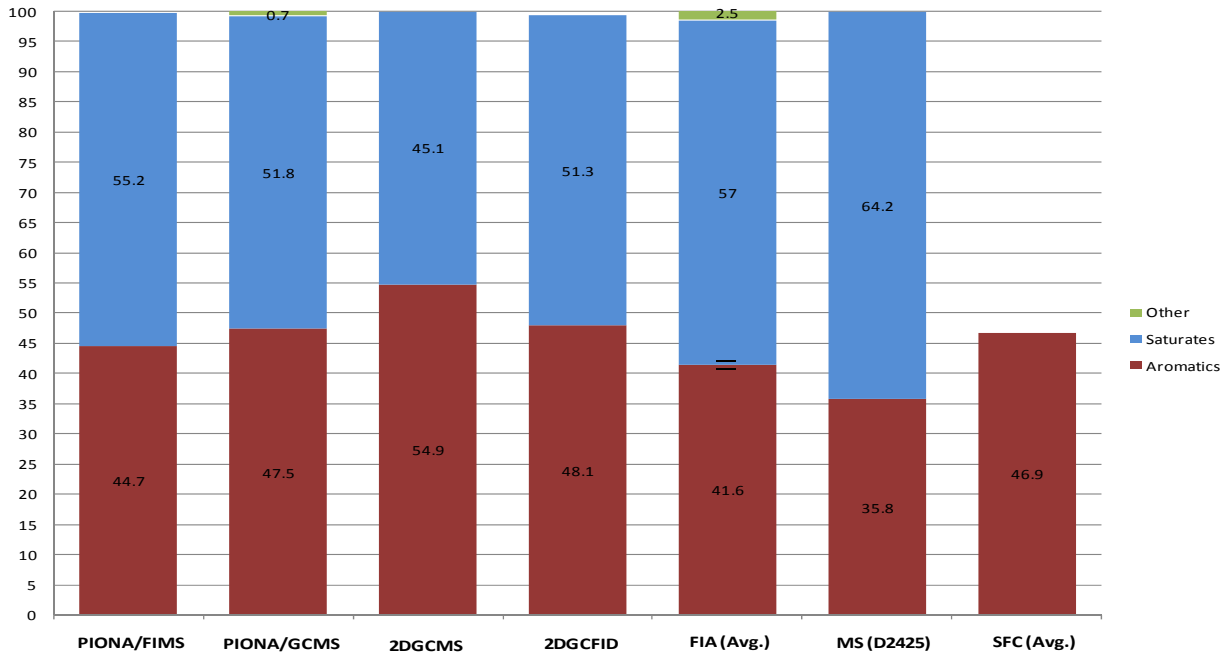

Figure 12.7. Comparison of results for FD7A.

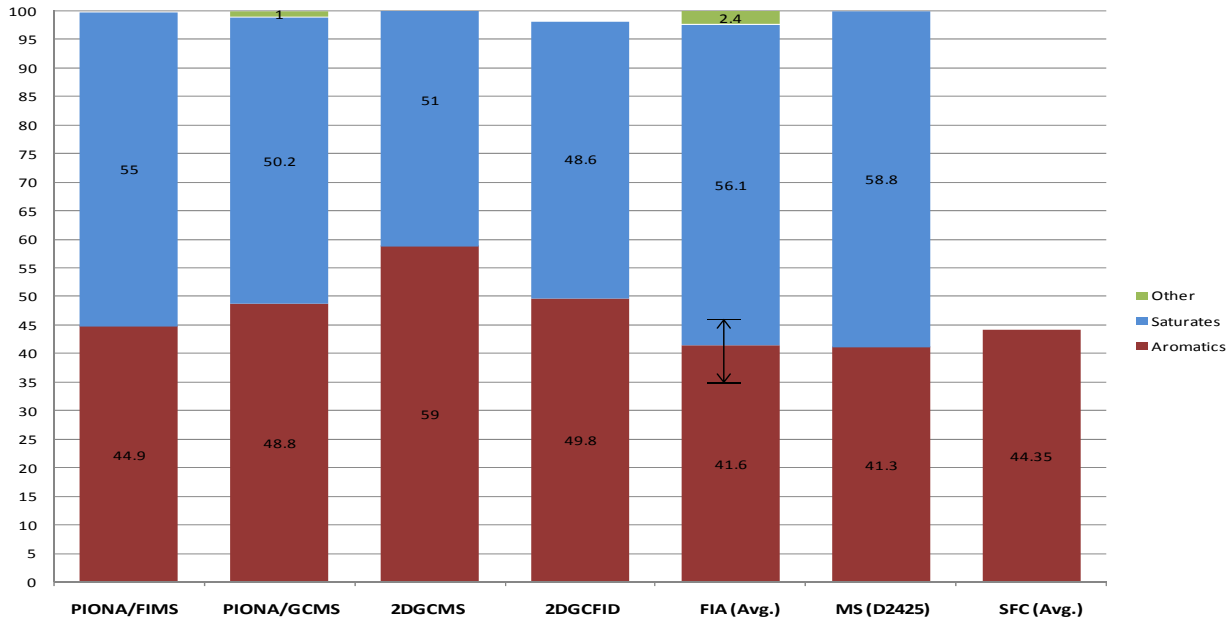

Figure 12.8. Comparison of results for FD8A.

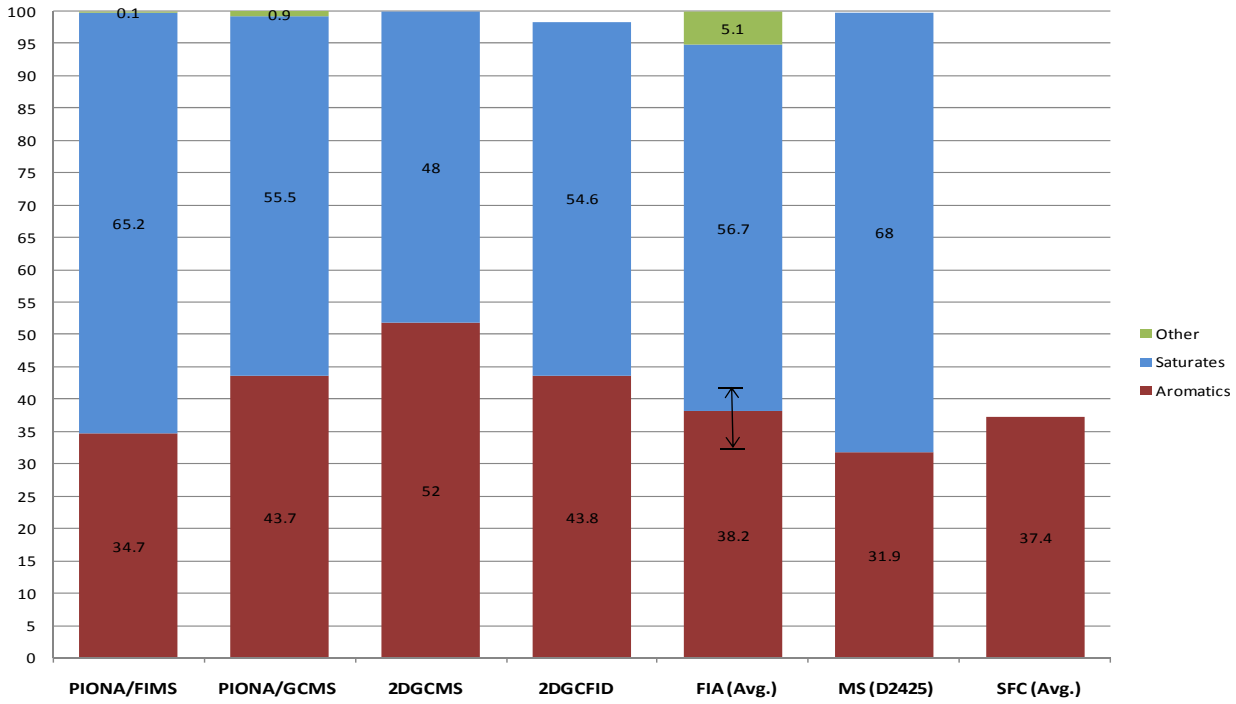

Figure 12.9. Comparison of results for FD9A.

A more detailed breakdown of products for the nine FACE diesel fuels is provided in Figures 12.10–12.18. In these figures, saturates are broken down into n-paraffins, isoparaffins, and cycloparaffins. Aromatics are broken down into monoaromatics having one aromatic ring (alkylbenzenes, indans, teralins, indenes) and polyaromatics containing two or more aromatic rings. For the PIONA GC-MS and MS methods, it was not possible to speciate the n-paraffins and isoparaffins from each other and so only the total of n-paraffins + isoparaffins is reported. Similarly, for the 2-D GC-FID method, only the total aromatics values are reported. Although that method is capable of speciating the various aromatic compounds from each other, the task of identifying each specific compound is herculean and has not been fully completed at this point. Those efforts are continuing at NCUT.

For FD1A and FD2A, shown in Figures 12.10 and 12.11, the monoaromatic results from the 2-D GC-MS method are in very good agreement with those from the MS ASTM D2425 and SFC methods. The n-paraffin + isoparaffin levels are somewhat higher than the values from the MS method and the cycloparaffin values are lower. With regard to the NCUT PIONA FIMS and PIONA GC-MS methods, the monoaromatic levels are significantly higher and the n-paraffin + isoparaffin levels are significantly lower than the MS and SFC values. As discussed previously, this was caused by a large peak near the split point that was not totally captured. The cycloparaffin values are in reasonably good agreement with the MS values.

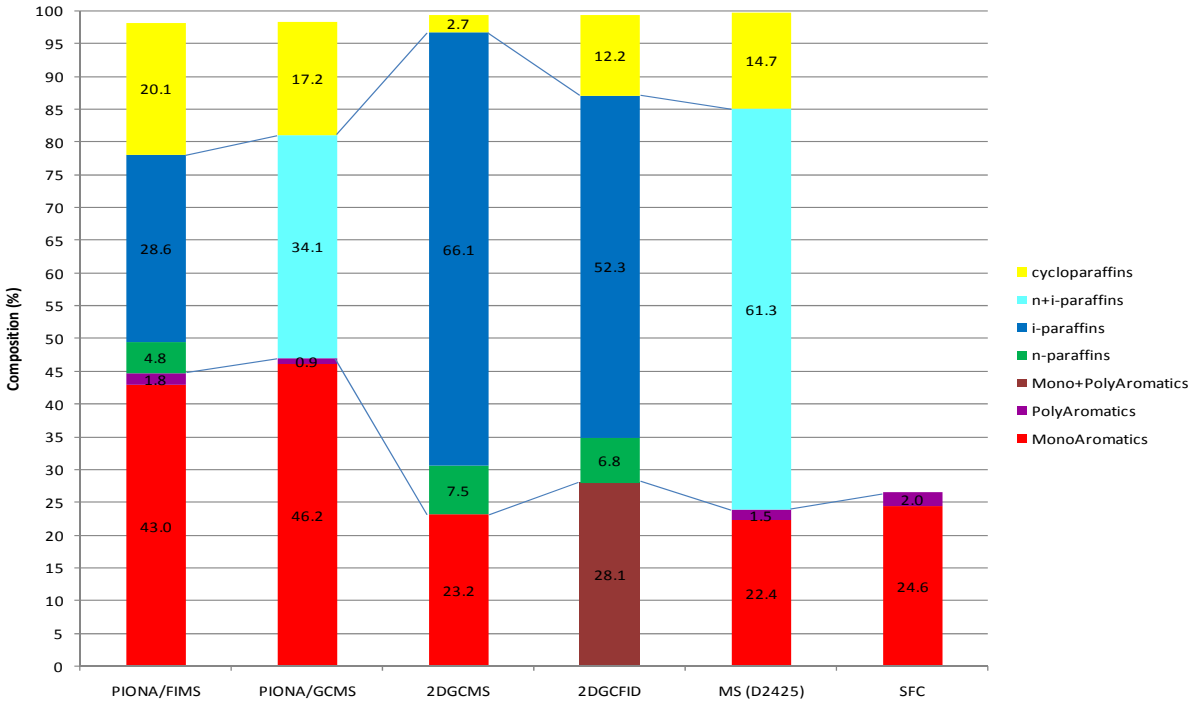

Figure 12.10. Comparison of detailed paraffin and aromatic classes for FD1A.

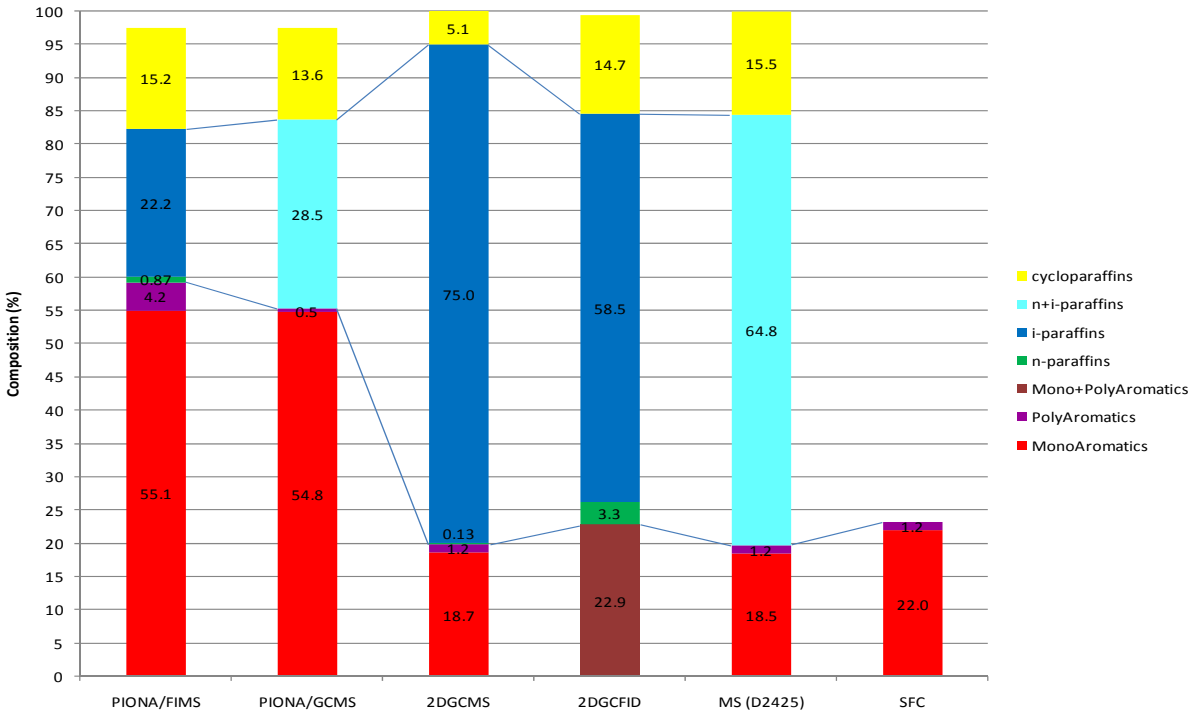

Figure 12.11. Comparison of detailed paraffin and aromatic classes for FD2A.

For FD3A (Figure 12.12), the total (mono + poly) aromatics levels of all four advanced characterization techniques are higher than those from the MS method. However, the total and individual values are fairly close to the values obtained by SFC. The n-paraffin + isoparaffin values

from the PIONA FIMS and PIONA GC-MS methods are fairly close to the value from MS while the cycloparaffin values are a bit lower than those from the MS method. For the 2-D GC-MS and 2-D GC-FID techniques, the area percent n-paraffin + isoparaffin values are higher and the cycloparaffin area percent values are significantly lower than the weight percent values from MS.

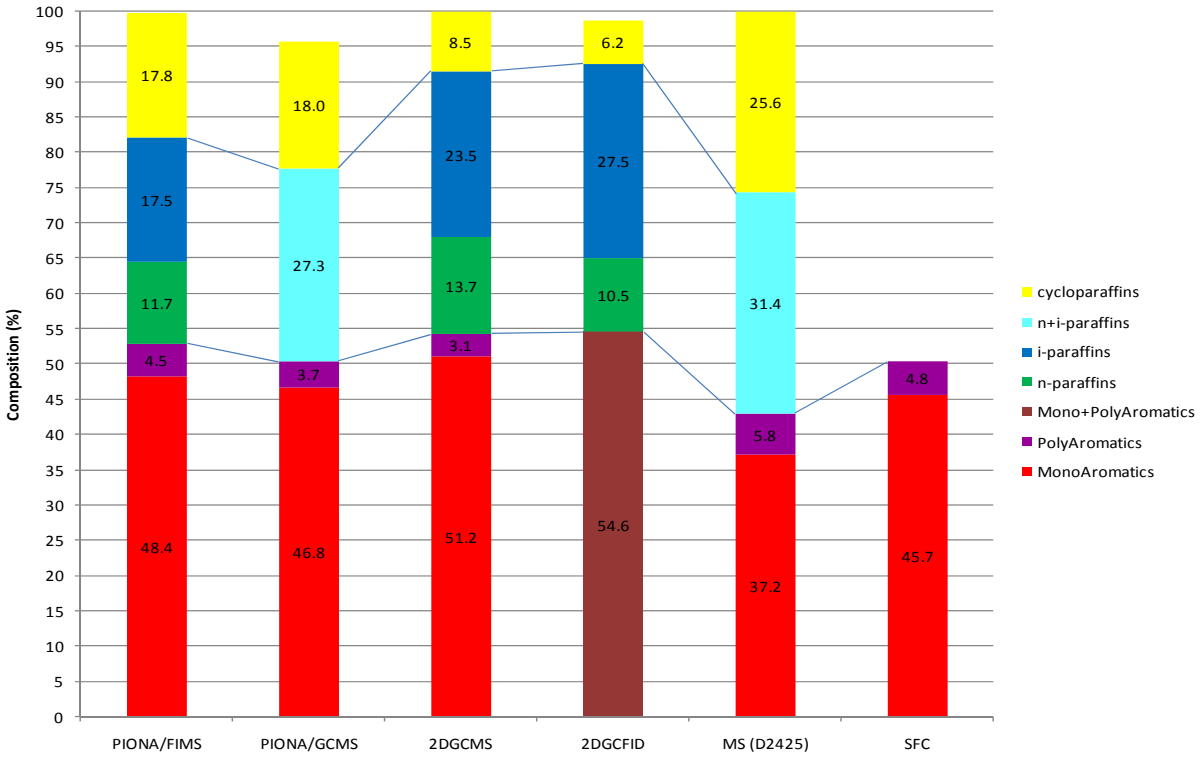

Figure 12.12. Comparison of detailed paraffin and aromatic classes for FD3A.

For FD4A (Figure 12.13), the monoaromatics value from PIONA GC-MS is very close to the SFC value and slightly higher than the MS value. The values from PIONA/FIMS and 2-D GC-MS are higher than the MS and SFC values. The polyaromatics value from PIONA FIMS is somewhat higher than the values from MS and SFC (although the absolute values are relatively small), but PIONA GC-MS and 2-D GC-MS values are close. Once again the total aromatics levels of all four advanced characterization techniques are higher than those from the MS method, especially those from the PIONA FIMS method. However, the PIONA GC-MS and 2-D GC-FID total aromatics levels come very close to matching that from the SFC method. Correspondingly, the n-paraffin + isoparaffin levels from the PIONA FIMS method are considerably lower than that from the MS method, although cycloparaffin levels are essentially identical. In contrast, the n-paraffin + isoparaffin levels from the 2-D GC-MS and 2-D GC-FIMS are higher and the cycloparaffin levels are very significantly lower than the values from MS.

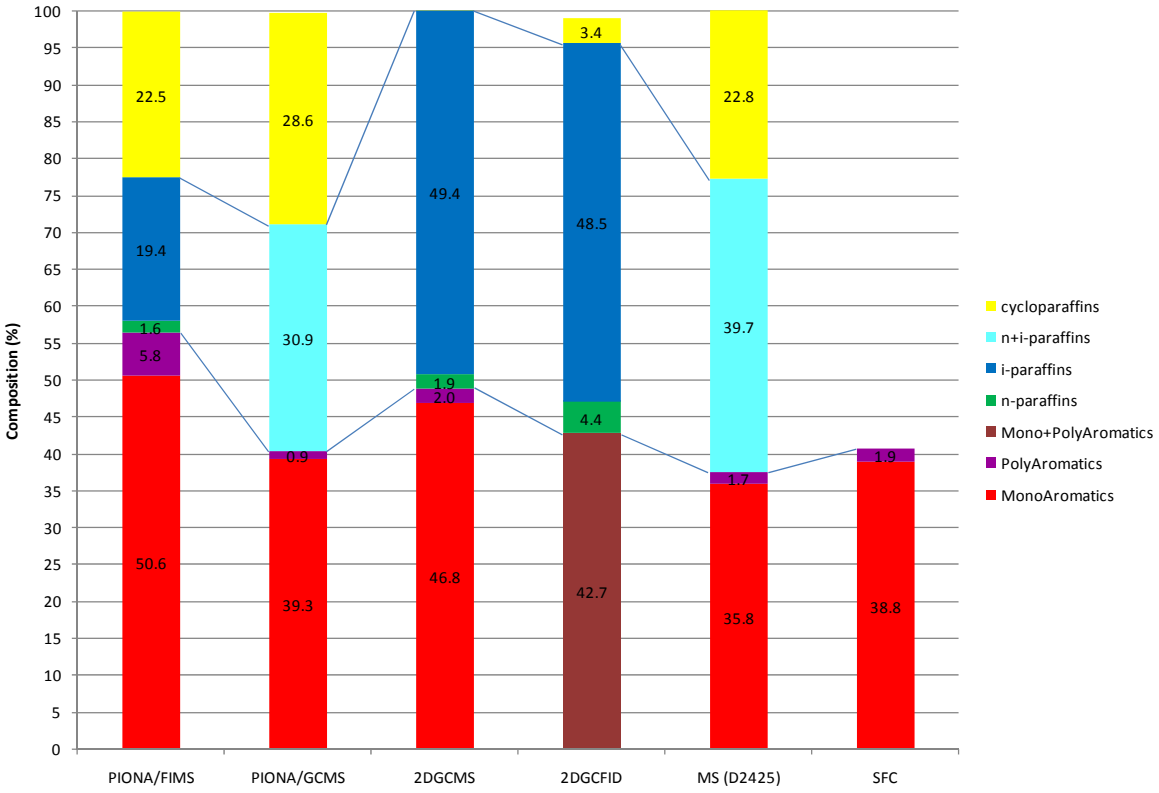

Figure 12.13. Comparison of detailed paraffin and aromatic classes for FD4A.

For FD5A (Figure 12.14), the monoaromatics values from PIONA FIMS and PIONA GC-MS are very close to the value from SFC and slightly higher than the value from MS. The 2-D GC-MS monoaromatics value is higher than from MS and SFC. The polyaromatics values from all three methods are very close to the values from MS and SFC. Once again the aromatic levels of all four advanced characterization techniques are higher than those from the MS method, especially those from the 2-D GC-MS method. However, the PIONA GC-MS and PIONA FIMS monoaromatic + polyaromatic levels come very close to matching those from the SFC method. The n-paraffin + isoparaffin levels from the PIONA FIMS, PIONA GC-MS, and 2-D GC-MS methods are very close to those obtained from the MS method. Furthermore, the cycloparaffin levels of the PIONA FIMS and PIONA GC-MS are nearly identical to those from MS. For the 2-D GC-FID method, the n-paraffin + isoparaffin level is higher than the MS value while the cycloparaffin level is significantly lower.

For FD6A (Figure 12.15), the monoaromatic, polyaromatic, and total aromatics levels for all advanced characterization techniques except 2-D GC-FID were very close to the values obtained from the MS and SFC methods. The n-paraffin + isoparaffin levels from PIONA FIMS and PIONA GC-MS were lower than those from MS, while the values from 2-D GC-MS and 2-D GC-FID were higher. The cycloparaffin value from PIONA FIMS were close to those from MS, while the value from PIONA GC-MS were higher and the values from 2-D GC-MS and 2-D GC-FID were significantly lower.

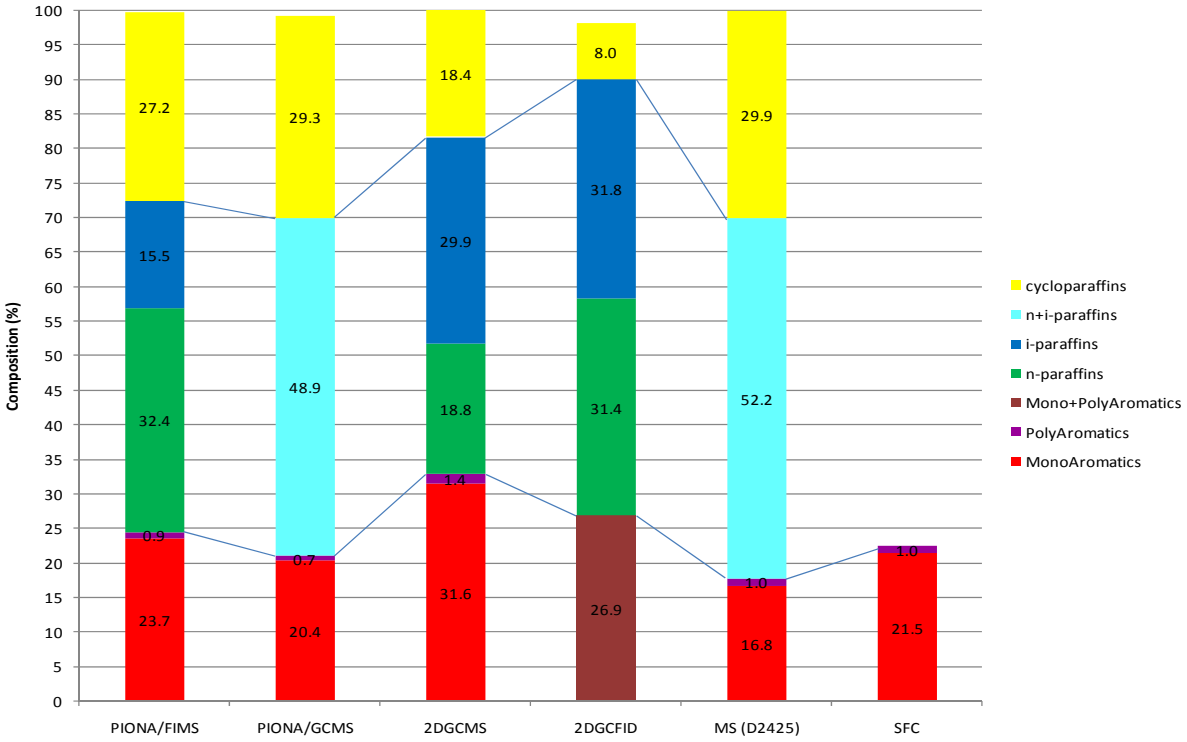

Figure 12.14. Comparison of detailed paraffin and aromatic classes for FD5A.

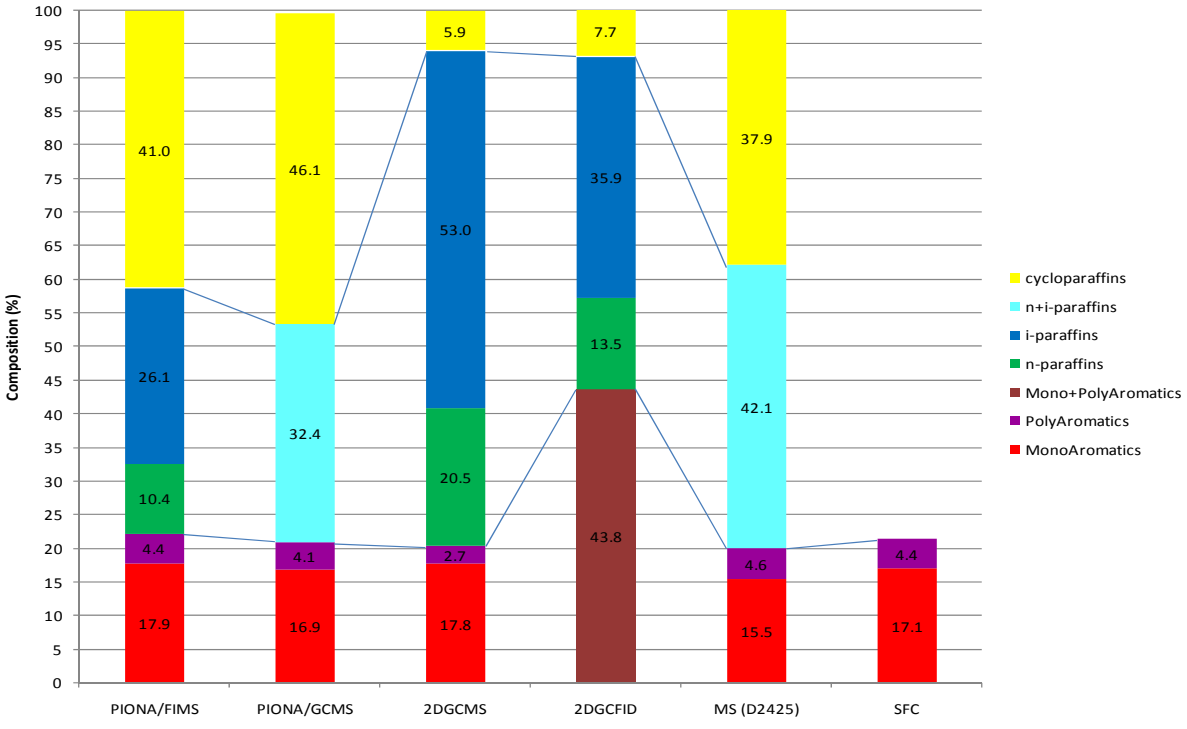

Figure 12.15. Comparison of detailed paraffin and aromatic classes for FD6A.

For FD7A (Figure 12.16), the monoaromatic values from PIONA FIMS and PIONA GC-MS were very close to the values from MS and SFC, while the 2-D GC-MS value was a bit higher. The polyaromatics levels from all three methods were close to the SFC value, but quite a bit higher than the MS value. The total aromatics value for all advanced characterization techniques was somewhat higher than that from MS, although not too far off from the value from SFC. The n-paraffin + isoparaffin levels from 2-D GC-FID were very close to the total value from MS, while the values from the other techniques were somewhat lower. The cycloparaffin values from all techniques were lower than those from MS, with the PIONA GC-MS coming closest to matching the MS value.

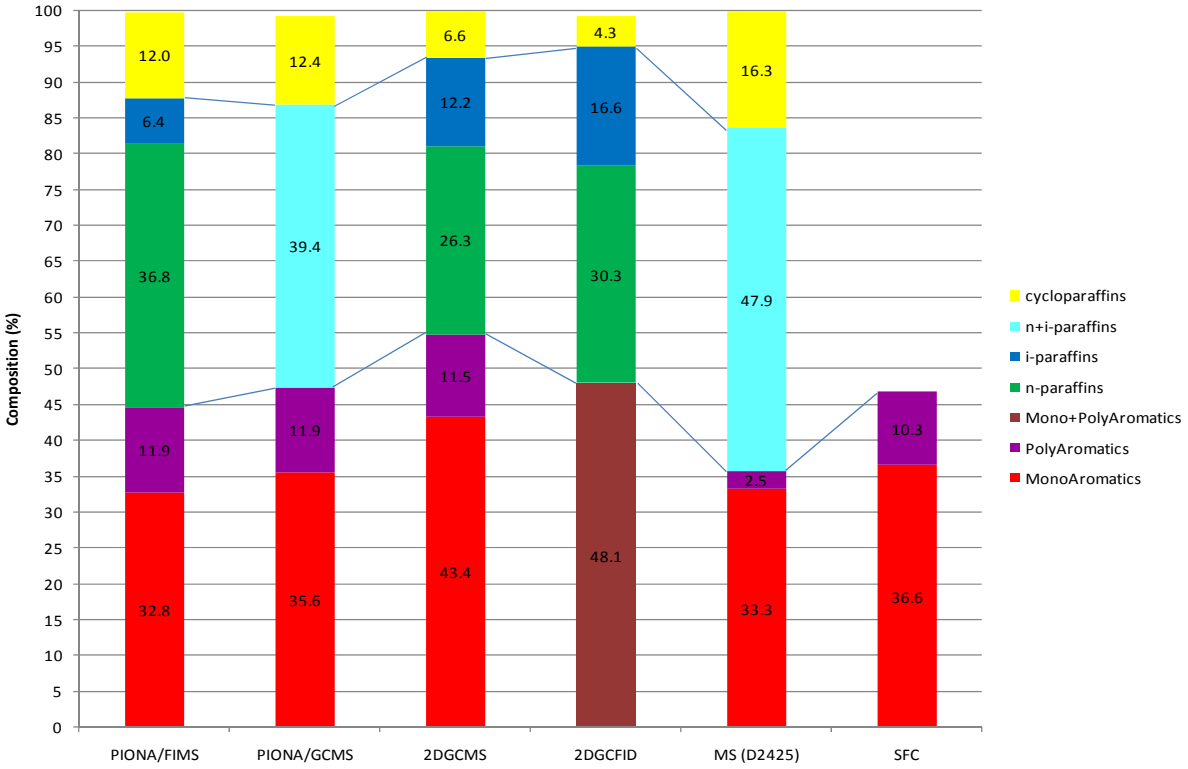

Figure 12.16. Comparison of detailed paraffin and aromatic classes for FD7A.

For FD8A (Figure 12.17), the monoaromatic values from PIONA FIMS and PIONA GC-MS were very close to the values from MS and SFC, while the 2-D GC-MS values were higher. The polyaromatic values from these advanced techniques were close to the values from MS and SFC. The value for total aromatics from PIONA FIMS was essentially the same as the values from MS and SFC, while the values for the other techniques were a bit higher. The n-paraffin + isoparaffin levels from 2-D GC-MS and 2-D GC-FID were very close to the total value from MS, while the values from PIONA FIMS and PIONA GC-MS were lower. The cycloparaffin values from these latter two techniques were fairly close to the value from MS, while the values from 2-D GC-MS and 2-D GC-FID were very significantly lower.

For FD9A, the center-point fuel (Figure 12.18), the monoaromatics value from PIONA FIMS was very close to the values from MS and SFC, while the values from the other advanced characterization

techniques were higher, especially for the 2-D GC-MS method. The polyaromatics values from all techniques were very close to the MS and SFC values. The total aromatics value from PIONA FIMS was very close to the MS and SFC values while the values from the other techniques were higher. The total n-paraffin + isoparaffin levels for 2-D GC-MS were close to the total value from MS, while the values from PIONA FIMS and PIONA GC-MS were quite a bit lower. However, the cycloparaffin values from PIONA FIMS and PIONA GC-MS were close to the value from MS, while the values from 2-D GC-MS and 2-D GC-FID were considerably lower.

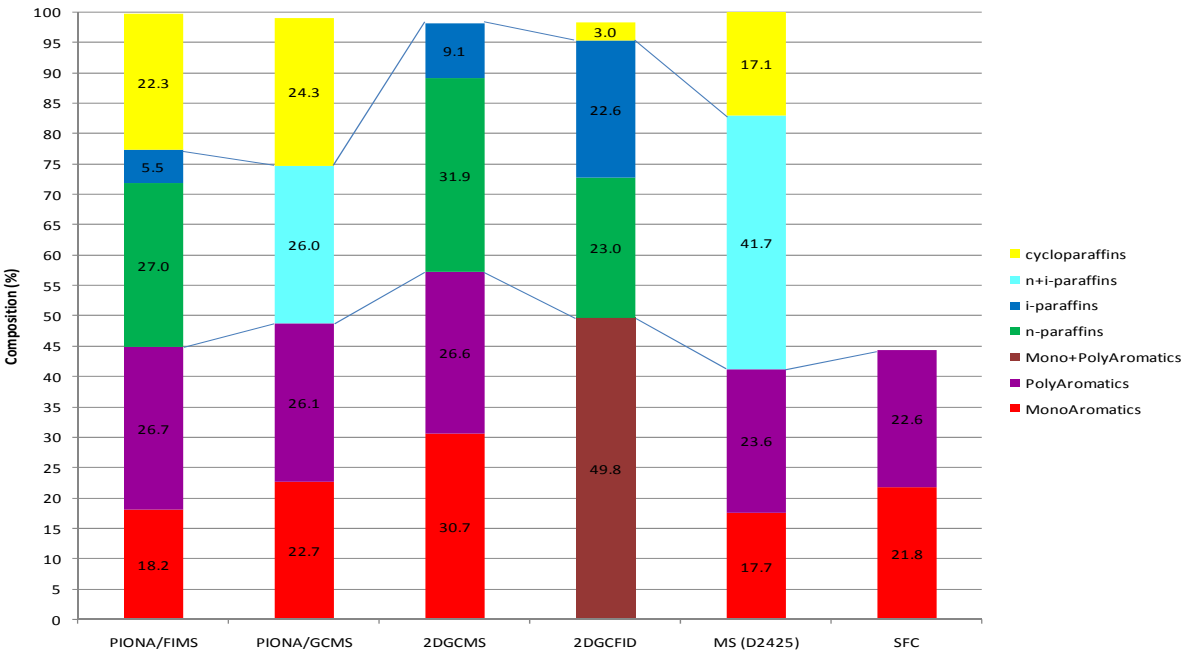

Figure 12.17. Comparison of detailed paraffin and aromatic classes for FD8A.

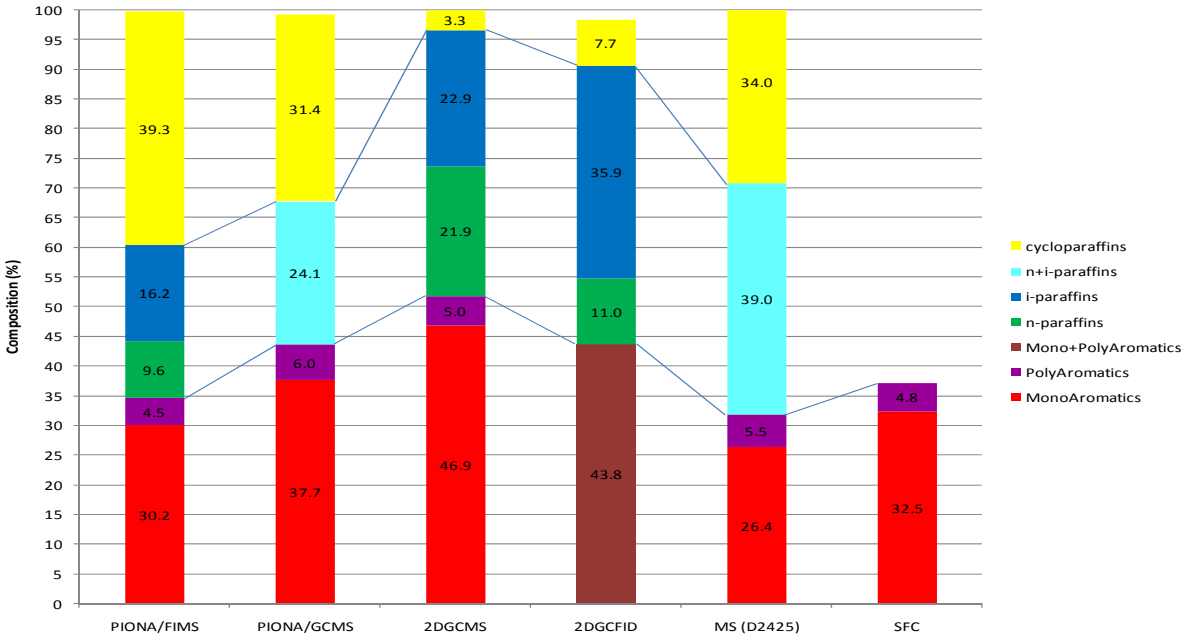

Figure 12.18. Comparison of detailed paraffin and aromatic classes for FD9A.

APPENDIX A. SIMULATED DISTILLATION DATA

APPENDIX A. SIMULATED DISTILLATION DATA

Table A.1. Simulated Distillation Table (°C)

	Weight loss (%)	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SIMDIS	0.5	139.6	140.4	118.6	139.6	132.8	123.2	140.4	182	125.2
SIMDIS	1	141.2	141.2	136	140.4	140.4	138.2	150.2	182.6	138.2
SIMDIS	2	146.4	146.4	140.4	142	147.2	157.2	160.6	183.4	143.4
SIMDIS	3	160	157.2	145	146.4	154.4	166.2	164.2	184.8	146.4
SIMDIS	4	162	162	146.4	146.4	160.6	173.8	166.8	218	154.4
SIMDIS	5	162.8	162.8	147.2	148	162.8	180.6	170.4	226.8	160.6
SIMDIS	6	163.4	163.4	153	158.6	163.4	186	170.4	237	162.8
SIMDIS	7	164.8	163.4	158.6	161.4	164.8	192.2	171	241	162.8
SIMDIS	8	166.8	164.8	161.4	162	166.8	195.6	171	247.2	163.4
SIMDIS	9	169.6	166.2	162.8	162.8	169.6	201	171.6	252.6	164.2
SIMDIS	10	170.4	169.6	163.4	163.4	170.4	205.6	173.8	253.2	166.2
SIMDIS	11	171	170.4	163.4	163.4	171	209.4	176.4	253.8	169.6
SIMDIS	12	173.8	171	163.4	164.2	173.8	214	177.2	253.8	170.4
SIMDIS	13	176.4	171	164.2	164.2	174.4	216	179.2	254.6	170.4
SIMDIS	14	179.2	173.8	164.2	164.2	175.2	218.8	182	254.6	171
SIMDIS	15	180	176.4	164.8	164.8	177.2	222.8	183.4	254.6	173.8
SIMDIS	16	181.2	179.2	165.4	165.4	179.2	226.2	183.4	255.2	177.2
SIMDIS	17	182.6	180	166.2	165.4	181.2	228.8	184	255.2	181.2
SIMDIS	18	183.4	181.2	167.6	166.8	182.6	231.6	184.8	255.2	183.4
SIMDIS	19	184	182.6	169	167.6	184	234.2	185.4	255.2	184.8
SIMDIS	20	184	183.4	170.4	170.4	184.8	235.6	186	255.8	187.4
SIMDIS	21	184.8	183.4	171	171	186	237.6	188.2	255.8	189.6
SIMDIS	22	186.8	184	171	171	187.4	239	189.6	255.8	193
SIMDIS	23	187.4	184.8	171.6	171	188.8	241.8	190.2	255.8	195.6
SIMDIS	24	187.4	186	171.6	171.6	190.2	244.4	191.6	255.8	198.4
SIMDIS	25	188.2	186.8	172.4	171.6	191.6	246.4	194.2	255.8	202.2
SIMDIS	26	188.2	187.4	173.8	171.6	194.2	247.8	195.6	256.4	205.6
SIMDIS	27	188.8	187.4	174.4	173.8	195.6	249.8	197	256.4	208.8
SIMDIS	28	188.8	188.2	176.4	176.4	195.6	251.2	198.4	256.4	212
SIMDIS	29	189.6	188.2	177.2	177.8	196.4	253.2	199.6	259.2	215.4
SIMDIS	30	189.6	188.8	179.2	182	197	253.8	202.2	263	217.4

Table A.1. (continued)

	Weight loss (%)	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SIMDIS	31	190.2	188.8	180.6	183.4	197.6	255.2	204.2	266.4	220.8
SIMDIS	32	190.2	189.6	182.6	184	199	256.4	206.2	267	224.8
SIMDIS	33	190.8	189.6	183.4	184.8	201	257.8	208.2	267	227.6
SIMDIS	34	191.6	190.2	184	186	202.8	259.8	210.2	267.6	230.8
SIMDIS	35	192.2	190.2	184.8	188.8	204.2	261.8	212	267.6	233
SIMDIS	36	192.2	190.2	185.4	190.2	205.6	263	214.8	267.6	235
SIMDIS	37	193	190.8	186.8	191.6	206.8	264.4	216	268.2	237
SIMDIS	38	193	191.6	188.2	197.6	208.2	265.6	218	268.2	238.4
SIMDIS	39	193	192.2	189.6	199	209.4	267	220	268.2	241.8
SIMDIS	40	193.6	192.2	190.2	202.8	210.8	269	223.4	268.2	244.4
SIMDIS	41	194.2	192.2	191.6	206.2	213.4	270.2	226.8	269	246.4
SIMDIS	42	195	193	193	210.2	214.8	271	229.6	271	248.4
SIMDIS	43	195.6	193	195	211.4	216	272.2	232.2	271.6	250.4
SIMDIS	44	196.4	193.6	196.4	216	216	273.6	235	271.6	252.6
SIMDIS	45	196.4	193.6	197	220	216.6	274.8	235.6	272.2	253.8
SIMDIS	46	197	194.2	198.4	221.4	218.8	277.4	238.4	272.2	254.6
SIMDIS	47	197.6	195	199	222.8	220	278.8	241.8	272.8	255.8
SIMDIS	48	198.4	195	201	224.8	222.2	280.2	246.4	274.2	257.8
SIMDIS	49	199.6	195.6	202.8	226.2	224.8	281.4	249.8	275.6	259.8
SIMDIS	50	200.2	196.4	204.8	228.2	226.8	282.8	253.2	278.2	261.8
SIMDIS	51	201	197	206.2	229.6	228.8	284	253.8	279.4	263
SIMDIS	52	201.6	197	207.4	230.8	230.2	286	253.8	282	265
SIMDIS	53	202.2	197.6	209.4	232.2	232.2	287.4	254.6	285.4	266.4
SIMDIS	54	202.8	198.4	210.8	233.6	235	288	254.6	287.4	267.6
SIMDIS	55	204.2	199	213.4	235.6	235.6	289.2	255.2	289.2	270.2
SIMDIS	56	204.8	200.2	215.4	237.6	237	290.6	255.2	291.8	271
SIMDIS	57	206.2	201	216	239.6	239	292.4	255.2	293	272.2
SIMDIS	58	207.4	201.6	217.4	241.8	243	294.4	255.2	293	273.6
SIMDIS	59	208.2	202.2	219.4	244.4	246.4	295	255.8	293.8	275.6
SIMDIS	60	209.4	202.2	221.4	246.4	249.2	296.2	255.8	293.8	278.2
SIMDIS	61	210.2	202.8	224.2	247.8	253.2	297.6	255.8	294.4	279.4
SIMDIS	62	210.8	203.6	226.8	249.8	253.8	299.4	255.8	296.2	280.8
SIMDIS	63	211.4	204.8	228.8	252.6	254.6	301.4	255.8	297.6	282

Table A.1. (continued)

	Weight loss (%)	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SIMDIS	64	212	205.6	230.8	254.6	254.6	302.6	255.8	298.2	284
SIMDIS	65	212.8	207.4	232.2	257.2	254.6	303.4	256.4	298.8	286.6
SIMDIS	66	214	208.2	234.2	260.4	255.2	304.6	256.4	300.2	287.4
SIMDIS	67	216	209.4	235.6	263	255.2	306.4	256.4	302.6	288.6
SIMDIS	68	218	210.2	237	265.6	255.2	308.4	256.4	304	289.8
SIMDIS	69	220.8	210.8	238.4	269.6	255.2	310.2	256.4	305.8	292.4
SIMDIS	70	222.8	211.4	241	272.2	255.8	312.2	256.4	308.4	294.4
SIMDIS	71	226.2	211.4	243.8	276.2	255.8	314.6	257.2	311.6	295.6
SIMDIS	72	229.6	212	246.4	279.4	255.8	316.6	257.2	314	297
SIMDIS	73	233	213.4	249.2	282.8	255.8	318.6	259.2	316	298.2
SIMDIS	74	236.2	214.8	251.2	286.6	256.4	321.4	263	318.6	300.8
SIMDIS	75	241	216.6	253.2	289.2	259.8	324	266.4	321.4	302
SIMDIS	76	246.4	219.4	254.6	293	263.8	326.8	267	324	303.4
SIMDIS	77	250.4	222.2	255.8	295.6	266.4	330.2	267.6	327.4	304.6
SIMDIS	78	253.8	226.2	258.4	298.8	270.2	332.8	267.6	330.8	307
SIMDIS	79	256.4	234.2	261	302.6	271	336.2	270.2	333.6	309.6
SIMDIS	80	260.4	255.2	263.8	307	271.6	339.6	271	337.6	311.6
SIMDIS	81	264.4	271.6	266.4	311.6	271.6	343	271.6	341.6	314.6
SIMDIS	82	268.2	286	269	317.2	272.2	345.6	272.2	345.6	316.6
SIMDIS	83	271	300.8	271	324	272.8	349	272.2	349	318.6
SIMDIS	84	274.8	320	272.8	330.2	277.4	352.2	272.2	352.2	322
SIMDIS	85	280.2	338.2	276.2	336.2	280.2	354.8	272.8	355.4	325.4
SIMDIS	86	284.6	347	279.4	342.4	284	357.4	274.2	358	329.4
SIMDIS	87	287.4	352.2	282	347.6	287.4	359.4	278.2	360.6	332.2
SIMDIS	88	292.4	355.4	286	351.6	289.2	361.2	283.4	362.6	336.2
SIMDIS	89	297	358.6	288	355.4	293	363.8	287.4	365.2	341
SIMDIS	90	301.4	362	291.2	358.6	295.6	365.8	291.2	367.8	345.6
SIMDIS	91	304.6	363.8	295	362	298.2	367.8	293	369.8	350.8
SIMDIS	92	310.2	366.4	298.8	364.6	302	369.8	294.4	371.6	355.4
SIMDIS	93	315.4	369	302	367.2	305.8	371.6	297.6	374.2	360
SIMDIS	94	320.6	371.6	305.2	369.8	310.8	374.2	302	376.8	363.8
SIMDIS	95	328.2	374.2	310.2	373	316.6	376.8	307	379.4	367.8
SIMDIS	96	335	377.6	316	375.6	323.4	379.4	314	382	371.6

Table A.1. (continued)

	Weight loss (%)	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SIMDIS	97	343.8	380.8	320.6	379.4	330.2	382.8	322	386	376.2
SIMDIS	98	356	385.4	329.4	384	337.6	388	332.2	391.2	382
SIMDIS	99	374.2	393.2	343	392.4	348.2	397	351.6	400.8	391.2
SIMDIS	99.5	393.2	402.8	357.4	402.2	356.8	411.2	374.2	413.8	404

Table A.2. Simulated Distillation Table (°F)

	Weight loss (%)	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SIMDIS	0.5	283.28	284.72	245.48	283.28	271.04	253.76	284.72	359.6	257.36
SIMDIS	1	286.16	286.16	276.8	284.72	284.72	280.76	302.36	360.68	280.76
SIMDIS	2	295.52	295.52	284.72	287.6	296.96	314.96	321.08	362.12	290.12
SIMDIS	3	320	314.96	293	295.52	309.92	331.16	327.56	364.64	295.52
SIMDIS	4	323.6	323.6	295.52	295.52	321.08	344.84	332.24	424.4	309.92
SIMDIS	5	325.04	325.04	296.96	298.4	325.04	357.08	338.72	440.24	321.08
SIMDIS	6	326.12	326.12	307.4	317.48	326.12	366.8	338.72	458.6	325.04
SIMDIS	7	328.64	326.12	317.48	322.52	328.64	377.96	339.8	465.8	325.04
SIMDIS	8	332.24	328.64	322.52	323.6	332.24	384.08	339.8	476.96	326.12
SIMDIS	9	337.28	331.16	325.04	325.04	337.28	393.8	340.88	486.68	327.56
SIMDIS	10	338.72	337.28	326.12	326.12	338.72	402.08	344.84	487.76	331.16
SIMDIS	11	339.8	338.72	326.12	326.12	339.8	408.92	349.52	488.84	337.28
SIMDIS	12	344.84	339.8	326.12	327.56	344.84	417.2	350.96	488.84	338.72
SIMDIS	13	349.52	339.8	327.56	327.56	345.92	420.8	354.56	490.28	338.72
SIMDIS	14	354.56	344.84	327.56	327.56	347.36	425.84	359.6	490.28	339.8
SIMDIS	15	356	349.52	328.64	328.64	350.96	433.04	362.12	490.28	344.84
SIMDIS	16	358.16	354.56	329.72	329.72	354.56	439.16	362.12	491.36	350.96
SIMDIS	17	360.68	356	331.16	329.72	358.16	443.84	363.2	491.36	358.16
SIMDIS	18	362.12	358.16	333.68	332.24	360.68	448.88	364.64	491.36	362.12
SIMDIS	19	363.2	360.68	336.2	333.68	363.2	453.56	365.72	491.36	364.64
SIMDIS	20	363.2	362.12	338.72	338.72	364.64	456.08	366.8	492.44	369.32
SIMDIS	21	364.64	362.12	339.8	339.8	366.8	459.68	370.76	492.44	373.28
SIMDIS	22	368.24	363.2	339.8	339.8	369.32	462.2	373.28	492.44	379.4
SIMDIS	23	369.32	364.64	340.88	339.8	371.84	467.24	374.36	492.44	384.08
SIMDIS	24	369.32	366.8	340.88	340.88	374.36	471.92	376.88	492.44	389.12

Table A.2. (continued)

	Weight loss (%)	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SIMDIS	25	370.76	368.24	342.32	340.88	376.88	475.52	381.56	492.44	395.96
SIMDIS	26	370.76	369.32	344.84	340.88	381.56	478.04	384.08	493.52	402.08
SIMDIS	27	371.84	369.32	345.92	344.84	384.08	481.64	386.6	493.52	407.84
SIMDIS	28	371.84	370.76	349.52	349.52	384.08	484.16	389.12	493.52	413.6
SIMDIS	29	373.28	370.76	350.96	352.04	385.52	487.76	391.28	498.56	419.72
SIMDIS	30	373.28	371.84	354.56	359.6	386.6	488.84	395.96	505.4	423.32
SIMDIS	31	374.36	371.84	357.08	362.12	387.68	491.36	399.56	511.52	429.44
SIMDIS	32	374.36	373.28	360.68	363.2	390.2	493.52	403.16	512.6	436.64
SIMDIS	33	375.44	373.28	362.12	364.64	393.8	496.04	406.76	512.6	441.68
SIMDIS	34	376.88	374.36	363.2	366.8	397.04	499.64	410.36	513.68	447.44
SIMDIS	35	377.96	374.36	364.64	371.84	399.56	503.24	413.6	513.68	451.4
SIMDIS	36	377.96	374.36	365.72	374.36	402.08	505.4	418.64	513.68	455
SIMDIS	37	379.4	375.44	368.24	376.88	404.24	507.92	420.8	514.76	458.6
SIMDIS	38	379.4	376.88	370.76	387.68	406.76	510.08	424.4	514.76	461.12
SIMDIS	39	379.4	377.96	373.28	390.2	408.92	512.6	428	514.76	467.24
SIMDIS	40	380.48	377.96	374.36	397.04	411.44	516.2	434.12	514.76	471.92
SIMDIS	41	381.56	377.96	376.88	403.16	416.12	518.36	440.24	516.2	475.52
SIMDIS	42	383	379.4	379.4	410.36	418.64	519.8	445.28	519.8	479.12
SIMDIS	43	384.08	379.4	383	412.52	420.8	521.96	449.96	520.88	482.72
SIMDIS	44	385.52	380.48	385.52	420.8	420.8	524.48	455	520.88	486.68
SIMDIS	45	385.52	380.48	386.6	428	421.88	526.64	456.08	521.96	488.84
SIMDIS	46	386.6	381.56	389.12	430.52	425.84	531.32	461.12	521.96	490.28
SIMDIS	47	387.68	383	390.2	433.04	428	533.84	467.24	523.04	492.44
SIMDIS	48	389.12	383	393.8	436.64	431.96	536.36	475.52	525.56	496.04
SIMDIS	49	391.28	384.08	397.04	439.16	436.64	538.52	481.64	528.08	499.64
SIMDIS	50	392.36	385.52	400.64	442.76	440.24	541.04	487.76	532.76	503.24
SIMDIS	51	393.8	386.6	403.16	445.28	443.84	543.2	488.84	534.92	505.4
SIMDIS	52	394.88	386.6	405.32	447.44	446.36	546.8	488.84	539.6	509
SIMDIS	53	395.96	387.68	408.92	449.96	449.96	549.32	490.28	545.72	511.52
SIMDIS	54	397.04	389.12	411.44	452.48	455	550.4	490.28	549.32	513.68
SIMDIS	55	399.56	390.2	416.12	456.08	456.08	552.56	491.36	552.56	518.36
SIMDIS	56	400.64	392.36	419.72	459.68	458.6	555.08	491.36	557.24	519.8
SIMDIS	57	403.16	393.8	420.8	463.28	462.2	558.32	491.36	559.4	521.96

Table A.2. (continued)

	Weight loss (%)	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SIMDIS	58	405.32	394.88	423.32	467.24	469.4	561.92	491.36	559.4	524.48
SIMDIS	59	406.76	395.96	426.92	471.92	475.52	563	492.44	560.84	528.08
SIMDIS	60	408.92	395.96	430.52	475.52	480.56	565.16	492.44	560.84	532.76
SIMDIS	61	410.36	397.04	435.56	478.04	487.76	567.68	492.44	561.92	534.92
SIMDIS	62	411.44	398.48	440.24	481.64	488.84	570.92	492.44	565.16	537.44
SIMDIS	63	412.52	400.64	443.84	486.68	490.28	574.52	492.44	567.68	539.6
SIMDIS	64	413.6	402.08	447.44	490.28	490.28	576.68	492.44	568.76	543.2
SIMDIS	65	415.04	405.32	449.96	494.96	490.28	578.12	493.52	569.84	547.88
SIMDIS	66	417.2	406.76	453.56	500.72	491.36	580.28	493.52	572.36	549.32
SIMDIS	67	420.8	408.92	456.08	505.4	491.36	583.52	493.52	576.68	551.48
SIMDIS	68	424.4	410.36	458.6	510.08	491.36	587.12	493.52	579.2	553.64
SIMDIS	69	429.44	411.44	461.12	517.28	491.36	590.36	493.52	582.44	558.32
SIMDIS	70	433.04	412.52	465.8	521.96	492.44	593.96	493.52	587.12	561.92
SIMDIS	71	439.16	412.52	470.84	529.16	492.44	598.28	494.96	592.88	564.08
SIMDIS	72	445.28	413.6	475.52	534.92	492.44	601.88	494.96	597.2	566.6
SIMDIS	73	451.4	416.12	480.56	541.04	492.44	605.48	498.56	600.8	568.76
SIMDIS	74	457.16	418.64	484.16	547.88	493.52	610.52	505.4	605.48	573.44
SIMDIS	75	465.8	421.88	487.76	552.56	499.64	615.2	511.52	610.52	575.6
SIMDIS	76	475.52	426.92	490.28	559.4	506.84	620.24	512.6	615.2	578.12
SIMDIS	77	482.72	431.96	492.44	564.08	511.52	626.36	513.68	621.32	580.28
SIMDIS	78	488.84	439.16	497.12	569.84	518.36	631.04	513.68	627.44	584.6
SIMDIS	79	493.52	453.56	501.8	576.68	519.8	637.16	518.36	632.48	589.28
SIMDIS	80	500.72	491.36	506.84	584.6	520.88	643.28	519.8	639.68	592.88
SIMDIS	81	507.92	520.88	511.52	592.88	520.88	649.4	520.88	646.88	598.28
SIMDIS	82	514.76	546.8	516.2	602.96	521.96	654.08	521.96	654.08	601.88
SIMDIS	83	519.8	573.44	519.8	615.2	523.04	660.2	521.96	660.2	605.48
SIMDIS	84	526.64	608	523.04	626.36	531.32	665.96	521.96	665.96	611.6
SIMDIS	85	536.36	640.76	529.16	637.16	536.36	670.64	523.04	671.72	617.72
SIMDIS	86	544.28	656.6	534.92	648.32	543.2	675.32	525.56	676.4	624.92
SIMDIS	87	549.32	665.96	539.6	657.68	549.32	678.92	532.76	681.08	629.96
SIMDIS	88	558.32	671.72	546.8	664.88	552.56	682.16	542.12	684.68	637.16
SIMDIS	89	566.6	677.48	550.4	671.72	559.4	686.84	549.32	689.36	645.8
SIMDIS	90	574.52	683.6	556.16	677.48	564.08	690.44	556.16	694.04	654.08

Table A.2. (continued)

	Weight loss (%)	FD1A	FD2A	FD3A	FD4A	FD5A	FD6A	FD7A	FD8A	FD9A
SIMDIS	91	580.28	686.84	563	683.6	568.76	694.04	559.4	697.64	663.44
SIMDIS	92	590.36	691.52	569.84	688.28	575.6	697.64	561.92	700.88	671.72
SIMDIS	93	599.72	696.2	575.6	692.96	582.44	700.88	567.68	705.56	680
SIMDIS	94	609.08	700.88	581.36	697.64	591.44	705.56	575.6	710.24	686.84
SIMDIS	95	622.76	705.56	590.36	703.4	601.88	710.24	584.6	714.92	694.04
SIMDIS	96	635	711.68	600.8	708.08	614.12	714.92	597.2	719.6	700.88
SIMDIS	97	650.84	717.44	609.08	714.92	626.36	721.04	611.6	726.8	709.16
SIMDIS	98	672.8	725.72	624.92	723.2	639.68	730.4	629.96	736.16	719.6
SIMDIS	99	705.56	739.76	649.4	738.32	658.76	746.6	664.88	753.44	736.16
SIMDIS	99.5	739.76	757.04	675.32	755.96	674.24	772.16	705.56	776.84	759.2

APPENDIX B. GAS CHROMATOGRAPHY-FIELD IONIZATION MASS SPECTROMETRY DATA

APPENDIX B. GAS CHROMATOGRAPHY-FIELD IONIZATION MASS SPECTROMETRY DATA

Table B.1. GC-FIMS Data for FD1A

Sample ID	FD1A															GC-FIMS	PIONA	Total
Lab ID	08-881															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.00**	**0.12**	**1.80**	**4.79**	**6.58**	**7.19**	**6.50**	**4.84**	**3.77**	**3.54**	**1.92**	**0.89**	**41.95**	**11.54**	**53.49**
Iso- + n-Paraffins		**0.00**	**0.00**	**0.00**	**0.00**	**0.66**	**3.04**	**4.25**	**4.34**	**4.18**	**2.98**	**2.23**	**2.19**	**0.94**	**0.19**	**25.00**	**8.41**	**33.41**
isoparaffins	2	0.00	0.00	0.00	0.00	0.51	3.00	4.05	3.85	3.61	2.45	1.46	1.55	0.70	0.15	21.32	7.26	28.58
n-Paraffins	2	0.00	0.00	0.00	0.00	0.15	0.04	0.20	0.49	0.57	0.53	0.77	0.64	0.25	0.03	3.68	1.15	4.83
Cycloparaffins		**0.00**	**0.00**	**0.00**	**0.12**	**1.14**	**1.75**	**2.33**	**2.85**	**2.32**	**1.86**	**1.54**	**1.35**	**0.98**	**0.71**	**16.95**	**3.13**	**20.08**
Monocycloparaffins	0	0.00	0.00	0.00	0.02	0.68	0.81	0.95	1.15	1.00	0.90	0.74	0.65	0.50	0.33	7.73	3.13	10.86
Dicycloparaffins	-2	0.00	0.00	0.00	0.07	0.39	0.71	0.96	1.18	0.83	0.57	0.47	0.42	0.30	0.24	6.14	0.00	6.14
Polycycloparaffins	-4	0.00	0.00	0.00	0.03	0.07	0.23	0.42	0.52	0.49	0.39	0.33	0.28	0.18	0.13	3.07	0.00	3.07
Aromatics		**0.00**	**0.02**	**0.42**	**1.52**	**1.00**	**1.02**	**1.00**	**0.93**	**0.78**	**0.59**	**0.44**	**0.31**	**0.22**	**0.14**	**8.38**	**36.37**	**44.75**
Monoaromatics		**0.00**	**0.00**	**0.41**	**1.21**	**0.80**	**0.80**	**0.80**	**0.72**	**0.58**	**0.44**	**0.34**	**0.25**	**0.17**	**0.08**	**6.60**	**36.37**	**42.97**
Alkylbenzenes	-6	0.00	0.00	0.19	0.80	0.30	0.27	0.27	0.24	0.19	0.15	0.12	0.09	0.06	0.03	2.71	36.37	39.08
Benzocycloalkanes	-8	0.00	0.00	0.22	0.40	0.48	0.47	0.39	0.30	0.22	0.16	0.12	0.09	0.06	0.03	2.93	0.00	2.93
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.01	0.02	0.07	0.14	0.18	0.17	0.13	0.10	0.07	0.04	0.02	0.95	0.00	0.95
Diaromatics		**0.00**	**0.00**	**0.00**	**0.30**	**0.18**	**0.20**	**0.18**	**0.17**	**0.15**	**0.11**	**0.08**	**0.05**	**0.05**	**0.05**	**1.53**	**0.00**	**1.53**
Naphthalenes	-12	0.00	0.00	0.00	0.30	0.17	0.16	0.10	0.06	0.05	0.05	0.04	0.04	0.05	0.05	1.07	0.00	1.07
Biphenyls	-14	0.00	0.00	0.00	0.00	0.01	0.02	0.05	0.06	0.06	0.04	0.02	0.01	0.00	0.00	0.27	0.00	0.27
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.03	0.02	0.01	0.01	0.00	0.00	0.00	0.12	0.00	0.12
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.01	0.01	0.00	0.00	0.00	0.07	0.00	0.07
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**	**0.01**	**0.01**	**0.00**	**0.01**
Phenanthrenes	-18	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	0.00	0.01
Phenanthrocyclolalkanes	-20	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
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**	**0.00**
Pyrenes	-22	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
Crysenes	-24	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
Aromatic Sulfur		**0.00**	**0.02**	**0.01**	**0.00**	**0.02**	**0.02**	**0.02**	**0.04**	**0.05**	**0.04**	**0.03**	**0.01**	**0.00**	**0.00**	**0.25**	**0.00**	**0.25**
Benzothiophenes	-10S	0.00	0.02	0.01	0.00	0.00	0.01	0.01	0.02	0.03	0.02	0.02	0.01	0.00	0.00	0.15	0.00	0.15
Dibenzothiophenes	-16S	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.00	0.00	0.00	0.11	0.00	0.11
Benzonaphthothiophenes	-22S	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
Olefins																**0.00**	**1.76**	**1.76**
Polars																**0.00**	**0.00**	**0.00**
Total																**50.33**	**49.67**	**100.00**

Table B.2. GC-FIMS Data for FD2A

Sample ID	FD2A															GC-FIMS	PIONA	Total
Lab ID	08-882															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.00**	**0.11**	**3.62**	**9.92**	**6.97**	**2.08**	**1.33**	**0.93**	**1.08**	**1.35**	**1.26**	**2.48**	**31.14**	**7.10**	**38.24**
Iso- + n-Paraffins		**0.00**	**0.00**	**0.00**	**0.00**	**1.22**	**7.78**	**5.50**	**1.15**	**0.59**	**0.26**	**0.12**	**0.07**	**0.02**	**0.02**	**16.74**	**6.32**	**23.06**
isoparaffins	2	0.00	0.00	0.00	0.00	1.14	7.78	5.48	1.14	0.56	0.24	0.09	0.07	0.02	0.02	16.53	5.65	22.18
n-Paraffins	2	0.00	0.00	0.00	0.00	0.07	0.00	0.02	0.01	0.04	0.03	0.04	0.00	0.00	0.00	0.20	0.67	0.87
Cycloparaffins		**0.00**	**0.00**	**0.00**	**0.11**	**2.40**	**2.14**	**1.48**	**0.93**	**0.74**	**0.67**	**0.95**	**1.29**	**1.24**	**2.46**	**14.40**	**0.78**	**15.18**
Monocycloparaffins	0	0.00	0.00	0.00	0.02	2.21	1.75	1.06	0.66	0.60	0.61	0.81	0.65	0.18	0.32	8.86	0.78	9.64
Dicycloparaffins	-2	0.00	0.00	0.00	0.02	0.19	0.37	0.35	0.23	0.13	0.04	0.05	0.18	0.31	0.75	2.63	0.00	2.63
Polycycloparaffins	-4	0.00	0.00	0.00	0.07	0.00	0.03	0.07	0.03	0.01	0.01	0.09	0.46	0.75	1.39	2.92	0.00	2.92
Aromatics		**0.00**	**0.06**	**1.68**	**4.81**	**1.82**	**1.53**	**1.09**	**0.65**	**0.34**	**0.15**	**0.17**	**0.31**	**0.25**	**0.20**	**13.03**	**46.22**	**59.25**
Monoaromatics		**0.00**	**0.00**	**1.68**	**3.47**	**1.00**	**0.83**	**0.64**	**0.39**	**0.20**	**0.08**	**0.07**	**0.15**	**0.20**	**0.18**	**8.88**	**46.22**	**55.10**
Alkylbenzenes	-6	0.00	0.00	1.12	2.86	0.36	0.24	0.22	0.14	0.08	0.05	0.06	0.13	0.18	0.17	5.60	46.22	51.82
Benzocycloalkanes	-8	0.00	0.00	0.56	0.56	0.62	0.52	0.32	0.18	0.09	0.03	0.01	0.02	0.03	0.02	2.93	0.00	2.93
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.05	0.02	0.06	0.10	0.07	0.04	0.01	0.00	0.00	0.00	0.00	0.35	0.00	0.35
Diaromatics		**0.00**	**0.00**	**0.00**	**1.34**	**0.76**	**0.69**	**0.45**	**0.25**	**0.09**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**3.59**	**0.00**	**3.59**
Naphthalenes	-12	0.00	0.00	0.00	1.34	0.73	0.57	0.24	0.07	0.01	0.00	0.00	0.00	0.00	0.00	2.97	0.00	2.97
Biphenyls	-14	0.00	0.00	0.00	0.00	0.02	0.06	0.12	0.10	0.06	0.01	0.00	0.00	0.00	0.00	0.37	0.00	0.37
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.01	0.05	0.07	0.06	0.01	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.20
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.06
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**	**0.01**	**0.01**	**0.00**	**0.01**
Phenanthrenes	-18	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	0.00	0.01
Phenanthrocyclolalkanes	-20	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	0.00	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**	**0.00**
Pyrenes	-22	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
Crysenes	-24	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
Aromatic Sulfur		**0.00**	**0.06**	**0.00**	**0.00**	**0.06**	**0.01**	**0.01**	**0.01**	**0.04**	**0.05**	**0.10**	**0.16**	**0.04**	**0.00**	**0.54**	**0.00**	**0.54**
Benzothiophenes	-10S	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.05	0.10	0.16	0.04	0.00	0.47	0.00	0.47
Dibenzothiophenes	-16S	0.00	0.00	0.00	0.00	0.06	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.07
Benzonaphthothiophenes	-22S	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
Olefins																**0.00**	**2.50**	**2.50**
Polars																**0.00**	**0.00**	**0.00**
Total																**44.17**	**55.82**	**99.99**

Table B.3. GC-FIMS Data for FD3A

Sample ID	FD3A															GC-FIMS	PIONA	Total
Lab ID	08-883															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.01**	**1.32**	**7.26**	**8.42**	**5.61**	**5.58**	**2.59**	**0.99**	**0.30**	**0.01**	**0.00**	**0.00**	**32.08**	**14.85**	**46.93**
Iso- + n-Paraffins		**0.00**	**0.00**	**0.00**	**0.00**	**2.92**	**4.47**	**3.21**	**4.17**	**2.05**	**0.89**	**0.28**	**0.00**	**0.00**	**0.00**	**18.01**	**11.17**	**29.18**
isoparaffins	2	0.00	0.00	0.00	0.00	0.94	3.13	1.89	2.81	1.07	0.29	0.00	0.00	0.00	0.00	10.14	7.34	17.48
n-Paraffins	2	0.00	0.00	0.00	0.00	1.98	1.34	1.33	1.36	0.98	0.60	0.28	0.00	0.00	0.00	7.87	3.83	11.70
Cycloparaffins		**0.00**	**0.00**	**0.01**	**1.32**	**4.34**	**3.95**	**2.39**	**1.41**	**0.54**	**0.09**	**0.02**	**0.01**	**0.00**	**0.00**	**14.07**	**3.68**	**17.75**
Monocycloparaffins	0	0.00	0.00	0.00	0.33	2.13	2.38	1.41	0.74	0.32	0.07	0.00	0.00	0.00	0.00	7.39	3.68	11.07
Dicycloparaffins	-2	0.00	0.00	0.00	0.95	2.13	1.37	0.70	0.55	0.17	0.01	0.02	0.01	0.00	0.00	5.92	0.00	5.92
Polycycloparaffins	-4	0.00	0.00	0.01	0.04	0.08	0.19	0.28	0.12	0.05	0.01	0.00	0.00	0.00	0.00	0.76	0.00	0.76
Aromatics		**0.00**	**0.00**	**1.55**	**4.60**	**4.38**	**3.66**	**3.08**	**1.91**	**0.91**	**0.24**	**0.07**	**0.01**	**0.01**	**0.00**	**20.42**	**32.42**	**52.84**
Monoaromatics		**0.00**	**0.00**	**1.40**	**3.85**	**3.48**	**2.67**	**2.17**	**1.39**	**0.68**	**0.22**	**0.07**	**0.01**	**0.01**	**0.00**	**15.95**	**32.42**	**48.37**
Alkylbenzenes	-6	0.00	0.00	0.76	2.58	1.48	1.04	0.95	0.54	0.32	0.10	0.04	0.00	0.01	0.00	7.82	32.42	40.24
Benzocycloalkanes	-8	0.00	0.00	0.64	1.26	1.94	1.46	0.93	0.56	0.29	0.11	0.03	0.00	0.00	0.00	7.21	0.00	7.21
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.02	0.05	0.17	0.30	0.28	0.08	0.02	0.00	0.00	0.00	0.00	0.92	0.00	0.92
Diaromatics		**0.00**	**0.00**	**0.14**	**0.74**	**0.89**	**0.98**	**0.91**	**0.52**	**0.23**	**0.02**	**0.00**	**0.00**	**0.00**	**0.00**	**4.44**	**0.00**	**4.44**
Naphthalenes	-12	0.00	0.00	0.14	0.74	0.82	0.70	0.38	0.14	0.03	0.00	0.00	0.00	0.00	0.00	2.96	0.00	2.96
Biphenyls	-14	0.00	0.00	0.00	0.00	0.06	0.16	0.31	0.19	0.12	0.01	0.00	0.00	0.00	0.00	0.86	0.00	0.86
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.01	0.12	0.20	0.17	0.07	0.00	0.00	0.00	0.00	0.00	0.57	0.00	0.57
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.06
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**	**0.00**
Phenanthrenes	-18	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
Phenanthrocyclolalkanes	-20	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
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**	**0.00**
Pyrenes	-22	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
Crysenes	-24	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
Aromatic Sulfur		**0.00**	**0.00**	**0.01**	**0.00**	**0.01**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.03**	**0.00**	**0.03**
Benzothiophenes	-10S	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	0.00	0.01	0.00	0.01
Dibenzothiophenes	-16S	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.02
Benzonaphthothiophenes	-22S	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
Olefins																**0.00**	**0.23**	**0.23**
Polars																**0.00**	**0.00**	**0.00**
Total																**52.50**	**47.50**	**100.00**

Table B.4. GC-FIMS Data for FD4A

Sample ID	FD4A															GC-FIMS	PIONA	Total
Lab ID	08-884(090324)															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.00**	**0.18**	**0.51**	**5.14**	**10.78**	**7.67**	**5.02**	**3.55**	**2.93**	**2.29**	**1.23**	**1.19**	**40.48**	**2.99**	**43.47**
Iso- + n-Paraffins		**0.00**	**0.00**	**0.00**	**0.00**	**0.17**	**4.14**	**7.75**	**3.55**	**1.36**	**0.75**	**0.21**	**0.09**	**0.00**	**0.00**	**18.02**	**2.92**	**20.94**
isoparaffins	2	0.00	0.00	0.00	0.00	0.17	4.14	7.75	3.54	1.35	0.75	0.21	0.09	0.00	0.00	18.00	1.37	19.37
n-Paraffins	2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.03	1.55	1.58
Cycloparaffins		**0.00**	**0.00**	**0.00**	**0.18**	**0.34**	**1.00**	**3.03**	**4.12**	**3.66**	**2.80**	**2.71**	**2.20**	**1.23**	**1.19**	**22.45**	**0.07**	**22.52**
Monocycloparaffins	0	0.00	0.00	0.00	0.01	0.34	0.98	2.64	3.04	1.90	1.24	1.46	0.99	0.28	0.10	12.98	0.07	13.05
Dicycloparaffins	-2	0.00	0.00	0.00	0.00	0.00	0.02	0.27	0.59	0.80	0.70	0.52	0.47	0.35	0.28	4.00	0.00	4.00
Polycycloparaffins	-4	0.00	0.00	0.00	0.17	0.00	0.00	0.11	0.49	0.96	0.86	0.74	0.74	0.60	0.80	5.48	0.00	5.48
Aromatics		**0.00**	**0.09**	**3.64**	**11.63**	**1.85**	**1.16**	**0.65**	**0.34**	**0.15**	**0.12**	**0.18**	**0.22**	**0.15**	**0.09**	**20.26**	**36.19**	**56.45**
Monoaromatics		**0.00**	**0.00**	**3.63**	**9.39**	**0.56**	**0.10**	**0.04**	**0.05**	**0.05**	**0.08**	**0.14**	**0.15**	**0.14**	**0.08**	**14.42**	**36.19**	**50.61**
Alkylbenzenes	-6	0.00	0.00	1.78	8.48	0.40	0.07	0.03	0.02	0.03	0.08	0.13	0.13	0.13	0.07	11.37	36.19	47.56
Benzocycloalkanes	-8	0.00	0.00	1.85	0.80	0.14	0.03	0.01	0.03	0.02	0.00	0.01	0.01	0.01	0.01	2.92	0.00	2.92
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.11	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.13
Diaromatics		**0.00**	**0.00**	**0.00**	**2.25**	**1.23**	**1.05**	**0.60**	**0.26**	**0.07**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**5.47**	**0.00**	**5.47**
Naphthalenes	-12	0.00	0.00	0.00	2.25	1.20	0.90	0.36	0.06	0.00	0.00	0.00	0.00	0.00	0.00	4.77	0.00	4.77
Biphenyls	-14	0.00	0.00	0.00	0.00	0.02	0.07	0.13	0.11	0.05	0.01	0.00	0.00	0.00	0.00	0.39	0.00	0.39
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.01	0.07	0.07	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.19
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.05	0.02	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.12
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**	**0.01**	**0.00**	**0.01**
Phenanthrenes	-18	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	0.01	0.00	0.01
Phenanthrocyclolalkanes	-20	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
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**	**0.00**
Pyrenes	-22	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
Crysenes	-24	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
Aromatic Sulfur		**0.00**	**0.09**	**0.00**	**0.00**	**0.06**	**0.01**	**0.00**	**0.02**	**0.02**	**0.04**	**0.04**	**0.08**	**0.01**	**0.00**	**0.37**	**0.00**	**0.37**
Benzothiophenes	-10S	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.04	0.04	0.08	0.01	0.00	0.30	0.00	0.30
Dibenzothiophenes	-16S	0.00	0.00	0.00	0.00	0.06	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.07
Benzonaphthothiophenes	-22S	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
Olefins																**0.00**	**0.09**	**0.09**
Polars																**0.00**	**0.00**	**0.00**
Total																**60.74**	**39.27**	**100.01**

Table B.5. GC-FIMS Data for FD5A

Sample ID	FD5A															GC-FIMS	PIONA	Total
Lab ID	08-885															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.01**	**1.83**	**11.57**	**10.06**	**15.97**	**9.56**	**3.98**	**2.00**	**0.90**	**0.46**	**0.15**	**0.00**	**56.50**	**18.70**	**75.20**
Paraffins		**0.00**	**0.00**	**0.00**	**0.00**	**5.81**	**5.49**	**14.25**	**7.99**	**1.44**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**34.99**	**12.96**	**47.95**
isoparaffins	2	0.00	0.00	0.00	0.00	2.30	3.14	2.25	0.98	0.49	0.00	0.00	0.00	0.00	0.00	9.16	6.32	15.48
n-Paraffins	2	0.00	0.00	0.00	0.00	3.51	2.35	12.00	7.01	0.95	0.00	0.00	0.00	0.00	0.00	25.82	6.64	32.46
Cycloparaffins		**0.00**	**0.00**	**0.01**	**1.83**	**5.76**	**4.57**	**1.72**	**1.58**	**2.54**	**2.00**	**0.90**	**0.46**	**0.15**	**0.00**	**21.51**	**5.74**	**27.25**
Monocycloparaffins	0	0.00	0.00	0.00	0.55	3.55	3.48	1.05	0.29	0.08	0.03	0.03	0.04	0.00	0.00	9.10	5.74	14.84
Dicycloparaffins	-2	0.00	0.00	0.00	1.22	2.14	1.04	0.37	0.34	0.59	0.61	0.17	0.06	0.02	0.00	6.57	0.00	6.57
Polycycloparaffins	-4	0.00	0.00	0.01	0.06	0.06	0.05	0.30	0.94	1.87	1.36	0.70	0.36	0.13	0.00	5.84	0.00	5.84
Aromatics		**0.00**	**0.00**	**1.21**	**4.34**	**2.98**	**1.56**	**0.58**	**0.04**	**0.03**	**0.09**	**0.14**	**0.03**	**0.00**	**0.00**	**11.00**	**13.62**	**24.62**
MonoAromatics		**0.00**	**0.00**	**1.14**	**3.84**	**2.70**	**1.52**	**0.58**	**0.04**	**0.03**	**0.09**	**0.14**	**0.03**	**0.00**	**0.00**	**10.11**	**13.62**	**23.73**
Alkylbenzenes	-6	0.00	0.00	0.60	2.64	1.61	0.90	0.44	0.03	0.03	0.09	0.14	0.03	0.00	0.00	6.52	13.62	20.14
Benzocycloalkanes	-8	0.00	0.00	0.54	1.18	1.07	0.60	0.13	0.01	0.00	0.00	0.00	0.00	0.00	0.00	3.54	0.00	3.54
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.01	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.05
Diaromatics		**0.00**	**0.00**	**0.07**	**0.50**	**0.28**	**0.05**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.90**	**0.00**	**0.90**
Naphthalenes	-12	0.00	0.00	0.07	0.50	0.26	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.86	0.00	0.86
Biphenyls	-14	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.03
Naphthocycloalkanes	-14	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
Fluorenes	-16	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**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Phenanthrenes	-18	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
Phenanthrocyclolalkanes	-20	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
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**	**0.00**
Pyrenes	-22	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
Crysenes	-24	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
Aromatic Sulfur		**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**
Benzothiophenes	-10S	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
Dibenzothiophenes	-16S	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
Benzonaphthothiophenes	-22S	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
Olefins																**0.00**	**0.18**	**0.18**
Polars																**0.00**	**0.00**	**0.00**
Total																**67.50**	**32.50**	**100.00**

Table B.6. GC-FIMS Data for FD6A

Sample ID	FD6A															GC-FIMS	PIONA	Total
Lab ID	08-886															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.00**	**0.88**	**3.79**	**6.03**	**10.56**	**15.47**	**15.03**	**8.44**	**4.55**	**3.31**	**1.79**	**1.30**	**71.16**	**6.40**	**77.56**
Iso- + n-Paraffins		**0.00**	**0.00**	**0.00**	**0.00**	**1.03**	**2.51**	**6.38**	**10.04**	**8.27**	**2.83**	**0.71**	**0.15**	**0.00**	**0.00**	**31.93**	**4.64**	**36.57**
isoparaffins	2	0.00	0.00	0.00	0.00	0.11	1.57	4.97	8.16	6.93	2.01	0.44	0.00	0.00	0.00	24.18	1.96	26.14
n-Paraffins	2	0.00	0.00	0.00	0.00	0.92	0.95	1.42	1.89	1.34	0.82	0.27	0.15	0.00	0.00	7.75	2.68	10.43
Cycloparaffins		**0.00**	**0.00**	**0.00**	**0.88**	**2.76**	**3.52**	**4.17**	**5.43**	**6.76**	**5.61**	**3.84**	**3.16**	**1.79**	**1.30**	**39.22**	**1.76**	**40.98**
Monocycloparaffins	0	0.00	0.00	0.00	0.16	0.99	1.75	1.89	1.68	1.56	0.87	0.54	0.18	0.02	0.00	9.63	1.76	11.39
Dicycloparaffins	-2	0.00	0.00	0.00	0.72	1.73	1.38	1.16	1.80	2.27	1.98	1.30	0.86	0.34	0.28	13.83	0.00	13.83
Polycycloparaffins	-4	0.00	0.00	0.00	0.01	0.05	0.39	1.12	1.95	2.92	2.75	2.00	2.12	1.42	1.02	15.77	0.00	15.77
Aromatics		**0.00**	**0.00**	**0.29**	**1.65**	**3.32**	**3.56**	**3.59**	**2.62**	**1.74**	**0.91**	**0.75**	**0.54**	**0.65**	**0.42**	**20.04**	**2.29**	**22.33**
Monoaromatics		**0.00**	**0.00**	**0.27**	**1.46**	**2.61**	**2.52**	**2.49**	**1.83**	**1.26**	**0.85**	**0.74**	**0.54**	**0.65**	**0.42**	**15.64**	**2.29**	**17.93**
Alkylbenzenes	-6	0.00	0.00	0.09	0.57	0.72	0.74	1.03	0.72	0.60	0.54	0.62	0.50	0.60	0.42	7.16	2.29	9.45
Benzocycloalkanes	-8	0.00	0.00	0.18	0.88	1.84	1.58	1.07	0.71	0.43	0.24	0.10	0.04	0.04	0.00	7.11	0.00	7.11
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.01	0.05	0.21	0.38	0.40	0.24	0.07	0.02	0.00	0.00	0.00	1.37	0.00	1.37
Diaromatics		**0.00**	**0.00**	**0.01**	**0.19**	**0.71**	**1.04**	**1.10**	**0.77**	**0.46**	**0.06**	**0.01**	**0.00**	**0.00**	**0.00**	**4.34**	**0.00**	**4.34**
Naphthalenes	-12	0.00	0.00	0.01	0.19	0.66	0.73	0.46	0.20	0.09	0.01	0.00	0.00	0.00	0.00	2.34	0.00	2.34
Biphenyls	-14	0.00	0.00	0.00	0.00	0.05	0.17	0.36	0.30	0.25	0.03	0.00	0.00	0.00	0.00	1.16	0.00	1.16
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.01	0.13	0.22	0.20	0.10	0.02	0.00	0.00	0.00	0.00	0.67	0.00	0.67
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.07	0.02	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.17
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**	**0.00**
Phenanthrenes	-18	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
Phenanthrocyclolalkanes	-20	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
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**	**0.00**
Pyrenes	-22	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
Crysenes	-24	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
Aromatic Sulfur		**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.02**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.05**	**0.00**	**0.05**
Benzothiophenes	-10S	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.05
Dibenzothiophenes	-16S	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
Benzonaphthothiophenes	-22S	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
Olefins																**0.00**	**0.12**	**0.12**
Polars																**0.00**	**0.00**	**0.00**
Total																**91.20**	**8.81**	**100.01**

Table B.7. GC-FIMS Data for FD7A

Sample ID	FD7A															GC-FIMS	PIONA	Total
Lab ID	08-887															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.03**	**0.94**	**5.24**	**5.17**	**20.65**	**10.98**	**1.81**	**0.56**	**0.02**	**0.53**	**0.00**	**0.00**	**45.93**	**9.30**	**55.23**
Iso- + n-Paraffins		**0.00**	**0.00**	**0.00**	**0.00**	**2.42**	**2.67**	**19.22**	**10.38**	**1.66**	**0.08**	**0.00**	**0.00**	**0.00**	**0.00**	**36.43**	**6.77**	**43.20**
isoparaffins	2	0.00	0.00	0.00	0.00	0.75	1.45	1.01	0.29	0.20	0.00	0.00	0.00	0.00	0.00	3.71	2.71	6.42
n-Paraffins	2	0.00	0.00	0.00	0.00	1.67	1.22	18.21	10.09	1.46	0.08	0.00	0.00	0.00	0.00	32.73	4.06	36.79
Cycloparaffins		**0.00**	**0.00**	**0.03**	**0.94**	**2.82**	**2.50**	**1.43**	**0.60**	**0.15**	**0.48**	**0.02**	**0.53**	**0.00**	**0.00**	**9.49**	**2.53**	**12.02**
Monocycloparaffins	0	0.00	0.00	0.00	0.26	1.61	1.70	0.99	0.21	0.00	0.42	0.00	0.53	0.00	0.00	5.72	2.53	8.25
Dicycloparaffins	-2	0.00	0.00	0.00	0.62	1.14	0.73	0.23	0.31	0.07	0.02	0.01	0.00	0.00	0.00	3.14	0.00	3.14
Polycycloparaffins	-4	0.00	0.00	0.03	0.06	0.07	0.07	0.20	0.08	0.08	0.04	0.01	0.00	0.00	0.00	0.63	0.00	0.63
Aromatics		**0.00**	**0.00**	**1.46**	**3.92**	**2.84**	**1.69**	**6.80**	**0.40**	**4.41**	**0.02**	**2.44**	**0.01**	**0.88**	**0.00**	**24.87**	**19.76**	**44.63**
Monoaromatics		**0.00**	**0.00**	**1.33**	**3.22**	**2.35**	**1.27**	**3.90**	**0.29**	**0.47**	**0.00**	**0.10**	**0.01**	**0.00**	**0.00**	**12.95**	**19.76**	**32.71**
Alkylbenzenes	-6	0.00	0.00	0.77	2.51	1.26	0.53	2.85	0.08	0.03	0.00	0.00	0.01	0.00	0.00	8.05	19.76	27.81
Benzocycloalkanes	-8	0.00	0.00	0.56	0.70	1.03	0.68	0.69	0.19	0.12	0.00	0.00	0.00	0.00	0.00	3.98	0.00	3.98
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.02	0.06	0.06	0.36	0.02	0.32	0.00	0.10	0.00	0.00	0.00	0.93	0.00	0.93
Diaromatics		**0.00**	**0.00**	**0.14**	**0.69**	**0.49**	**0.42**	**2.90**	**0.10**	**3.94**	**0.02**	**2.34**	**0.00**	**0.88**	**0.00**	**11.91**	**0.00**	**11.91**
Naphthalenes	-12	0.00	0.00	0.14	0.69	0.46	0.29	0.60	0.01	1.06	0.00	1.33	0.00	0.84	0.00	5.40	0.00	5.40
Biphenyls	-14	0.00	0.00	0.00	0.00	0.02	0.09	2.24	0.07	2.79	0.01	0.97	0.00	0.04	0.00	6.25	0.00	6.25
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.01	0.04	0.06	0.02	0.05	0.00	0.01	0.00	0.00	0.00	0.20	0.00	0.20
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.00	0.03	0.00	0.00	0.00	0.07	0.00	0.07
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**	**0.00**
Phenanthrenes	-18	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
Phenanthrocyclolalkanes	-20	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
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**	**0.00**
Pyrenes	-22	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
Crysenes	-24	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
Aromatic Sulfur		**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**	**0.01**	**0.00**	**0.01**
Benzothiophenes	-10S	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	0.01	0.00	0.01
Dibenzothiophenes	-16S	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
Benzonaphthothiophenes	-22S	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
Olefins																**0.00**	**0.10**	**0.10**
Polars																**0.00**	**0.00**	**0.00**
Total																**70.80**	**29.16**	**99.96**

Table B.8. GC-FIMS Data for FD8A

Sample ID	FD8A															GC-FIMS	PIONA	Total
Lab ID	08-888															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.00**	**0.02**	**0.14**	**1.33**	**19.24**	**13.30**	**4.52**	**5.52**	**0.99**	**6.12**	**1.52**	**1.98**	**54.67**	**0.30**	**54.97**
Iso- + n-Paraffins		**0.00**	**0.00**	**0.00**	**0.02**	**0.09**	**0.37**	**18.27**	**9.98**	**2.19**	**1.43**	**0.00**	**0.00**	**0.00**	**0.00**	**32.35**	**0.30**	**32.65**
isoparaffins	2	0.00	0.00	0.00	0.00	0.00	0.00	1.83	1.47	1.07	1.10	0.00	0.00	0.00	0.00	5.47	0.2.	5.47
n-Paraffins	2	0.00	0.00	0.00	0.02	0.09	0.37	16.44	8.51	1.12	0.33	0.00	0.00	0.00	0.00	26.89	0.13	27.02
Cycloparaffins		**0.00**	**0.00**	**0.00**	**0.00**	**0.04**	**0.95**	**0.97**	**3.32**	**2.34**	**4.08**	**0.99**	**6.12**	**1.52**	**1.98**	**22.32**	**0.00**	**22.32**
Monocycloparaffins	0	0.00	0.00	0.00	0.00	0.00	0.88	0.27	1.69	0.08	1.82	0.03	4.67	0.04	0.25	9.73	0.00	9.73
Dicycloparaffins	-2	0.00	0.00	0.00	0.00	0.00	0.01	0.10	0.85	0.73	0.89	0.29	0.40	0.33	0.44	4.04		4.04
Polycycloparaffins	-4	0.00	0.00	0.00	0.00	0.04	0.06	0.60	0.78	1.53	1.37	0.67	1.06	1.14	1.29	8.54		8.54
Aromatics		**0.00**	**0.00**	**0.02**	**0.11**	**2.78**	**1.14**	**14.49**	**0.60**	**10.54**	**0.26**	**6.95**	**0.27**	**4.33**	**0.35**	**41.83**	**3.11**	**44.94**
Monaaromatics		**0.00**	**0.00**	**0.01**	**0.05**	**2.62**	**0.86**	**8.03**	**0.34**	**1.23**	**0.06**	**0.88**	**0.25**	**0.47**	**0.34**	**15.14**	**3.11**	**18.25**
Alkylbenzenes	-6	0.00	0.00	0.01	0.02	1.36	0.15	6.08	0.04	0.09	0.06	0.14	0.23	0.31	0.33	8.83	3.11	11.94
Benzocycloalkanes	-8	0.00	0.00	0.01	0.03	1.12	0.62	1.18	0.25	0.29	0.00	0.04	0.01	0.04	0.01	3.61		3.61
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.00	0.13	0.09	0.77	0.05	0.85	0.00	0.70	0.00	0.12	0.00	2.71		2.71
Diaromatics		**0.00**	**0.00**	**0.00**	**0.05**	**0.16**	**0.28**	**6.46**	**0.25**	**9.30**	**0.20**	**6.07**	**0.02**	**3.75**	**0.00**	**26.56**		**26.56**
Naphthalenes	-12	0.00	0.00	0.00	0.05	0.14	0.08	1.20	0.01	2.53	0.00	3.35	0.00	3.20	0.00	10.57		10.57
Biphenyls	-14	0.00	0.00	0.00	0.00	0.01	0.13	5.14	0.17	6.44	0.17	2.37	0.01	0.32	0.00	14.78		14.78
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.01	0.07	0.12	0.05	0.19	0.00	0.04	0.00	0.00	0.00	0.49		0.49
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.14	0.02	0.31	0.01	0.23	0.00	0.72		0.72
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**	**0.10**	**0.00**	**0.11**		**0.11**
Phenanthrenes	-18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.11		0.11
Phenanthrocyclolalkanes	-20	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	-22	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
Crysenes	-24	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**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.02**		**0.02**
Benzothiophenes	-10S	0.00	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		0.02
Dibenzothiophenes	-16S	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
Benzonaphthothiophenes	-22S	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**	**0.02**	**0.02**
Polars																**0.00**	**0.00**	**0.00**
Total																**96.50**	**3.43**	**99.93**

Table B.9. GC-FIMS Data for FD9A

Sample ID	FD9A															GC-FIMS	PIONA	Total
Lab ID	08-889															200°C+	200°C-	Sum
		C1 to														%of	%of	IBP
HC Type	Z No	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	Total	Total	FBP
Saturates		**0.00**	**0.00**	**0.01**	**0.65**	**3.20**	**7.83**	**7.38**	**12.82**	**8.77**	**10.84**	**3.91**	**2.32**	**1.08**	**0.51**	**59.30**	**5.90**	**65.20**
Iso- + n-Paraffins		**0.00**	**0.00**	**0.00**	**0.00**	**0.89**	**1.95**	**4.21**	**4.94**	**4.32**	**3.65**	**1.62**	**0.39**	**0.00**	**0.00**	**21.98**	**3.90**	**25.88**
isoparaffins	2	0.00	0.00	0.00	0.00	0.14	1.03	2.99	3.27	3.33	2.61	1.22	0.16	0.00	0.00	14.74	1.50	16.24
n-Paraffins	2	0.00	0.00	0.00	0.00	0.75	0.91	1.22	1.68	0.99	1.04	0.40	0.24	0.00	0.00	7.24	2.42	9.66
Cycloparaffins		**0.00**	**0.00**	**0.01**	**0.65**	**2.31**	**5.88**	**3.17**	**7.88**	**4.45**	**7.19**	**2.29**	**1.93**	**1.08**	**0.51**	**37.33**	**2.00**	**39.33**
Monocycloparaffins	0	0.00	0.00	0.00	0.11	0.86	4.42	1.52	5.12	1.15	3.81	0.31	0.24	0.02	0.01	17.58	1.96	19.54
Dicycloparaffins	-2	0.00	0.00	0.00	0.51	1.40	1.13	0.87	1.48	1.47	1.55	0.82	0.43	0.31	0.16	10.15	0.00	10.15
Polycycloparaffins	-4	0.00	0.00	0.01	0.02	0.05	0.33	0.78	1.27	1.83	1.82	1.15	1.25	0.75	0.34	9.59	0.00	9.59
Aromatics		**0.00**	**0.00**	**0.59**	**2.02**	**2.51**	**2.55**	**2.84**	**1.90**	**1.75**	**0.67**	**0.79**	**0.34**	**0.25**	**0.08**	**16.30**	**18.42**	**34.72**
Monoaromatics		**0.00**	**0.00**	**0.52**	**1.68**	**1.93**	**1.78**	**1.92**	**1.27**	**0.94**	**0.60**	**0.51**	**0.34**	**0.19**	**0.08**	**11.78**	**18.42**	**30.20**
Alkylbenzenes	-6	0.00	0.00	0.23	0.97	0.55	0.54	0.84	0.49	0.40	0.37	0.40	0.32	0.18	0.08	5.37	18.42	23.79
Benzocycloalkanes	-8	0.00	0.00	0.29	0.71	1.34	1.10	0.77	0.50	0.33	0.18	0.07	0.01	0.01	0.00	5.31	0.00	5.31
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.01	0.04	0.15	0.30	0.29	0.21	0.06	0.03	0.01	0.00	0.00	1.09	0.00	1.09
Diaromatics		**0.00**	**0.00**	**0.06**	**0.34**	**0.57**	**0.76**	**0.92**	**0.59**	**0.79**	**0.07**	**0.28**	**0.00**	**0.06**	**0.00**	**4.45**	**0.00**	**4.45**
Naphthalenes	-12	0.00	0.00	0.06	0.34	0.52	0.54	0.35	0.16	0.25	0.01	0.24	0.00	0.06	0.00	2.53	0.00	2.53
Biphenyls	-14	0.00	0.00	0.00	0.00	0.05	0.13	0.35	0.23	0.43	0.05	0.03	0.00	0.00	0.00	1.26	0.00	1.26
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.01	0.10	0.17	0.15	0.08	0.01	0.00	0.00	0.00	0.00	0.53	0.00	0.53
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.06	0.02	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.14
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**	**0.00**
Phenanthrenes	-18	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
Phenanthrocyclolalkanes	-20	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
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**	**0.00**
Pyrenes	-22	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
Crysenes	-24	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
Aromatic Sulfur		**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.03**	**0.02**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.07**	**0.00**	**0.07**
Benzothiophenes	-10S	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.06
Dibenzothiophenes	-16S	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	0.01	0.00	0.01
Benzonaphthothiophenes	-22S	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
Olefins																**0.00**	**0.13**	**0.13**
Polars																**0.00**	**0.00**	**0.00**
Total																**75.60**	**24.45**	**100.05**

APPENDIX C. PIONA DATA

APPENDIX C. PIONA DATA

Table C.1. PIONA Data for FD1A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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	0.00	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	0.05	0.07
7	0.02	0.01	0.02	0.06	0.01	0.00	0.10	0.24
8	0.30	0.10	0.02	0.00	0.00	0.00	5.02	5.44
9	0.57	0.52	0.29	0.00	0.00	0.01	26.99	28.38
10	0.97	1.96	0.39	0.00	0.04	0.01	4.21	7.57
11	1.25	4.67	0.41	0.00	1.63	0.00	0.00	7.96
Totals	3.13	7.26	1.15	0.06	1.68	0.02	36.37	49.67

Table C.2. PIONA Data for FD2A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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 C.3. PIONA Data for FD3A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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	0.00	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	0.01	0.01	0.00	0.01	0.01	0.04	0.08
7	0.06	0.03	0.04	0.05	0.00	0.00	0.14	0.32
8	0.41	0.43	0.15	0.00	0.00	0.01	5.40	6.39
9	0.75	0.72	0.57	0.00	0.00	0.01	26.78	28.82
10	1.65	2.92	1.66	0.00	0.02	0.02	0.07	6.33
11	0.81	3.23	1.40	0.01	0.09	0.02	0.00	5.56
Totals	3.68	7.34	3.83	0.06	0.11	0.06	32.42	47.50

Table C.4. PIONA Data for FD4A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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 C.5. PIONA Data for FD5A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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	0.05
7	0.03	0.06	0.04	0.05	0.00	0.00	0.08	0.27
8	0.35	0.20	0.11	0.00	0.00	0.00	1.76	2.43
9	0.98	0.76	0.65	0.00	0.00	0.01	11.68	14.08
10	2.93	3.26	2.91	0.00	0.00	0.03	0.06	9.19
11	1.43	2.04	2.92	0.00	0.07	0.01	0.00	6.47
Totals	5.74	6.32	6.64	0.05	0.08	0.05	13.62	32.50

Table C.6. PIONA Data for FD6A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.02
6	0.01	0.01	0.01	0.00	0.01	0.01	0.04	0.07
7	0.05	0.04	0.05	0.06	0.00	0.00	0.15	0.34
8	0.37	0.24	0.15	0.00	0.00	0.00	0.47	1.23
9	0.53	0.48	0.33	0.00	0.00	0.00	1.60	2.94
10	0.79	0.94	0.84	0.00	0.00	0.01	0.04	2.61
11	0.00	0.25	1.32	0.00	0.02	0.01	0.00	1.59
Totals	1.76	1.96	2.68	0.06	0.03	0.03	2.29	8.81

Table C.7. PIONA Data for FD7A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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

Table C.8. PIONA Data for FD8A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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	0.02	0.00	0.00	0.00	0.00	0.03
5	0.00	0.06	0.00	0.01	0.00	0.00	0.00	0.07
6	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.04
7	0.00	0.03	0.00	0.00	0.00	0.00	0.02	0.05
8	0.00	0.10	0.00	0.00	0.00	0.00	0.13	0.22
9	0.00	0.00	0.00	0.00	0.00	0.00	2.92	2.92
10	0.00	0.00	0.05	0.00	0.00	0.00	0.02	0.07
11	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.06
Totals	0.00	0.20	0.13	0.01	0.01	0.00	3.11	3.46

Table C.9. PIONA Data for FD9A

Carbon Number	Saturated Hydrocarbon Content			Unsaturated Hydrocarbon Content			Monoaromatic Hydrocarbon Content	Totals
	Paraffins			Olefins				
	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	0.01
6	0.01	0.02	0.01	0.00	0.01	0.01	0.03	0.08
7	0.04	0.02	0.04	0.06	0.00	0.00	0.16	0.31
8	0.32	0.16	0.13	0.00	0.00	0.00	3.12	3.74
9	0.90	0.00	0.36	0.00	0.00	0.01	15.06	16.32
10	0.69	1.09	0.79	0.00	0.00	0.01	0.05	2.63
11	0.00	0.20	1.09	0.00	0.04	0.00	0.00	1.33
Totals	1.96	1.50	2.42	0.06	0.05	0.02	18.42	24.42

APPENDIX D. SPE GC-MS + PIONA DATA

APPENDIX D. SPE GC-MS + PIONA Data

Table D.1. SPE GC-MS + PIONA Data for Face Diesel Fuels FD1A, FD2A, and FD3A

Method	FD1A			FD2A			FD3A		
	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	**11.5**	**39.7**	**51.3**	**7.1**	**34.9**	**42.0**	**14.9**	**30.4**	**45.2**
Total paraffins	**8.4**	**25.7**	**34.1**	**6.3**	**22.1**	**28.5**	**11.2**	**16.1**	**27.3**
Isoparaffins	7.3			5.7			7.3		
n-Paraffins	1.2			0.7			3.8		
Cycloparaffins	**3.1**	**14.0**	**17.2**	**0.8**	**12.8**	**13.6**	**3.7**	**14.3**	**18.0**
Monocycloparaffins	3.1	6.6	9.8	0.8	5.7	6.5	3.7	7.6	11.3
Dicycloparaffins		5.1	5.1		3.7	3.7		5.8	5.8
Tricycloparaffins		2.3	2.3		2.0	2.0		0.9	0.9
4-Rings cycloparaffins		0.0	0.0		1.4	1.4		0.0	0.0
5-Rings cycloparaffins		0.0	0.0		0.1	0.1		0.0	0.0
6-Rings cycloparaffins		0.0	0.0		0.0	0.0		0.0	0.0
AROMATICS	**36.4**	**10.3**	**46.6**	**46.2**	**9.1**	**55.3**	**32.4**	**18.1**	**50.5**
Monoaromatics	**36.4**	**9.3**	**45.7**	**46.2**	**8.5**	**54.8**	**32.4**	**14.4**	**46.8**
Alkylbenzenes	36.4	6.9	43.3	46.2	8.4	54.7	32.4	7.6	40.0
Benzocycloalkanes		1.8	1.8		0.1	0.1		5.4	5.4
Benzodicycloalkanes		0.6	0.6		0.0	0.0		1.4	1.4
Diaromatics		**0.9**	**0.9**		**0.5**	**0.5**		**3.6**	**3.6**
Naphthalenes		0.7	0.7		0.5	0.5		2.6	2.6
Naphthocycloalkanes		0.1	0.1		0.0	0.0		0.8	0.8
Fluorenes		0.1	0.1		0.1	0.1		0.2	0.2
Triaromatics		**0.0**	**0.0**		**0.0**	**0.0**		**0.1**	**0.1**
Phenanthrenes		0.0	0.0		0.0	0.0		0.1	0.1
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**
Benzpyrenes/Perylenes		0.0	0.0		0.0	0.0		0.0	0.0
Dibenzanthracenes		0.0	0.0		0.0	0.0		0.0	0.0
Aromatic Sulfur		**0.0**	**0.0**		**0.0**	**0.0**		**0.1**	**0.1**
Benzothiophenes		0.0	0.0		0.0	0.0		0.1	0.1
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
POLARS		0.0	0.0		0.0	0.0		0.0	0.0
OLEFINS	**1.8**	**0.3**	**2.1**	**2.5**	**0.2**	**2.7**	**0.2**	**4.0**	**4.2**
TOTAL	**49.7**	**50.3**	**100.0**	**55.8**	**44.2**	**100.0**	**47.5**	**52.5**	**100.0**

Table D.2. SPE GC-MS + PIONA Data for Face Diesel Fuels FD4A, FD5A, and FD6A

Method	FD4A			FD5A			FD6A		
	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	**3.0**	**56.5**	**59.5**	**18.7**	**59.5**	**78.2**	**6.4**	**72.1**	**78.5**
Total paraffins	**2.9**	**28.0**	**30.9**	**13.0**	**36.0**	**48.9**	**4.6**	**27.8**	**32.4**
isoparaffins	1.4			6.3			2.0		
n-paraffins	1.6			6.6			2.7		
Cycloparaffins	**0.1**	**28.5**	**28.6**	**5.7**	**23.6**	**29.3**	**1.8**	**44.4**	**46.1**
Monocycloparaffins	0.1	13.0	13.1	5.7	9.4	15.1	1.8	15.7	17.5
Dicycloparaffins		8.5	8.5		8.8	8.8		14.5	14.5
Tricycloparaffins		4.9	4.9		5.0	5.0		10.4	10.4
4-Rings cycloparaffins		2.1	2.1		0.4	0.4		3.7	3.7
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	**36.2**	**4.0**	**40.2**	**13.6**	**7.4**	**21.1**	**2.3**	**18.8**	**21.0**
Monoaromatics	**36.2**	**3.1**	**39.3**	**13.6**	**6.7**	**20.4**	**2.3**	**14.6**	**16.9**
Alkylbenzenes	36.2	2.8	39.0	13.6	4.8	18.4	2.3	6.0	8.3
Benzocycloalkanes		0.3	0.3		1.9	1.9		6.6	6.6
Benzodicycloalkanes		0.0	0.0		0.0	0.0		2.0	2.0
Diaromatics		**0.9**	**0.9**		**0.6**	**0.6**		**3.9**	**3.9**
Naphthalenes		0.8	0.8		0.6	0.6		2.5	2.5
Naphthocycloalkanes		0.0	0.0		0.0	0.0		1.1	1.1
Fluorenes		0.0	0.0		0.0	0.0		0.3	0.3
Triaromatics		**0.0**	**0.0**		**0.0**	**0.0**		**0.1**	**0.1**
Phenanthrenes		0.0	0.0		0.0	0.0		0.1	0.1
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**
Benzpyrenes/Perylenes		0.0	0.0		0.0	0.0		0.0	0.0
Dibenzanthracenes		0.0	0.0		0.0	0.0		0.0	0.0
Aromatic Sulfur		**0.0**	**0.0**		**0.1**	**0.1**		**0.2**	**0.2**
Benzothiophenes		0.0	0.0		0.1	0.1		0.2	0.2
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
POLARS		0.0	0.0		0.0	0.0		0.0	0.0
OLEFINS	**0.1**	**0.3**	**0.4**	**0.2**	**0.5**	**0.7**	**0.1**	**0.3**	**0.4**
TOTAL	**39.3**	**60.7**	**100.0**	**32.5**	**67.500**	**100.0**	**8.8**	**91.2**	**100.0**

Table D.3. SPE GC-MS + PIONA Data for Face Diesel Fuels FD7A, FD8A, and FD9A

Method	FD7A			FD8A			FD9A		
	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	**9.3**	**42.5**	**51.8**	**0.3**	**49.9**	**50.2**	**5.9**	**49.6**	**55.5**
Total paraffins	**6.8**	**32.6**	**39.4**	**0.3**	**25.6**	**26.0**	**3.9**	**20.2**	**24.1**
isoparaffins	2.7			0.2			1.5		
n-paraffins	4.1			0.1			2.4		
Cycloparaffins	**2.5**	**9.9**	**12.4**	**0.0**	**24.3**	**24.3**	**2.0**	**29.4**	**31.4**
Monocycloparaffins	2.5	5.2	7.8	0.0	7.8	7.8	2.0	10.9	12.8
Dicycloparaffins		4.3	4.3		8.6	8.6		10.0	10.0
Tricycloparaffins		0.4	0.4		6.6	6.6		6.8	6.8
4-Rings cycloparaffins		0.0	0.0		1.2	1.2		1.8	1.8
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	**19.8**	**27.8**	**47.5**	**3.1**	**45.7**	**48.8**	**18.4**	**25.2**	**43.7**
Monoaromatics	**19.8**	**15.9**	**35.6**	**3.1**	**19.6**	**22.7**	**18.4**	**19.3**	**37.7**
Alkylbenzenes	19.8	9.3	29.0	3.1	8.5	11.6	18.4	8.8	27.2
Benzocycloalkanes		4.5	4.5		6.0	6.0		8.0	8.0
Benzodicycloalkanes		2.0	2.0		5.1	5.1		2.4	2.4
Diaromatics		**10.7**	**10.7**		**22.0**	**22.0**		**5.5**	**5.5**
Naphthalenes		4.1	4.1		5.9	5.9		3.7	3.7
Naphthocycloalkanes		5.9	5.9		14.5	14.5		1.4	1.4
Fluorenes		0.7	0.7		1.6	1.6		0.4	0.4
Triaromatics		**0.3**	**0.3**		**0.7**	**0.7**		**0.1**	**0.1**
Phenanthrenes		0.3	0.3		0.7	0.7		0.1	0.1
Phenanthrocycloalkanes		0.0	0.0		0.0	0.0		0.0	0.0
Tetraaromatics		**0.0**	**0.0**		**0.1**	**0.1**		**0.0**	**0.0**
Pyrenes/Benzofluorenes		0.0	0.0		0.1	0.1		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**
Benzpyrenes/Perylenes		0.0	0.0		0.0	0.0		0.0	0.0
Dibenzanthracenes		0.0	0.0		0.0	0.0		0.0	0.0
Aromatic Sulfur		**1.0**	**1.0**		**3.3**	**3.3**		**0.2**	**0.2**
Benzothiophenes		0.9	0.9		2.4	2.4		0.2	0.2
Dibenzothiophenes		0.1	0.1		0.9	0.9		0.0	0.0
Benzonaphthothiophenes		0.0	0.0		0.0	0.0		0.0	0.0
POLARS		0.0	0.0		0.0	0.0		0.0	0.0
OLEFINS	**0.1**	**0.6**	**0.7**	**0.0**	**1.0**	**1.0**	**0.1**	**0.8**	**0.9**
TOTAL	**29.2**	**70.8**	**100.0**	**3.5**	**96.5**	**100.0**	**24.4**	**75.580**	**100.0**

APPENDIX E. HYDROCARBON ANALYSIS DATA BY CARBON NUMBER AND BOILING POINT

APPENDIX E. HYDROCARBON ANALYSIS DATA BY CARBON NUMBER AND BOILING POINT

Table E.1. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD1A

Report in Weight % for Simdist ≤ 200	49.67						
C-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	0.01	0.00		0.01
6	0.00	0.00	0.00	0.02	0.00		0.03
7	0.03	0.03	0.00	0.13	0.06		0.25
8	0.03	0.15	0.03	0.39	5.63		6.23
9	0.41	0.56	0.19	1.40	19.35		21.92
10	0.68	10.18	0.23	0.77	4.34		16.20
11	0.01	2.44	0.00	0.00	0.06		2.51
Totals	1.16	13.36	0.45	2.73	29.45	2.52	49.67

Table E.2. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD2A

Report in Weight % for Simdist ≤ 200	55.83						
C-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 E.3. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD3A

Report in Weight % for Simdist ≤ 200	47.50						
C-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		0.01
6	0.01	0.01	0.06	0.02	0.00		0.11
7	0.05	0.07	0.03	0.16	0.27		0.57
8	0.20	0.47	0.02	0.58	6.95		8.21
9	0.80	0.99	0.58	1.27	25.53		29.17
10	1.54	3.98	0.19	0.11	1.76		7.59
11	0.00	0.74	0.00	0.00	0.01		0.75
Total	2.60	6.27	0.87	2.15	34.52	1.09	47.50

Table E.4. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD4A

Report in Weight % for Simdist ≤ 200	39.26						
C-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 E.5. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD5A

Report in Weight % for Simdist ≤ 200	32.50						
C-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	0.01	0.00		0.01
6	0.00	0.00	0.01	0.01	0.00		0.02
7	0.05	0.08	0.00	0.09	0.07		0.29
8	0.12	0.23	0.02	0.40	1.90		2.67
9	0.76	0.68	0.44	1.26	10.40		13.54
10	3.11	3.83	0.24	0.96	4.18		12.32
11	0.02	1.98	0.00	0.00	0.23		2.23
12	0.00	0.01	0.00	0.00	0.00		0.01
Totals	4.06	6.82	0.71	2.72	16.79	1.40	32.50

Table E.6. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD6A

Report in Weight % for Simdist ≤ 200	8.81						
C-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	0.01	0.00		0.01
6	0.00	0.01	0.02	0.01	0.00		0.05
7	0.04	0.05	0.01	0.09	0.12		0.31
8	0.12	0.23	0.10	0.38	0.37		1.20
9	0.29	0.42	0.23	0.48	0.92		2.33
10	0.58	0.92	0.07	0.21	1.14		2.92
11	0.42	0.65	0.00	0.00	0.19		1.27
Totals	1.45	2.29	0.44	1.18	2.75	0.71	8.81

Table E.7. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD7A

Report in Weight % for Simdist ≤ 200	29.15						
C-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 E.8. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD8A

Report in Weight % for Simdist ≤ 200	3.46						
C-number	**n-Paraffins**	**Isoparaffins**	**Olefins**	**Naphthenes**	**Aromatics**	**Unknown**	**Totals**
3	0.00	0.00	0.00	0.00	0.00		0.00
4	0.01	0.00	0.00	0.00	0.00		0.01
5	0.00	0.05	0.00	0.00	0.00		0.05
6	0.00	0.01	0.00	0.00	0.00		0.01
7	0.00	0.04	0.00	0.00	0.00		0.04
8	0.00	0.12	0.00	0.00	0.08		0.20
9	0.00	0.06	0.02	0.01	0.38		0.47
10	0.04	0.03	0.00	0.00	2.54		2.61
11	0.02	0.01	0.00	0.00	0.00		0.03
Totals	0.08	0.31	0.02	0.01	3.01	0.04	3.46

Table E.9. Detailed Hydrocarbon Analysis by Carbon Number (C-number) for FD9A

Report in Weight % for Simdist ≤ 200	24.42						
C-number	**n-Paraffins**	**Isoparaffins**	**Olefins**	**Naphthenes**	**Aromatics**	**Unknown**	**Totals**
1	0.00	0.00	0.00	0.00	0.00		0.00
2	0.00	0.00	0.00	0.00	0.00		0.00
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		0.01
6	0.00	0.02	0.01	0.01	0.00		0.04
7	0.04	0.02	0.00	0.09	0.15		0.30
8	0.12	0.17	0.05	0.34	2.89		3.57
9	0.36	0.71	0.22	0.57	11.99		13.86
10	0.74	1.18	0.09	0.20	3.02		5.23
11	0.01	0.79	0.00	0.00	0.16		0.96
Total	1.28	2.89	0.38	1.21	18.21	0.45	24.42

Table E.10. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD1A

Start BP	Initial	(ibp)139.6	150	160	170	180	190	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	(ibp)139.6	150	160	170	180	190	200			
Simdist %off	0.50	1.76	0.74	6.50	5.50	15.67	19.00			
n-Paraffins	0.02	0.00	0.13	0.00	0.28	0.00	0.16	0.60	1.16	1.04
Isoparaffins	0.08	0.14	0.10	0.52	3.82	2.89	9.78	17.32	13.36	7.65
Olefins	0.03	0.02	0.04	0.05	0.00	0.00	0.00	0.15	0.45	1.51
Naphthenes	0.20	0.07	0.13	0.07	0.27	1.22	0.00	1.97	2.73	3.37
Aromatics	0.15	1.52	0.27	5.78	0.98	8.35	7.51	24.57	29.45	36.10
Unknown	0.02	0.01	0.05	0.08	0.14	3.21	1.55	5.07	2.52	0.00
Totals	0.50	1.76	0.74	6.50	5.50	15.67	19.00	49.67	49.67	49.67

Table E.11. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD2A

Start BP	0	140.4	160	170	180	190	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	140.4	160	170	180	190	200			
Simdist %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	0.64
Isoparaffins	0.10	0.09	0.39	0.48	3.69	2.97	7.71	5.50	6.17
Olefins	0.07	0.02	0.00	0.00	0.00	0.00	0.10	0.29	0.15
Naphthenes	0.07	0.05	0.00	0.05	0.07	0.00	0.25	0.53	0.60
Aromatics	0.16	2.80	6.51	5.61	9.50	15.48	40.06	45.31	48.27
Unknown	0.07	0.03	0.01	0.13	3.40	3.46	7.10	3.32	0.00
Totals	0.50	3.08	6.92	6.50	16.67	22.17	55.83	55.83	55.83

Table E.12. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD3A

Start BP	0	(ibp)118.6	130	140	150	160	170	180	190	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	(ibp)118.6	130	140	150	160	170	180	190	200			
Simdist %off	0.5	0.3	1.1	3.6	2.0	12.2	10.9	9.1	7.8			
n-Paraffins	0.03	0.09	0.00	0.00	0.53	0.00	1.38	0.00	0.00	2.03	2.60	3.83
Isoparaffins	0.16	0.10	0.13	0.34	0.41	1.77	0.93	1.53	1.33	6.69	6.27	7.34
Olefins	0.04	0.01	0.04	0.13	0.23	0.05	0.00	0.00	0.00	0.50	0.87	0.23
Naphthenes	0.11	0.13	0.35	0.12	0.34	0.19	0.06	0.16	0.00	1.45	2.15	3.68
Aromatics	0.13	0.00	0.53	2.98	0.51	10.15	8.11	5.35	5.89	33.65	34.52	32.42
Unknown	0.03	0.00	0.02	0.01	0.00	0.06	0.37	2.05	0.62	3.16	1.09	
Totals	0.50	0.33	1.08	3.57	2.02	12.21	10.86	9.10	7.83	47.50	47.50	47.50

Table E.13. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD4A

Start BP	0	(ibp)139.6	150	160	170	180	190	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	(ibp)139.6	150	160	170	180	190	200			
Simdist %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	1.55
Isoparaffins	0.12	0.14	0.23	0.80	0.69	0.40	0.00	2.38	2.60	1.37
Olefins	0.03	0.06	0.02	0.00	0.00	0.00	0.00	0.12	0.19	0.09
Naphthenes	0.04	0.01	0.14	0.01	0.01	0.02	0.00	0.24	0.29	0.07
Aromatics	0.28	4.47	0.67	12.54	8.55	5.76	2.96	35.22	35.35	36.19
Unknown	0.02	0.00	0.10	0.00	0.12	0.15	0.45	0.83	0.31	0.00
Total	0.50	4.69	1.31	13.36	9.67	6.33	3.41	39.26	39.26	39.26

Table E.14. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD5A

Start BP	0	(ibp)132.8	150	160	170	180	190	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	(ibp)132.8	150	160	170	180	190	200			
Simdist %off	0.5	1.9	1.5	5.6	6.9	7.5	8.6			
n-Paraffins	0.09	0.00	0.50	0.00	2.17	0.00	0.15	2.90	4.06	6.64
Isoparaffins	0.18	0.37	0.34	1.43	1.05	1.56	2.24	7.16	6.82	6.32
Olefins	0.02	0.08	0.27	0.06	0.00	0.00	0.00	0.44	0.71	0.18
Naphthenes	0.17	0.36	0.21	0.28	0.07	1.11	0.00	2.20	2.72	5.74
Aromatics	0.04	1.06	0.19	3.69	3.17	4.30	5.38	17.82	16.79	13.62
Unknown	0.00	0.02	0.00	0.13	0.45	0.49	0.88	1.98	1.40	0.00
Total	0.50	1.89	1.51	5.60	6.90	7.46	8.64	32.50	32.50	32.50

Table E.15. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD6A

Start BP	0	(ibp)123.2	140	150	160	170	180	190	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	(ibp)123.2	140	150	160	170	180	190	200			
Simdist %off	0.5	0.6	0.5	0.7	1.2	1.4	1.7	2.2			
n-Paraffins	0.02	0.07	0.00	0.29	0.00	0.54	0.00	0.71	1.64	1.45	2.68
Isoparaffins	0.18	0.07	0.23	0.14	0.52	0.30	0.44	0.29	2.18	2.29	1.96
Olefins	0.05	0.08	0.05	0.12	0.02	0.00	0.00	0.00	0.33	0.44	0.11
Naphthenes	0.15	0.23	0.08	0.11	0.09	0.02	0.26	0.00	0.93	1.18	1.76
Aromatics	0.08	0.10	0.15	0.03	0.43	0.40	0.91	0.85	2.96	2.75	2.29
Unknown	0.02	0.05	0.01	0.00	0.13	0.14	0.11	0.32	0.78	0.71	0.00
Total	0.50	0.59	0.53	0.69	1.19	1.41	1.73	2.17	8.81	8.81	8.81

Table E.16. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD7A

Start BP	0	(ibp)140.4	160	170	180	190	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	(ibp)140.4	160	170	180	190	200			
Simdist %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	4.06
Isoparaffins	0.08	0.46	0.70	0.54	1.06	1.06	3.90	3.97	2.71
Olefins	0.09	0.20	0.05	0.00	0.00	0.00	0.34	0.80	0.10
Naphthenes	0.18	0.25	0.13	0.03	0.51	0.00	1.10	1.73	2.53
Aromatics	0.07	0.22	2.01	6.62	7.34	4.34	20.59	19.41	19.76
Unknown	0.05	0.01	0.06	0.15	0.47	0.51	1.25	0.88	0.00
Total	0.50	1.44	2.95	8.40	9.38	6.49	29.15	29.15	29.15

Table E.17. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD8A

Start BP	0	(ibp)182	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	(ibp)182	200			
Simdist %off	0.50	2.96			
n-Paraffins	0.04	0.02	0.06	0.08	0.13
Isoparaffins	0.27	0.00	0.27	0.31	0.20
Olefins	0.02	0.00	0.02	0.02	0.02
Naphthenes	0.01	0.00	0.01	0.01	0.00
Aromatics	0.14	2.93	3.07	3.01	3.11
Unknown	0.03	0.01	0.03	0.04	0.00
Total	0.50	2.96	3.46	3.46	3.46

Table E.18. Detailed Hydrocarbon Analysis by Boiling Point (degrees C) for FD9A

Start BP	0	(ibp)125.2	140	150	160	170	180	190	Sum of By BP	Totals By C-number	PIONA ≤200
End BP	(ibp)125.2	140	150	160	170	180	190	200			
Simdist %off	0.50	0.85	2.10	1.45	6.60	5.20	4.42	3.30			
n-Paraffins	0.03	0.11	0.00	0.43	0.00	0.63	0.00	0.06	1.26	1.28	2.42
Isoparaffins	0.14	0.08	0.39	0.21	0.65	0.36	0.67	0.41	2.91	2.89	1.93
Olefins	0.03	0.07	0.06	0.15	0.04	0.00	0.00	0.00	0.34	0.38	0.13
Naphthenes	0.19	0.25	0.08	0.25	0.07	0.02	0.31	0.00	1.16	1.21	1.53
Aromatics	0.10	0.31	1.58	0.37	5.76	4.12	3.30	2.47	18.02	18.21	18.41
Unknown	0.01	0.02	0.00	0.04	0.08	0.07	0.14	0.36	0.73	0.45	0.00
Total	0.50	0.85	2.10	1.45	6.60	5.20	4.42	3.30	24.42	24.42	24.42

Table E.19. GC-FIMS Data >200°C for FD1A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	
End Bp		**210**	**220**	**230**	**240**	**250**	**260**	**270**	**280**	**290**	**300**	**310**	**320**	**330**	**340**	**350**	**360**	**370**	**380**	**390**	
HC Type	**Z No**																				**Totals**
Saturates		**7.98**	**6.86**	**2.70**	**2.15**	**1.89**	**2.77**	**2.64**	**2.05**	**2.46**	**1.90**	**2.21**	**1.91**	**1.21**	**1.36**	**0.87**	**0.52**	**0.31**	**0.14**	**0.00**	**41.95**
Iso- + n-Paraffins		**5.26**	**4.66**	**1.27**	**1.21**	**0.82**	**1.77**	**1.78**	**0.91**	**1.67**	**0.93**	**1.60**	**1.24**	**0.52**	**0.81**	**0.41**	**0.11**	**0.03**	**0.00**	**0.00**	**25.00**
isoparaffins	2	5.26	4.05	1.26	1.17	0.82	1.61	1.54	0.77	1.26	0.92	1.19	0.63	0.45	0.22	0.11	0.06	0.00	0.00	0.00	21.32
n-Paraffins	2	0.00	0.61	0.00	0.05	0.00	0.16	0.24	0.14	0.41	0.01	0.41	0.61	0.07	0.59	0.30	0.05	0.03	0.00	0.00	3.68
Cycloparaffins		**2.72**	**2.21**	**1.44**	**0.94**	**1.07**	**1.00**	**0.86**	**1.14**	**0.79**	**0.97**	**0.62**	**0.66**	**0.69**	**0.55**	**0.46**	**0.41**	**0.27**	**0.14**	**0.00**	**16.95**
Monocycloparaffins	0	2.01	1.19	0.61	0.33	0.37	0.35	0.28	0.40	0.28	0.40	0.25	0.28	0.28	0.21	0.17	0.15	0.11	0.06	0.00	7.73
Dicycloparaffins	-2	0.59	0.84	0.66	0.46	0.51	0.44	0.37	0.43	0.28	0.31	0.20	0.20	0.22	0.18	0.17	0.14	0.09	0.04	0.00	6.14
Polycycloparaffins	-4	0.12	0.17	0.17	0.15	0.19	0.20	0.21	0.31	0.22	0.27	0.17	0.18	0.20	0.15	0.12	0.11	0.07	0.04	0.00	3.07
Aromatics		**2.09**	**1.00**	**0.63**	**0.64**	**0.24**	**0.36**	**0.25**	**0.41**	**0.31**	**0.36**	**0.27**	**0.26**	**0.27**	**0.23**	**0.21**	**0.27**	**0.30**	**0.28**	**0.00**	**8.38**
Monoaromatics		**2.08**	**0.99**	**0.62**	**0.32**	**0.22**	**0.26**	**0.21**	**0.30**	**0.23**	**0.27**	**0.19**	**0.18**	**0.17**	**0.13**	**0.11**	**0.11**	**0.11**	**0.09**	**0.00**	**6.60**
Alkylbenzenes	-6	1.33	0.60	0.22	0.08	0.07	0.06	0.04	0.07	0.04	0.05	0.03	0.03	0.03	0.02	0.02	0.02	0.01	0.01	0.00	2.71
Benzocycloalkanes	-8	0.75	0.38	0.38	0.23	0.14	0.18	0.13	0.16	0.10	0.11	0.06	0.06	0.05	0.04	0.04	0.04	0.04	0.03	0.00	2.93
Benzodicycloalkanes	-10	0.00	0.01	0.02	0.01	0.01	0.02	0.03	0.08	0.09	0.11	0.10	0.09	0.09	0.07	0.06	0.06	0.06	0.05	0.00	0.95
Diaromatics		**0.01**	**0.02**	**0.01**	**0.30**	**0.02**	**0.10**	**0.04**	**0.11**	**0.08**	**0.09**	**0.08**	**0.07**	**0.08**	**0.08**	**0.08**	**0.12**	**0.13**	**0.11**	**0.00**	**1.53**
Naphthalenes	-12	0.01	0.02	0.01	0.30	0.01	0.10	0.03	0.09	0.05	0.06	0.05	0.04	0.04	0.04	0.05	0.07	0.07	0.05	0.00	1.07
Biphenyls	-14	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.02	0.03	0.02	0.03	0.02	0.02	0.02	0.03	0.03	0.02	0.00	0.27
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.00	0.12
Fluorenes	-16	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	0.02	0.02	0.00	0.07
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**	**0.00**	**0.01**	**0.00**	**0.01**
Phenanthrenes	-18	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	0.01	0.00	0.01
Phenanthrocyclolalkanes	-20	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	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**	**0.00**	**0.00**	**0.00**	**0.00**
Pyrenes	-22	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	0.00	0.00	0.00
Crysenes	-24	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	0.00	0.00	0.00
Aromatic Sulfur		**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.01**	**0.01**	**0.02**	**0.02**	**0.01**	**0.04**	**0.05**	**0.07**	**0.00**	**0.25**
Benzothiophenes	-10S	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.00	0.15
Dibenzothiophenes	-16S	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	0.00	0.01	0.03	0.04	0.00	0.11
Benzonaphthothiophenes	-22S	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	0.00	0.00	0.00
																					50.33

Table E.20. GC-FIMS Data >200°C for FD2A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	
End Bp		**210**	**220**	**230**	**240**	**250**	**260**	**270**	**280**	**290**	**300**	**310**	**320**	**330**	**340**	**350**	**360**	**370**	**380**	**390**	**400**	
HC Type	**Z No**																					**Totals**
Saturates		**10.46**	**8.22**	**2.11**	**0.36**	**0.38**	**0.36**	**0.48**	**0.41**	**0.54**	**0.56**	**0.41**	**0.29**	**0.25**	**0.25**	**0.64**	**1.42**	**1.94**	**1.45**	**0.59**	**0.00**	**31.14**
Iso- + n-Paraffins		**7.48**	**6.35**	**1.34**	**0.22**	**0.24**	**0.20**	**0.26**	**0.04**	**0.23**	**0.12**	**0.12**	**0.11**	**0.00**	**0.00**	**0.03**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**16.74**
isoparaffins	2	7.48	6.25	1.34	0.22	0.24	0.19	0.26	0.04	0.21	0.12	0.10	0.06	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	16.53
n-Paraffins	2	0.00	0.10	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.02	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.20
Cycloparaffins		**2.98**	**1.87**	**0.76**	**0.14**	**0.14**	**0.17**	**0.22**	**0.37**	**0.32**	**0.44**	**0.29**	**0.19**	**0.25**	**0.25**	**0.61**	**1.42**	**1.94**	**1.45**	**0.59**	**0.00**	**14.40**
Monocycloparaffins	0	2.92	1.75	0.69	0.10	0.10	0.14	0.18	0.33	0.30	0.42	0.27	0.13	0.12	0.05	0.09	0.21	0.43	0.26	0.37	0.00	8.86
Dicycloparaffins	-2	0.05	0.11	0.08	0.04	0.04	0.03	0.03	0.04	0.01	0.02	0.02	0.04	0.05	0.08	0.24	0.60	0.67	0.49	0.00	0.00	2.63
Polycycloparaffins	-4	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.07	0.11	0.28	0.61	0.85	0.70	0.23	0.00	2.92
Aromatics		**3.50**	**1.71**	**0.82**	**0.93**	**0.16**	**0.58**	**0.39**	**0.81**	**0.54**	**0.46**	**0.42**	**0.35**	**0.23**	**0.14**	**0.19**	**0.37**	**0.52**	**0.52**	**0.37**	**0.00**	**13.03**
Monoaromatics		**3.49**	**1.69**	**0.81**	**0.18**	**0.12**	**0.17**	**0.18**	**0.21**	**0.16**	**0.13**	**0.10**	**0.09**	**0.08**	**0.07**	**0.16**	**0.31**	**0.47**	**0.40**	**0.04**	**0.00**	**8.88**
Alkylbenzenes	-6	2.46	1.40	0.27	0.06	0.03	0.02	0.03	0.03	0.02	0.02	0.01	0.02	0.06	0.07	0.14	0.25	0.37	0.33	0.00	0.00	5.60
Benzocycloalkanes	-8	1.03	0.28	0.49	0.12	0.09	0.14	0.13	0.13	0.08	0.07	0.04	0.03	0.01	0.00	0.02	0.06	0.10	0.07	0.04	0.00	2.93
Benzodicycloalkanes	-10	0.00	0.01	0.05	0.01	0.00	0.01	0.02	0.05	0.05	0.04	0.05	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35
Diaromatics		**0.01**	**0.02**	**0.01**	**0.75**	**0.05**	**0.41**	**0.20**	**0.60**	**0.38**	**0.32**	**0.32**	**0.23**	**0.12**	**0.05**	**0.03**	**0.03**	**0.02**	**0.02**	**0.02**	**0.00**	**3.59**
Naphthalenes	-12	0.01	0.02	0.01	0.75	0.04	0.40	0.18	0.56	0.32	0.26	0.24	0.13	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	2.97
Biphenyls	-14	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.04	0.04	0.06	0.05	0.07	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.37
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.03	0.04	0.02	0.01	0.02	0.01	0.01	0.01	0.00	0.20
Fluorenes	-16	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	0.00	0.01	0.01	0.00	0.01	0.00	0.06
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**	**0.00**	**0.01**	**0.00**	**0.00**	**0.01**
Phenanthrenes	-18	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	0.00	0.00	0.00	0.01
Phenanthrocyclolalkanes	-20	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	0.01	0.00	0.00	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**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Pyrenes	-22	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	0.00	0.00	0.00	0.00
Crysenes	-24	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	0.00	0.00	0.00	0.00
Aromatic Sulfur		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.03**	**0.02**	**0.02**	**0.01**	**0.03**	**0.04**	**0.09**	**0.30**	**0.00**	**0.54**
Benzothiophenes	-10S	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	0.00	0.03	0.03	0.09	0.29	0.00	0.47
Dibenzothiophenes	-16S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.07
Benzonaphthothiophenes	-22S	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	0.00	0.00	0.00	0.00
																						44.17

Table E.21. GC-FIMS Data >200°C for FD3A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	
End Bp		210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	
HC Type	Z No																Totals
Saturates		**3.78**	**5.41**	**3.83**	**3.74**	**3.31**	**3.35**	**2.68**	**1.42**	**2.15**	**0.50**	**1.09**	**0.82**	**0.00**	**0.00**	**0.00**	**32.08**
Iso- + n-Paraffins		**1.06**	**3.08**	**1.78**	**1.64**	**2.10**	**2.28**	**1.52**	**0.65**	**1.79**	**0.35**	**1.03**	**0.72**	**0.00**	**0.00**	**0.00**	**18.01**
isoparaffins	2	1.06	1.92	1.78	0.33	2.10	1.11	0.47	0.52	0.85	0.00	0.00	0.00	0.00	0.00	0.00	10.14
n-Paraffins	2	0.00	1.16	0.00	1.31	0.00	1.17	1.06	0.13	0.94	0.35	1.03	0.72	0.00	0.00	0.00	7.87
Cycloparaffins		**2.73**	**2.33**	**2.05**	**2.10**	**1.21**	**1.06**	**1.16**	**0.77**	**0.35**	**0.15**	**0.07**	**0.10**	**0.00**	**0.00**	**0.00**	**14.07**
Monocycloparaffins	0	1.44	1.19	1.23	1.09	0.68	0.45	0.57	0.43	0.12	0.12	0.07	0.00	0.00	0.00	0.00	7.39
Dicycloparaffins	-2	1.25	1.11	0.79	0.93	0.43	0.51	0.42	0.20	0.18	0.00	0.00	0.10	0.00	0.00	0.00	5.92
Polycycloparaffins	-4	0.04	0.03	0.04	0.08	0.10	0.10	0.16	0.15	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.76
Aromatics		**3.07**	**1.25**	**1.27**	**2.59**	**1.06**	**2.07**	**1.31**	**2.21**	**1.23**	**1.79**	**1.03**	**0.67**	**0.61**	**0.26**	**0.00**	**20.42**
Monoaromatics		**3.07**	**1.19**	**1.27**	**1.99**	**1.03**	**1.57**	**1.14**	**1.54**	**0.89**	**1.16**	**0.55**	**0.32**	**0.23**	**0.00**	**0.00**	**15.95**
Alkylbenzenes	-6	2.46	0.86	0.79	0.76	0.47	0.54	0.43	0.54	0.29	0.35	0.13	0.11	0.11	0.00	0.00	7.82
Benzocycloalkanes	-8	0.61	0.33	0.48	1.22	0.54	0.99	0.66	0.87	0.45	0.58	0.28	0.11	0.09	0.00	0.00	7.21
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.01	0.02	0.04	0.06	0.14	0.15	0.23	0.14	0.10	0.04	0.00	0.00	0.92
Diaromatics		**0.00**	**0.07**	**0.00**	**0.59**	**0.03**	**0.49**	**0.17**	**0.67**	**0.34**	**0.63**	**0.48**	**0.33**	**0.37**	**0.26**	**0.00**	**4.44**
Naphthalenes	-12	0.00	0.07	0.00	0.59	0.01	0.46	0.14	0.52	0.24	0.42	0.29	0.12	0.07	0.02	0.00	2.96
Biphenyls	-14	0.00	0.00	0.00	0.00	0.02	0.03	0.04	0.13	0.07	0.19	0.10	0.12	0.12	0.03	0.00	0.86
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.02	0.07	0.08	0.16	0.20	0.00	0.57
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.01	0.00	0.06
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	-18	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
Phenanthrocyclolalkanes	-20	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	-22	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
Crysenes	-24	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**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.01**	**0.00**	**0.00**	**0.03**
Benzothiophenes	-10S	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Dibenzothiophenes	-16S	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	0.00	0.00	0.02
Benzonaphthothiophenes	-22S	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
																	52.50

Table E.22. GC-FIMS Data >200°C for FD4A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	
End Bp		**210**	**220**	**230**	**240**	**250**	**260**	**270**	**280**	**290**	**300**	**310**	**320**	**330**	**340**	**350**	**360**	**370**	**380**	**390**	**400**	
HC Type	**Z No**																					**Totals**
Saturates		**0.94**	**2.60**	**6.71**	**4.34**	**4.77**	**2.91**	**2.63**	**2.21**	**2.15**	**2.39**	**1.50**	**0.93**	**0.73**	**0.70**	**0.85**	**1.10**	**1.50**	**1.29**	**0.23**	**0.00**	**40.48**
Iso- + n-Paraffins		**0.85**	**2.33**	**5.35**	**2.76**	**1.94**	**1.13**	**0.99**	**0.92**	**0.59**	**0.84**	**0.28**	**0.04**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**18.02**
isoparaffins	2	0.85	2.33	5.35	2.76	1.94	1.13	0.98	0.92	0.58	0.84	0.28	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18.00
n-Paraffins	2	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Cycloparaffins		**0.09**	**0.26**	**1.36**	**1.58**	**2.83**	**1.78**	**1.63**	**1.29**	**1.57**	**1.55**	**1.21**	**0.90**	**0.73**	**0.70**	**0.85**	**1.10**	**1.50**	**1.29**	**0.23**	**0.00**	**22.45**
Monocycloparaffins	0	0.08	0.26	1.35	1.53	2.64	1.55	1.22	0.85	0.99	0.93	0.64	0.36	0.17	0.09	0.03	0.02	0.05	0.12	0.11	0.00	12.98
Dicycloparaffins	-2	0.00	0.00	0.01	0.05	0.19	0.18	0.32	0.25	0.30	0.32	0.33	0.28	0.23	0.21	0.30	0.32	0.48	0.23	0.00	0.00	4.00
Polycycloparaffins	-4	0.01	0.01	0.00	0.00	0.00	0.04	0.10	0.20	0.28	0.29	0.24	0.26	0.33	0.40	0.53	0.76	0.97	0.95	0.12	0.00	5.48
Aromatics		**4.26**	**2.37**	**2.03**	**2.81**	**0.59**	**1.09**	**0.61**	**0.70**	**0.48**	**0.37**	**0.40**	**0.42**	**0.40**	**0.43**	**0.53**	**0.93**	**1.14**	**0.40**	**0.31**	**0.00**	**20.26**
Monoaromatics		**4.26**	**2.37**	**2.02**	**1.07**	**0.39**	**0.16**	**0.07**	**0.04**	**0.01**	**0.06**	**0.09**	**0.25**	**0.33**	**0.37**	**0.50**	**0.89**	**1.09**	**0.34**	**0.09**	**0.00**	**14.42**
Alkylbenzenes	-6	3.41	2.20	0.95	0.84	0.23	0.04	0.03	0.01	0.01	0.05	0.08	0.25	0.32	0.36	0.47	0.82	1.02	0.30	0.00	0.00	11.37
Benzocycloalkanes	-8	0.84	0.17	0.99	0.21	0.15	0.12	0.04	0.04	0.01	0.01	0.01	0.00	0.01	0.01	0.03	0.07	0.07	0.04	0.09	0.00	2.92
Benzodicycloalkanes	-10	0.00	0.00	0.09	0.02	0.01	0.01	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	0.13
Diaromatics		**0.00**	**0.00**	**0.00**	**1.73**	**0.20**	**0.92**	**0.54**	**0.66**	**0.47**	**0.31**	**0.31**	**0.13**	**0.05**	**0.04**	**0.02**	**0.02**	**0.02**	**0.02**	**0.03**	**0.00**	**5.47**
Naphthalenes	-12	0.00	0.00	0.00	1.73	0.18	0.91	0.49	0.60	0.37	0.23	0.20	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.77
Biphenyls	-14	0.00	0.00	0.00	0.00	0.02	0.02	0.04	0.05	0.06	0.07	0.06	0.04	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.39
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.01	0.03	0.03	0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.19
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.00	0.12
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**	**0.00**	**0.00**	**0.01**	**0.00**	**0.01**
Phenanthrenes	-18	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	0.00	0.01	0.00	0.01
Phenanthrocyclolalkanes	-20	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	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**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Pyrenes	-22	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	0.00	0.00	0.00	0.00
Crysenes	-24	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	0.00	0.00	0.00	0.00
Aromatic Sulfur		**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.03**	**0.02**	**0.02**	**0.01**	**0.02**	**0.03**	**0.04**	**0.19**	**0.00**	**0.37**
Benzothiophenes	-10S	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.03	0.04	0.19	0.00	0.30
Dibenzothiophenes	-16S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.07
Benzonaphthothiophenes	-22S	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	0.00	0.00	0.00	0.00
																						60.74

Table E.23. GC-FIMS Data >200°C for FD5A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	
End Bp		210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	
HC Type	Z No																Totals
Saturates		**5.65**	**7.18**	**4.43**	**3.99**	**2.54**	**14.27**	**2.80**	**6.78**	**2.59**	**2.26**	**1.50**	**0.88**	**0.86**	**0.76**	**0.00**	**56.50**
Iso- + n-Paraffins		**2.13**	**4.03**	**1.98**	**2.35**	**1.65**	**13.58**	**2.48**	**5.72**	**1.07**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**34.99**
isoparaffins	2	2.13	1.74	1.98	0.19	1.65	0.22	0.52	0.74	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.16
n-Paraffins	2	0.00	2.30	0.00	2.16	0.00	13.36	1.95	4.98	1.07	0.00	0.00	0.00	0.00	0.00	0.00	25.82
Cycloparaffins		**3.52**	**3.15**	**2.45**	**1.65**	**0.90**	**0.68**	**0.32**	**1.06**	**1.52**	**2.26**	**1.50**	**0.88**	**0.86**	**0.76**	**0.00**	**21.51**
Monocycloparaffins	0	2.25	2.20	1.82	1.14	0.58	0.44	0.10	0.14	0.08	0.08	0.14	0.00	0.13	0.00	0.00	9.10
Dicycloparaffins	-2	1.25	0.94	0.62	0.48	0.31	0.16	0.13	0.36	0.49	0.93	0.42	0.20	0.18	0.12	0.00	6.57
Polycycloparaffins	-4	0.03	0.01	0.01	0.02	0.01	0.09	0.09	0.56	0.94	1.25	0.93	0.68	0.56	0.64	0.00	5.84
Aromatics		**2.72**	**1.51**	**1.55**	**2.01**	**1.08**	**0.92**	**0.19**	**0.10**	**0.02**	**0.07**	**0.25**	**0.28**	**0.25**	**0.07**	**0.00**	**11.00**
Monoaromatics		**2.72**	**1.46**	**1.55**	**1.52**	**1.06**	**0.68**	**0.15**	**0.06**	**0.00**	**0.07**	**0.25**	**0.28**	**0.25**	**0.07**	**0.00**	**10.11**
Alkylbenzenes	-6	2.17	0.96	0.95	0.64	0.54	0.26	0.07	0.02	0.00	0.07	0.25	0.28	0.25	0.07	0.00	6.52
Benzocycloalkanes	-8	0.55	0.50	0.59	0.88	0.49	0.41	0.07	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.54
Benzodicycloalkanes	-10	0.00	0.00	0.01	0.01	0.03	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
Diaromatics		**0.00**	**0.05**	**0.00**	**0.49**	**0.03**	**0.24**	**0.04**	**0.04**	**0.02**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.90**
Naphthalenes	-12	0.00	0.05	0.00	0.49	0.01	0.22	0.04	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.86
Biphenyls	-14	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Naphthocycloalkanes	-14	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
Fluorenes	-16	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**	**0.00**	**0.00**	**0.00**	**0.00**
Phenanthrenes	-18	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
Phenanthrocyclolalkanes	-20	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	-22	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
Crysenes	-24	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**	**0.00**	**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**
Benzothiophenes	-10S	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
Dibenzothiophenes	-16S	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
Benzonaphthothiophenes	-22S	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
																	67.50

Table E.24. GC-FIMS Data >200°C for FD6A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	
End Bp		210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	410	
HC Type	Z No																						Totals
Saturates		**1.92**	**3.43**	**3.20**	**3.94**	**5.66**	**6.35**	**7.74**	**7.71**	**7.01**	**6.19**	**5.46**	**3.46**	**2.54**	**2.30**	**2.06**	**2.17**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**71.15**
Iso- + n-Paraffins		**0.17**	**1.89**	**1.58**	**1.82**	**4.27**	**4.07**	**5.89**	**5.30**	**2.62**	**1.86**	**1.90**	**0.40**	**0.16**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**31.93**
isoparaffins	2	0.17	1.19	1.58	0.66	4.27	2.60	4.84	4.98	1.30	1.81	0.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	24.18
n-Paraffins	2	0.00	0.71	0.00	1.16	0.00	1.47	1.05	0.31	1.32	0.05	1.13	0.40	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.75
Cycloparaffins		**1.74**	**1.54**	**1.62**	**2.13**	**1.39**	**2.28**	**1.85**	**2.41**	**4.39**	**4.33**	**3.56**	**3.06**	**2.38**	**2.30**	**2.06**	**2.17**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**39.22**
Monocycloparaffins	0	0.72	0.71	0.93	1.10	0.77	0.98	0.75	0.63	1.04	0.96	0.40	0.45	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.63
Dicycloparaffins	-2	1.02	0.81	0.68	0.94	0.47	0.84	0.62	0.87	1.60	1.55	1.49	1.08	0.66	0.46	0.40	0.33	0.00	0.00	0.00	0.00	0.00	13.83
Polycycloparaffins	-4	0.01	0.02	0.02	0.09	0.15	0.46	0.48	0.91	1.75	1.82	1.67	1.53	1.55	1.84	1.66	1.84	0.00	0.00	0.00	0.00	0.00	15.77
Aromatics		**0.57**	**0.43**	**0.67**	**1.86**	**0.76**	**2.14**	**0.99**	**1.30**	**1.66**	**1.36**	**1.58**	**1.16**	**0.63**	**0.48**	**0.65**	**1.05**	**2.73**	**0.00**	**0.00**	**0.00**	**0.00**	**20.04**
MonoAromatics		**0.57**	**0.43**	**0.67**	**1.64**	**0.73**	**1.58**	**0.83**	**0.83**	**1.11**	**0.86**	**0.89**	**0.73**	**0.36**	**0.35**	**0.61**	**1.04**	**2.41**	**0.00**	**0.00**	**0.00**	**0.00**	**15.64**
Alkylbenzenes	-6	0.31	0.16	0.21	0.24	0.16	0.27	0.17	0.17	0.20	0.22	0.23	0.30	0.26	0.33	0.51	1.00	2.41	0.00	0.00	0.00	0.00	7.16
Benzocycloalkanes	-8	0.26	0.27	0.46	1.38	0.55	1.24	0.59	0.53	0.63	0.41	0.33	0.23	0.06	0.02	0.10	0.04	0.00	0.00	0.00	0.00	0.00	7.11
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.01	0.02	0.06	0.07	0.13	0.28	0.24	0.33	0.19	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.37
Diaromatics		**0.00**	**0.00**	**0.00**	**0.22**	**0.03**	**0.56**	**0.16**	**0.47**	**0.55**	**0.49**	**0.69**	**0.41**	**0.27**	**0.12**	**0.04**	**0.01**	**0.32**	**0.00**	**0.00**	**0.00**	**0.00**	**4.34**
Naphthalenes	-12	0.00	0.00	0.00	0.22	0.00	0.50	0.11	0.35	0.34	0.28	0.34	0.15	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.34
Biphenyls	-14	0.00	0.00	0.00	0.00	0.02	0.05	0.05	0.12	0.16	0.20	0.21	0.19	0.11	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.16
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.01	0.08	0.06	0.06	0.07	0.03	0.01	0.32	0.00	0.00	0.00	0.00	0.67
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.06	0.01	0.05	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.17
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**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Phenanthrenes	-18	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	0.00	0.00	0.00	0.00	0.00
Phenanthrocyclolalkanes	-20	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	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**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Pyrenes	-22	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	0.00	0.00	0.00	0.00	0.00
Crysenes	-24	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	0.00	0.00	0.00	0.00	0.00
Aromatic Sulfur		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.02**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.05**
Benzothiophenes	-10S	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
Dibenzothiophenes	-16S	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	0.00	0.00	0.00	0.00	0.00
Benzonaphthothiophenes	-22S	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	0.00	0.00	0.00	0.00	0.00
																							91.19

Table E.25. GC-FIMS Data >200°C for FD7A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	
End Bp		**210**	**220**	**230**	**240**	**250**	**260**	**270**	**280**	**290**	**300**	**310**	**320**	**330**	**340**	**350**	**360**	**370**	**380**	**390**	**Totals**
HC Type	**Z No**																				
Saturates		**2.51**	**4.06**	**2.23**	**2.60**	**1.47**	**19.93**	**4.17**	**5.93**	**1.71**	**0.44**	**0.08**	**0.49**	**0.00**	**0.32**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**45.93**
Iso + n-Paraffins		**0.68**	**2.25**	**0.81**	**1.53**	**0.56**	**19.25**	**3.81**	**5.78**	**1.65**	**0.05**	**0.07**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**36.43**
isoparaffins	2	0.68	0.98	0.81	0.35	0.56	0.10	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.71
n-Paraffins	2	0.00	1.27	0.00	1.18	0.00	19.15	3.81	5.78	1.42	0.05	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	32.73
Cycloparaffins		**1.83**	**1.81**	**1.42**	**1.07**	**0.91**	**0.68**	**0.36**	**0.15**	**0.06**	**0.38**	**0.01**	**0.49**	**0.00**	**0.32**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**9.49**
Monocycloparaffins	0	1.04	1.12	0.92	0.67	0.61	0.38	0.13	0.06	0.00	0.00	0.00	0.46	0.00	0.32	0.00	0.00	0.00	0.00	0.00	5.72
Dicycloparaffins	-2	0.73	0.65	0.47	0.37	0.27	0.11	0.16	0.05	0.02	0.29	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.14
Polycycloparaffins	-4	0.06	0.05	0.03	0.03	0.03	0.18	0.07	0.04	0.05	0.09	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.63
Aromatics		**2.57**	**1.37**	**1.22**	**1.95**	**1.31**	**3.87**	**1.32**	**2.37**	**0.63**	**3.29**	**1.80**	**0.87**	**1.08**	**0.42**	**0.48**	**0.33**	**0.00**	**0.00**	**0.00**	**24.87**
MonoAromatics		**2.57**	**1.25**	**1.22**	**1.22**	**1.27**	**3.40**	**0.83**	**0.43**	**0.26**	**0.22**	**0.15**	**0.07**	**0.05**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**12.95**
Alkylbenzenes	-6	2.08	0.98	0.80	0.47	0.59	2.86	0.20	0.03	0.03	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	8.05
Benzocycloalkanes	-8	0.50	0.27	0.41	0.72	0.59	0.51	0.54	0.23	0.14	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.98
Benzodicycloalkanes	-10	0.00	0.00	0.01	0.03	0.08	0.04	0.09	0.17	0.10	0.14	0.14	0.07	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.93
Diaromatics		**0.00**	**0.12**	**0.00**	**0.72**	**0.04**	**0.47**	**0.49**	**1.93**	**0.36**	**3.08**	**1.66**	**0.80**	**1.03**	**0.41**	**0.48**	**0.33**	**0.00**	**0.00**	**0.00**	**11.91**
Naphthalenes	-12	0.00	0.12	0.00	0.72	0.03	0.41	0.19	0.50	0.25	0.47	0.69	0.38	0.60	0.31	0.44	0.29	0.00	0.00	0.00	5.40
Biphenyls	-14	0.00	0.00	0.00	0.00	0.01	0.06	0.30	1.42	0.07	2.59	0.90	0.39	0.41	0.07	0.03	0.00	0.00	0.00	0.00	6.25
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.01	0.04	0.03	0.01	0.02	0.01	0.03	0.00	0.00	0.00	0.20
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.07
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**	**0.00**	**0.00**	**0.00**	**0.00**
Phenanthrenes	-18	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	0.00	0.00	0.00
Phenanthrocyclolalkanes	-20	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	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**	**0.00**	**0.00**	**0.00**	**0.00**
Pyrenes	-22	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	0.00	0.00	0.00
Crysenes	-24	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	0.00	0.00	0.00
Aromatic Sulfur		**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**	**0.00**	**0.00**	**0.01**
Benzothiophenes	-10S	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	0.00	0.00	0.01
Dibenzothiophenes	-16S	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	0.00	0.00	0.00
Benzonaphthothiophenes	-22S	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	0.00	0.00	0.00
																					70.80

Table E.26. GC-FIMS Data >200°C for FD8A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	
End Bp		210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	410	
HC Type	Z No																						Totals
Saturates		**0.00**	**0.33**	**0.42**	**0.86**	**0.39**	**17.58**	**9.70**	**6.44**	**3.26**	**3.98**	**1.33**	**2.64**	**0.83**	**3.06**	**0.95**	**1.73**	**1.14**	**0.00**	**0.00**	**0.00**	**0.00**	**54.67**
Iso + n-Paraffins		**0.00**	**0.26**	**0.27**	**0.41**	**0.19**	**16.65**	**7.21**	**4.90**	**1.34**	**0.85**	**0.28**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	32.35
Isoparaffins	2	0.00	0.19	0.27	0.12	0.19	0.29	2.82	0.50	0.32	0.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.47
n-Paraffins	2	0.00	0.07	0.00	0.30	0.00	16.36	4.39	4.40	1.02	0.08	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	26.89
Cycloparaffins		**0.00**	**0.07**	**0.15**	**0.45**	**0.20**	**0.94**	**2.49**	**1.54**	**1.91**	**3.14**	**1.05**	**2.64**	**0.83**	**3.06**	**0.95**	**1.73**	**1.14**	**0.00**	**0.00**	**0.00**	**0.00**	**22.32**
Monocycloparaffins	0	0.00	0.06	0.14	0.44	0.19	0.43	1.24	1.06	0.44	0.33	0.36	2.03	0.10	2.55	0.19	0.16	0.00	0.00	0.00	0.00	0.00	9.73
Dicycloparaffins	-2	0.00	0.00	0.00	0.01	0.01	0.07	0.58	0.18	0.54	1.32	0.27	0.19	0.20	0.14	0.21	0.33	0.00	0.00	0.00	0.00	0.00	4.04
Polycycloparaffins	-4	0.00	0.01	0.01	0.00	0.00	0.43	0.67	0.30	0.94	1.49	0.42	0.42	0.52	0.37	0.55	1.25	1.14	0.00	0.00	0.00	0.00	8.54
Aromatics		**0.00**	**0.44**	**0.76**	**0.81**	**0.39**	**6.53**	**3.33**	**4.41**	**1.20**	**7.70**	**4.14**	**2.69**	**3.06**	**1.00**	**2.39**	**1.76**	**0.34**	**0.32**	**0.55**	**0.02**	**0.00**	**41.83**
Monoaromatics		**0.00**	**0.43**	**0.76**	**0.76**	**0.39**	**6.26**	**2.18**	**0.60**	**0.57**	**0.56**	**0.41**	**0.48**	**0.35**	**0.18**	**0.31**	**0.82**	**0.11**	**0.00**	**0.00**	**0.00**	**0.00**	**15.14**
Alkylbenzenes	-6	0.00	0.42	0.58	0.19	0.18	5.78	0.24	0.01	0.07	0.03	0.04	0.10	0.09	0.09	0.21	0.80	0.00	0.00	0.00	0.00	0.00	8.83
Benzocycloalkanes	-8	0.00	0.01	0.17	0.52	0.15	0.40	1.55	0.25	0.20	0.16	0.02	0.01	0.00	0.00	0.03	0.02	0.11	0.00	0.00	0.00	0.00	3.61
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.05	0.06	0.08	0.39	0.34	0.30	0.37	0.34	0.37	0.25	0.09	0.06	0.00	0.00	0.00	0.00	0.00	0.00	2.71
Diaromatics		**0.00**	**0.00**	**0.00**	**0.05**	**0.00**	**0.27**	**1.16**	**3.80**	**0.63**	**7.14**	**3.74**	**2.20**	**2.71**	**0.82**	**2.08**	**0.95**	**0.19**	**0.27**	**0.55**	**0.00**	**0.00**	**26.56**
Naphthalenes	-12	0.00	0.00	0.00	0.05	0.00	0.15	0.19	0.85	0.41	1.12	1.65	1.11	1.65	0.75	1.86	0.77	0.00	0.00	0.00	0.00	0.00	10.57
Biphenyls	-14	0.00	0.00	0.00	0.00	0.00	0.12	0.97	2.96	0.20	6.02	2.06	1.07	1.04	0.05	0.20	0.10	0.00	0.00	0.00	0.00	0.00	14.78
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.02	0.02	0.00	0.02	0.00	0.04	0.03	0.00	0.34	0.00	0.00	0.49
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.00	0.01	0.03	0.16	0.27	0.21	0.00	0.00	0.72
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**	**0.04**	**0.05**	**0.00**	**0.02**	**0.00**	**0.11**
Phenanthrenes	-18	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	0.04	0.05	0.00	0.02	0.00	0.11
Phenanthrocyclolalkanes	-20	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	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**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Pyrenes	-22	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	0.00	0.00	0.00	0.00	0.00
Crysenes	-24	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	0.00	0.00	0.00	0.00	0.00
Aromatic Sulfur		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.02**
Benzothiophenes	-10S	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Dibenzothiophenes	-16S	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	0.00	0.00	0.00	0.00	0.00
Benzonaphthothiophenes	-22S	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	0.00	0.00	0.00	0.00	0.00
																							96.50

Table E.27. GC-FIMS Data >200°C for FD9A by Boiling Point

Start BP		200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	
End Bp		210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	
HC Type	Z No																					Totals
Saturates		**1.86**	**3.18**	**2.79**	**4.03**	**4.26**	**4.89**	**5.72**	**6.50**	**5.71**	**5.31**	**5.09**	**3.58**	**2.00**	**1.88**	**1.44**	**1.06**	**0.00**	**0.00**	**0.00**	**0.00**	**59.30**
Iso + n-Paraffins		**0.34**	**1.21**	**0.97**	**1.77**	**2.02**	**2.61**	**3.60**	**2.44**	**1.95**	**2.69**	**1.20**	**0.74**	**0.43**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**21.98**
isoparaffins	2	0.34	0.53	0.97	0.90	2.02	1.08	2.52	2.18	0.91	2.61	0.24	0.26	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	14.74
n-Paraffins	2	0.00	0.67	0.00	0.87	0.00	1.54	1.07	0.26	1.05	0.09	0.97	0.48	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.24
Cycloparaffins		**1.52**	**1.98**	**1.83**	**2.27**	**2.24**	**2.27**	**2.12**	**4.05**	**3.76**	**2.62**	**3.89**	**2.84**	**1.56**	**1.88**	**1.44**	**1.06**	**0.00**	**0.00**	**0.00**	**0.00**	**37.33**
Monocycloparaffins	0	0.69	1.15	1.26	1.56	1.61	1.10	1.18	2.63	1.28	0.77	2.20	1.55	0.18	0.03	0.00	0.39	0.00	0.00	0.00	0.00	17.58
Dicycloparaffins	-2	0.80	0.82	0.55	0.62	0.46	0.72	0.54	0.77	1.20	0.88	0.86	0.54	0.43	0.44	0.31	0.22	0.00	0.00	0.00	0.00	10.15
Polycycloparaffins	-4	0.03	0.01	0.02	0.09	0.17	0.45	0.40	0.66	1.28	0.96	0.83	0.74	0.95	1.41	1.13	0.45	0.00	0.00	0.00	0.00	9.59
Aromatics		**1.25**	**0.65**	**0.60**	**1.40**	**0.80**	**2.15**	**0.96**	**1.09**	**1.62**	**0.93**	**0.99**	**1.04**	**0.76**	**0.59**	**0.49**	**0.98**	**0.00**	**0.00**	**0.00**	**0.00**	**16.30**
MonoAromatics		**1.25**	**0.59**	**0.60**	**1.09**	**0.77**	**1.50**	**0.78**	**0.70**	**0.92**	**0.54**	**0.55**	**0.55**	**0.35**	**0.31**	**0.33**	**0.94**	**0.00**	**0.00**	**0.00**	**0.00**	**11.78**
Alkylbenzenes	-6	0.85	0.32	0.27	0.28	0.25	0.34	0.23	0.19	0.22	0.17	0.18	0.27	0.26	0.27	0.32	0.94	0.00	0.00	0.00	0.00	5.37
Benzocycloalkanes	-8	0.40	0.26	0.33	0.79	0.49	1.08	0.48	0.40	0.46	0.21	0.18	0.13	0.05	0.03	0.02	0.00	0.00	0.00	0.00	0.00	5.31
Benzodicycloalkanes	-10	0.00	0.00	0.00	0.01	0.03	0.08	0.08	0.12	0.24	0.15	0.19	0.14	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.00	1.09
Diaromatics		**0.00**	**0.06**	**0.00**	**0.31**	**0.03**	**0.65**	**0.17**	**0.38**	**0.70**	**0.39**	**0.44**	**0.47**	**0.41**	**0.26**	**0.15**	**0.04**	**0.00**	**0.00**	**0.00**	**0.00**	**4.45**
Naphthalenes	-12	0.00	0.06	0.00	0.31	0.01	0.49	0.10	0.28	0.32	0.22	0.21	0.20	0.18	0.07	0.08	0.00	0.00	0.00	0.00	0.00	2.53
Biphenyls	-14	0.00	0.00	0.00	0.00	0.03	0.15	0.06	0.09	0.32	0.16	0.11	0.19	0.10	0.04	0.01	0.00	0.00	0.00	0.00	0.00	1.26
Naphthocycloalkanes	-14	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.05	0.01	0.08	0.07	0.08	0.13	0.05	0.03	0.00	0.00	0.00	0.00	0.53
Fluorenes	-16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.01	0.04	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.14
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**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Phenanthrenes	-18	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	0.00	0.00	0.00	0.00
Phenanthrocyclolalkanes	-20	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	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**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Pyrenes	-22	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	0.00	0.00	0.00	0.00
Crysenes	-24	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	0.00	0.00	0.00	0.00
Aromatic Sulfur		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.03**	**0.01**	**0.02**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.07**
Benzothiophenes	-10S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.06
Dibenzothiophenes	-16S	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	0.00	0.00	0.00	0.01
Benzonaphthothiophenes	-22S	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	0.00	0.00	0.00	0.00
																						75.60

APPENDIX F. CHEMICAL SHIFTS OF STRUCTURES IN THE DIESEL MOLECULAR WEIGHT RANGE

APPENDIX F. CHEMICAL SHIFTS OF STRUCTURES IN THE DIESEL MOLECULAR WEIGHT RANGE

The model systems below include predicted or, when available, experimental chemical shifts of structures in the diesel molecular weight range.

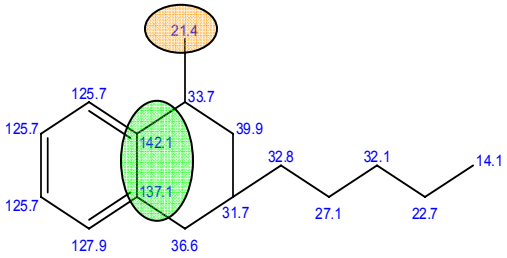

Figure F.1. Naphthenic-aromatic bridgehead carbon at 137–142 ppm and naphthenic methyl at 21 ppm.

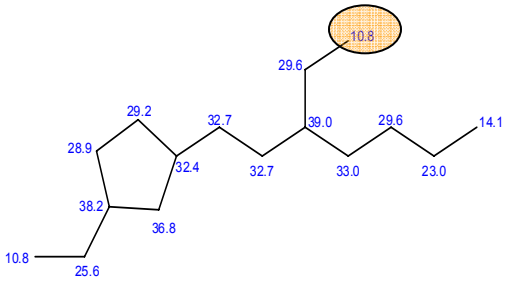

Figure F.2. Overlap of naphthenic transitions with n-alkanes, with methyl of pendant ethyl at 10.8 ppm.

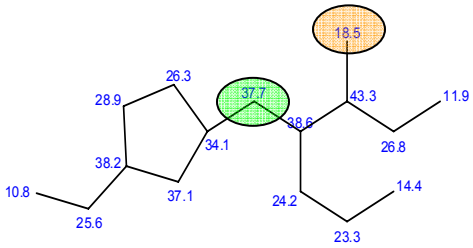

Figure F.3. Cyclopentyl carbons at 26–38 ppm and pendant methyl at 18.5 ppm.

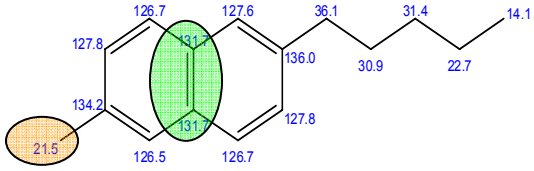

Figure F.4. Aromatic methyl at 21.5 ppm, naphthalene bridge carbon at 132 ppm.

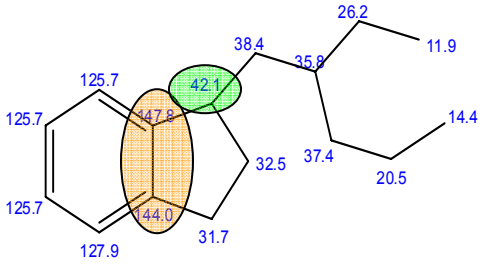

Figure F.5. Indan bridge carbons at 144 and 148 ppm and methine naphthenic carbon at 42 ppm.

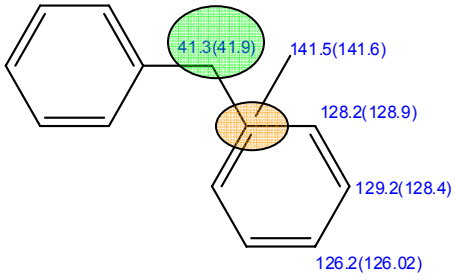

Figure F.6. Diaryl methane (6) shows CH_2 at 41.9 ppm and alkyl substituted aromatic carbon at 141.6 ppm.

APPENDIX G. STRUCTURAL REPRESENTATIONS BASED ON NUCLEAR MAGNETIC RESONANCE DATA

APPENDIX G. STRUCTURAL REPRESENTATIONS BASED ON NUCLEAR MAGNETIC RESONANCE DATA

The following molecular representations of carbon types were quantified using nuclear magnetic resonance data from Table 11.3 (Section 11, main body of report).

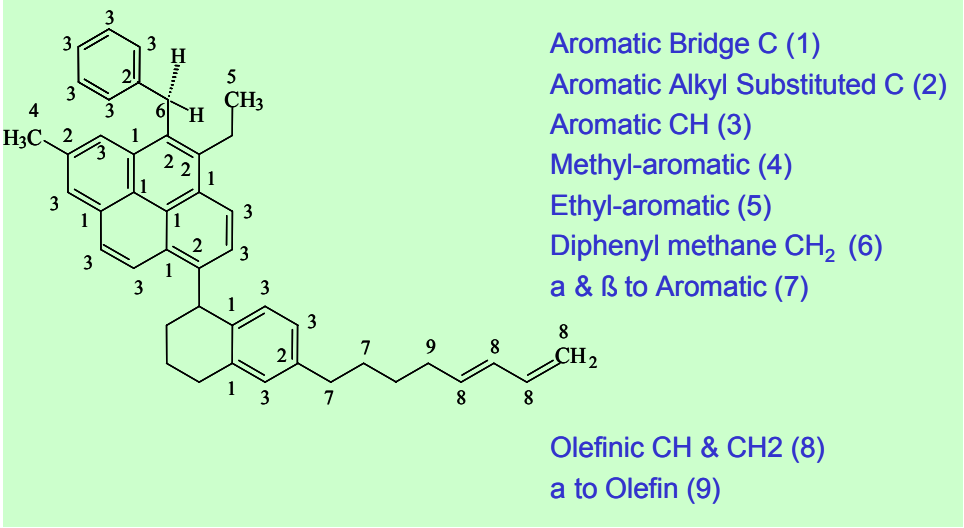

Figure G.1. A structure containing aromatic and olefinic carbon types.

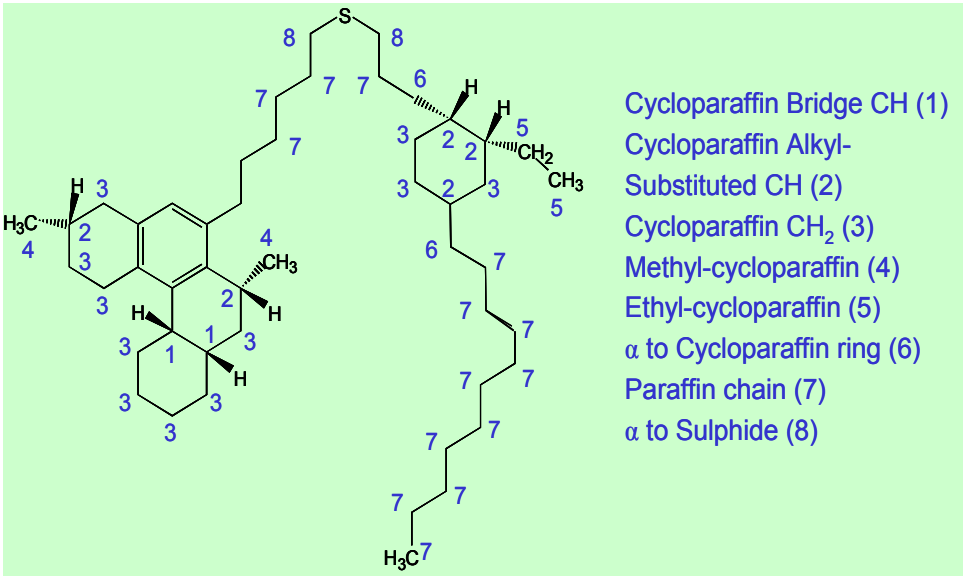

Figure G.2. A structure containing paraffinic and cycloparaffinic carbon types.

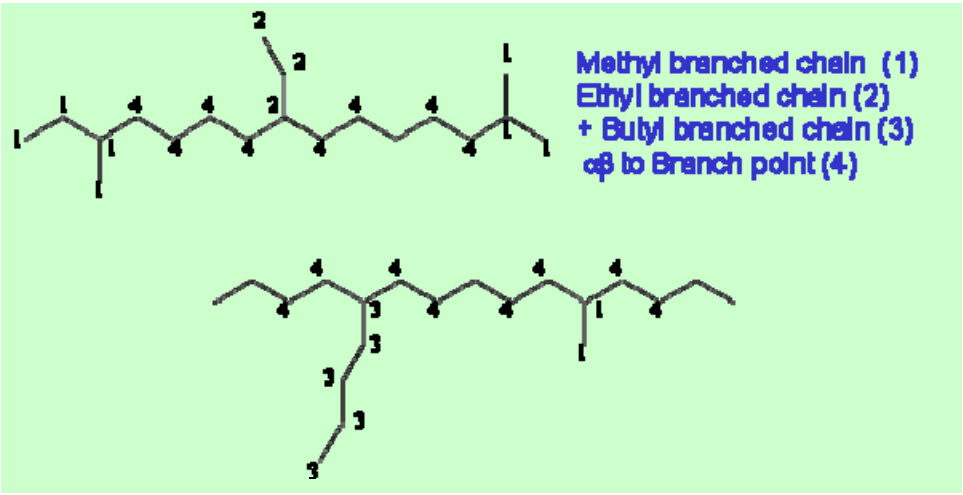

Figure G.3. Structures containing branched paraffinic carbon types.

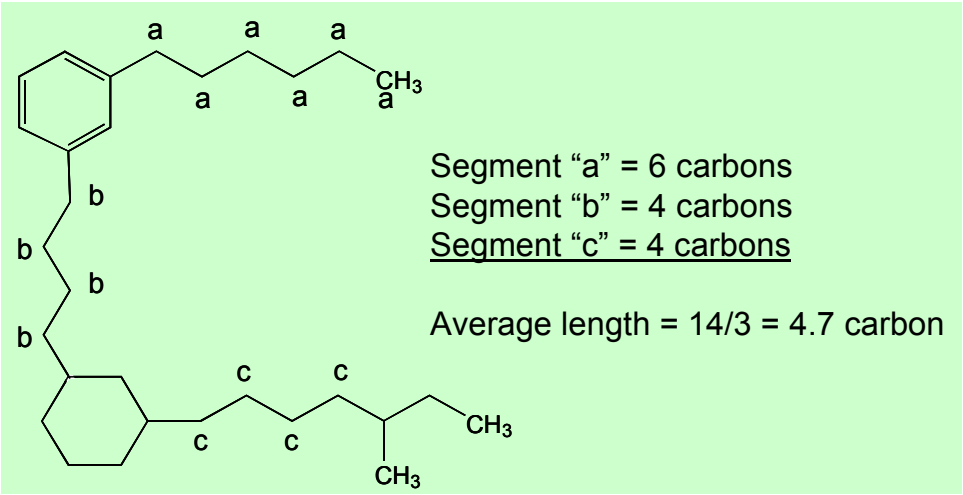

Figure G.4. Calculation of the average “chain segment length.”

APPENDIX H. LINEAR PARAFFIN AND TERMINAL AND PENDANT ALKYL STRUCTURES

APPENDIX H. LINEAR PARAFFIN AND TERMINAL AND PENDANT ALKYL STRUCTURES
(corresponding to Table 11.6 in the main body of the report)

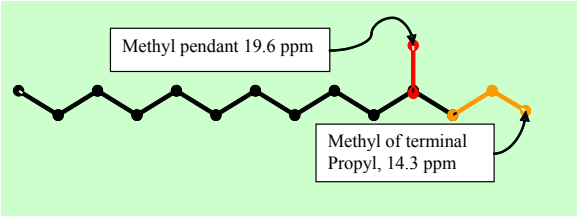

Figure H.1. Methyl branch and methyl on terminal propyl.

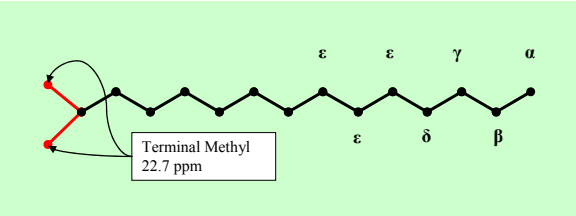

Figure H.2. Dual terminal methyl and methylene positions.

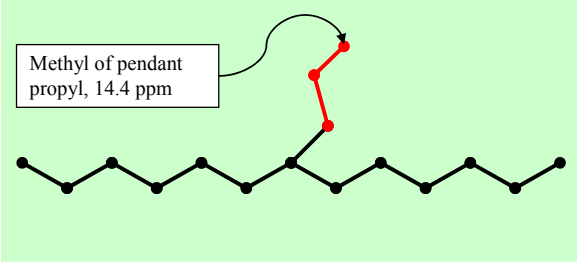

Figure H.3. Methyl on pendant propyl.

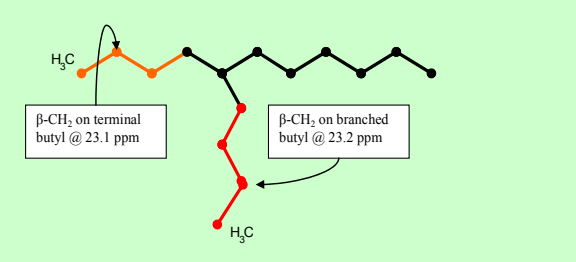

Figure H.4. β-CH_2 on terminal and pendant butyls.

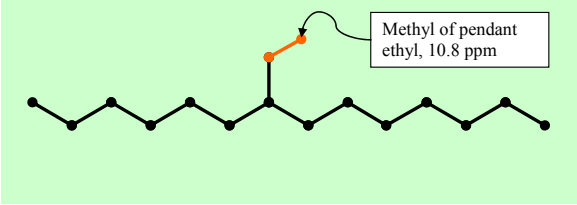

Figure H.5. Methyl on pendant ethyl.