

Fuels for Advanced Combustion Engines Research Diesel Fuels: Analysis of Physical and Chemical Properties

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ABSTRACT

The CRC Fuels for Advanced Combustion Engines working group has worked to identify a matrix of research diesel fuels for use in advanced combustion research applications. Nine fuels were specified and formulated to investigate the effects of cetane number aromatic content and 90% distillation fraction. Standard ASTM analyses were performed on the fuels as well as GC/MS and $^1\text{H}/^{13}\text{C}$ NMR analyses and thermodynamic characterizations. Details of the actual results of the fuel formulations compared with the design values are presented, as well as results from standard analyses, such as heating value, viscosity and density. Cetane number characterizations were accomplished by using both the engine method and the Ignition Quality Tester (IQT™) apparatus.

INTRODUCTION

The Fuels for Advanced Combustion Engines (FACE) Group is a working group of the Coordinating Research Council (CRC) Advanced Vehicle/Fuel/Lubricants (AVFL) Committee. The mission of the FACE Group is to recommend sets of test fuels well suited for research so that researchers evaluating advanced combustion systems may compare results from different laboratories

using the same set of fuels for consistency. Examples of advanced combustion systems include low-temperature combustion (LTC), homogenous charge compression ignition (HCCI), and high-efficiency clean combustion (HECC).

This report focuses on the results of standard ASTM-type analyses conducted to characterize the chemical and physical properties of a matrix of diesel test fuels, known as the FACE diesel fuels. However, due to the unusual chemical composition expected for the FACE fuels, it was decided that characterization by advanced analytical techniques would also be advantageous to researchers.

Although advanced analytical techniques, e.g., gas chromatography field ionization mass spectrometry (GC-FIMS) and nuclear magnetic resonance (NMR), have previously been used to characterize distillate fuels [1-5], a joint Natural Resources Canada (NRCan)/U.S. Department of Energy (DOE) workshop [6] recommended characterizing fuels derived from oil sand and shale oil to determine if the differences in the molecular structure of fuel would affect current property correlations and low-temperature combustion mechanisms. As a result of this recommendation, NRCan's National Centre for Upgrading Technology (NCUT) and DOE's Oak Ridge National Laboratory (ORNL) and Pacific Northwest National Laboratory

(PNNL) collaborated on characterizing fuels derived from unconventional hydrocarbons, using ^1H and ^{13}C NMR, GC-FIMS, and two dimensional gas chromatography (2D-GC) techniques. The knowledge from this collaboration was applied to the FACE fuels.

FUEL MATRIX

It was determined that three fuel properties were of primary importance to the performance of advanced combustion engines. These were (1) a measure of ignition quality, i.e., cetane number; (2) a measure of chemistry, i.e., aromatic content; and (3) volatility, i.e., T90 distillation. Target levels for these three variables were selected. In order 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:

- Cetane number: 30 and 55
- T90: 270 and 340°C
- Aromatics content: 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 cetane number of 42.5, T90 of 305°C, and aromatics content of 32.5%.

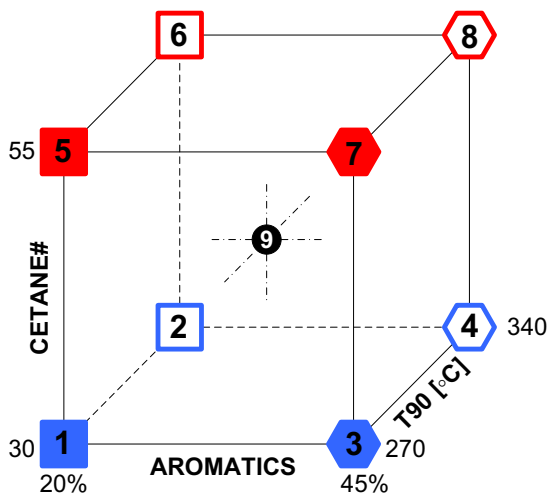


Figure 1. FACE Fuel Matrix

This resulted in a matrix containing 9 target fuels. A graphical representation of these fuels is shown in Figure 1. The nomenclature used to identify the FACE fuels relates to Figure 1 numerical designations and is defined as follows: FD-9A = FACE Diesel – Fuel 9, Batch A. Other constraints imposed on the fuels were a 15-ppm maximum sulfur content and a maximum of 4%, by volume, olefin content. While the importance of other design variables was recognized, e.g., fuel chemistry, the matrix neglected those variables in the interest of keeping the number of fuels to a manageable size. It was specified that all fuels should be formulated from

refinery streams, and blending of a small number of pure compounds to meet target properties was strongly discouraged. Beyond the T90 specification, all fuels should have a distillation curve that is similar in shape to those of current marketplace diesel fuels.

FUEL BLENDING

The fuels were manufactured and are being sold by Chevron-Phillips Chemical Company's Specialty Chemicals Group (CPChem). In general, the fuels were successfully formulated to match the target values. However, difficulty was encountered with two fuels that resulted in the need to accept values that were different from the target values. These two fuels were the high-cetane, high-aromatic, low- and high-T90 fuels, i.e., FD-7A and FD-8A, respectively.

FUEL CHARACTERIZATION

This report focuses on both the chemical and physical properties of the first production run of the FACE fuel set, as well as 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 the existing ORNL, PNNL, and NCUT collaboration, which focused on more complex fuels, such as those derived from oil sands and oil shale. Another motivation was to come up with a tractable parameter set, based on chemical composition, to relate to observed combustion behavior or physical properties, e.g., lubricity. By a well-characterized chemistry for the fuels would improve the possibility of developing robust predictive models for combustion behavior in both conventional and advanced combustion modes, whereby the predictive models could be applied to more complex fuel streams from non-traditional sources.

TRADITIONAL ASTM DIESEL FUEL ANALYSIS

A number of standardized ASTM tests [7] are available for diesel fuel characterization; many of these are widely used in producing certificates of analysis for fuels. One set of results for these analyses was obtained by subcontract through Southwest Research Institute (SwRI). NRCAN/NCUT also provided benchmark data for some of these analyses. Also included are the results provided on the CPChem Certificate of Analyses for the drums of fuel purchased by members. It is worth noting that the formulation of the FACE diesel fuels sometimes falls outside 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 lab to lab and test to test than is typically experienced with marketplace fuels.

- Cetane number/index
- Aromatic content
- T90 distillation
- Viscosity
- Specific gravity
- Cloud point
- Flash point
- Heat of combustion
- Ignition Quality Tester (IQT™) – DCN

Table 1 provides the results of this testing.

Cetane Number / Index

The cetane number (CN) for each fuel was measured by SwRI and CPChem per ASTM engine method D613. The values from these two sources differ by 1.5 units or less. The low-cetane fuels (FD-1A, 2A, 3A and 4A) have cetane numbers very close to the target value of 30. The values for fuels FD-5A and FD-6A were also very close to the target value of 55; however, the values for fuels FD-7A and FD-8A (approximately 45 and 50, respectively) were significantly low compared with the target value of 55. This difference was accepted to preserve better agreement between the target and actual values of the two other design variables. The center-point fuel (FD-9A) was produced on-target with a cetane number of 43. The cetane index (CI) results exhibited significant differences from the cetane number results. This is not too surprising since D976 CI 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, which incorporate unusual fuel chemistries.

Aromatic Content

The aromatic content for each fuel was determined by three laboratories (SwRI, NCUT, and CPChem) per ASTM D1319. In general the low-aromatic fuels (FD-1A, 2A, 5A and 6A) 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 FD-3A and FD-4A were at or slightly above the target aromatic content while fuels FD-7A and FD-8A were formulated below the target aromatic content. FD-9A was formulated slightly above the target aromatic content. In addition to these results the final CRC report includes aromatics by ASTM D5186 (Supercritical Fluid Chromatography) conducted by NCUT and SwRI laboratories.

T90 Distillation

The T90 values were measured by CPChem and SwRI per ASTM D86. In general there is very good agreement in the results from both laboratories. All 9 fuels were formulated within 6°C of the T90 target, with a separation between the high and low target of 70°C. Subsequent simulated distillation data (ASTM D2887) by NCUT was consistent with the ASTM D86 data. The final CRC report includes distillation curves for all fuels.

Kinematic Viscosity

Viscosity, determined by SwRI and NCUT using ASTM D445, shows good agreement among the laboratories. There was considerable variation in the kinematic viscosity as a result of the fuel formulation to meet the design criteria. The minimum kinematic viscosity was 1.319 cSt for FD-3A, and the maximum was 3.218 cSt for FD-8A. The variation in fuel property target values again resulted in fuels that exhibited viscosity outside the specification for #2 diesel fuel (1.90–4.1 cSt).

Specific Gravity

Specific gravity measured by all laboratories per ASTM D4052 was in good agreement for all fuels. The maximum percent difference between the three labs' results for any fuel was 0.14%. Because of the range of fuel chemistries, the specific gravity for some fuels exhibited values outside the typical range of 0.82–0.86 g/cc for commercial #2 diesel fuel. The center point fuel (FD-9A) that was designed as a near-marketplace-average fuel did fall within the limits of this specification.

Cloud Point

ASTM D2500 data were provided by both SwRI and NCUT. The laboratory-to-laboratory results agreed within a few degrees Celsius, with outliers for FD-2A and FD-4A, both of which are low-cetane, high-T90 fuels. All 9 fuels had cloud points well below zero, and actual values spanned a range from –19.5 to –59°C. A correlation between T90 and cloud point is not surprising; however, the variation in cloud point between high- and low-T90 blends was more pronounced for the low-cetane fuels than for the high-cetane fuels. Interestingly, the low-cetane fuels with high T90 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.

Flash Point

Flash points measured per ASTM D93 were obtained from SwRI, and CPChem. All 9 fuels had flash points higher than the 52°C specification for #2 diesel fuel.

Net Heat of Combustion

Net heats of combustion were obtained from SwRI per ASTM D240. All 9 fuels produced results that were within 2.4% difference of the average. The maximum value was 43,154 kJ/kg (FD-2A); the minimum was 42,147 kJ/kg (FD-3A).

Lubricity

Chevron measured the lubricity of all 9 fuels using the ASTM D6079 High-Frequency Reciprocating Rig (HFRR) method. The wear scar diameter (WSD) values

range from 492–687 microns WSD. Only FD-8A has a WSD that is below the ASTM specification of 520 microns for #2 diesel fuel.

Ignition Quality Tester (IQT™) - Derived Cetane Number (DCN)

The National Renewable Energy Laboratory (NREL) tested all 9 FACE diesel fuels using an Ignition Quality Tester (IQT™). The IQT™ is a constant-volume combustion apparatus developed specifically as a standard test device for fuel ignition delay [8-13], and ASTM D6890 was developed around this apparatus [14]. NREL tested all fuels according to ASTM D6980-08 and performed additional experiments to further study ignition quality, which is documented in a final CRC report. The additional analysis includes ignition delay calculations for a range of temperatures, pressures, and oxygen concentration with Arrhenius functions including apparent activation energy and oxygen order factor. Table 2 provides the DCN from the IQT™ and compares with the CN measured by ASTM D613.

As listed in Table 2, the IQT™-based ASTM D6890-08 DCN agree fairly well with the ASTM D613 engine-based CN, except for the lower cetane fuels. FD-5A, -6A, -7A, -8A, and -9A generally showed differences of DCN-CN around 0.1-1.2 cetane numbers. These differences fall within the same order of magnitude for DCN-CN data differences shown in ASTM's empirical model validation studies [15-17]. FD-1A, -2A, -3A, and -4A demonstrate a greater DCN-CN difference and the DCN values are consistently higher than the engine-based Cetane Numbers, 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 cetane numbers below 30 [18], but CPChem and SwRI results agree fairly well with each other for FD-1A, -2A, and -4A. FD-3A and FD-4A demonstrated ignition delay times corresponding to the discontinuous transition between correlation equations used in ASTM D6890 [14], yielding an additional possible uncertainty of approximately 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 the ASTM D6890-08 test method development [14] and research reports validating the empirical models [15-17] show the majority of experiments conducted to develop the empirical relations involved fuels with cetane numbers between 40–60, which is reasonable considering the ASTM test was primarily concerned with testing the traditional range of commercial diesel fuels. Only two fuels were studied with lower cetane numbers, 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 D6890-08 DCN in comparison to the ASTM D613 CN was not widely correlated for cetane numbers lower than 45, it is not

surprising the empirical correlations may not yield close agreement for the unique chemistry, low-cetane FACE diesel fuels.

CHEMICAL ANALYSIS

Because of the level of molecular and structural detail for each of the chemical analyses, discussion of results will be limited to a brief overview of key characteristics of the GC/MS analysis for each fuel. Data generated by NMR, GC-FIMS and 2D-GC is at a level of detail that including all the data on each fuel and a full discussion is beyond the scope of this paper. Therefore, only FACE fuel FD-9A (center-point) data will be provided as an example of the level of detail available with each fuel. The final CRC report includes all data and an in-depth discussion of the techniques and results.

GC/MS ANALYSIS

The 1-D GC/MS analyses were conducted by ORNL/NCUT per ASTM D2425. The GC/MS chromatograms identified the compounds that make up significant portions of the fuel. Minor compounds (at ppm concentrations) that do not make up significant portions of the fuel are neglected. The results from the chromatograms for fuels FD-1A–FD-9A are compiled in Table 3.

Low-Cetane Fuels (FD-1A, 2A, 3A and 4A)

FD-1A and FD-3A are the low-T90, low-cetane number fuels. Both of these fuels exhibit a normal alkane profile that is skewed toward lower carbon numbers compared with the distribution exhibited by FD-9A. This reflects the low T90 formulation of these fuels. FD-2A and FD-4A are the high-T90, low-cetane-number fuels, and neither fuel bears much resemblance to marketplace fuels. For example, FD-2A has a bimodal distribution of hydrocarbons, with most of the fuel mass made up of very volatile mono-aromatics and *iso*-paraffins plus some paraffins at boiling points between 340 and 400°C.

High-Cetane Fuels (FD-5A, 6A, 7A, and 8A)

FD-5A and FD-7A are the low-T90, high-cetane fuels. Both fuels exhibit the characteristic mono-aromatic blending stream at the low end of the distillation, suggesting that the most volatile components of the fuels have a low cetane number. Both fuels also exhibit normal and *iso*-paraffins from C11–C15, but not in a normal distribution. FD-7A also contains higher molecular weight diphenyl compounds near the end of the distillation.

FD-6A and FD-8A are the high-T90, high-cetane fuels. FD-6A exhibited a broad distribution of normal and *iso*-paraffins from C9-C20 with a higher molecular weight paraffin stream that is common to the high-T90 fuels. FD-8A is an unusual formulation, and exhibits a

