

Characterization of Dieseline with the Advanced Distillation Curve Method: Hydrocarbon Classification and Enthalpy of Combustion

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ABSTRACT: The use of fuel blends (incorporating fluids such as natural gas or gasoline) for compression ignition engines may aid in efforts to reduce nitrogen oxides (NO_x) and particulate matter emission. The consideration and design of such blends is dependent upon the detailed properties of the particular blend. In this work, we measured blends of 10, 20, 30, 50, 70, 80, and 90% (v/v) gasoline in diesel fuel by use of the advanced distillation curve (ADC) method to determine the hydrocarbon classifications in the various volume fractions. This allows us to track the hydrocarbon families throughout the volatility profile and, most importantly, observe changes in the aromatic content of the distillate cuts. In addition, we have used the composition explicit data channel (a unique capability to sample composition throughout the distillation curve) of the ADC to access thermochemical data, and related this to the temperature data grid reported earlier. This was done by calculating a composite enthalpy of combustion based on the enthalpy of combustion of the individual components of a distillate fraction. The addition of gasoline to diesel fuel increases the amount of light paraffins in early distillate cuts and increases the amount of aromatics in later distillate cuts. Also, the addition of gasoline to diesel fuel decreases the enthalpy of combustion especially in early distillate cuts on a molar, mass, and volume basis.

INTRODUCTION

Recent improvements on internal combustion for transport have mainly addressed the engines themselves (e.g., high-pressure fuel systems, multiple injections per stroke, improved combustion chamber architecture, turbo charging, exhaust gas recirculation, after-treatment, etc.).¹ In addition to the progress being made on engines, there is also opportunity for improvement in fuel properties. Environmental concerns and stringent regulations about pollutants and greenhouse-gas emissions, along with the increasing cost and dwindling reserves of low-cost petroleum-based fuels, add a sense of urgency to fuel research.

Compression ignition engines are approximately 30–35% more fuel-efficient than similar-sized spark ignition engines,² they still only transfer 30–40% of the fuel energy into useful work.^{1,3} Additionally, there is a trade-off between NO_x and particulate matter (PM) emissions from diesel engines. NO_x and PM formation in the combustion chamber is determined by local fuel-air equivalence ratios at given temperatures.⁴ It was shown that such combustion results in simultaneous reduction of both PM and NO_x .^{4–6} The trade off, however, in low-temperature combustion mode is usually reduced in cylinder oxygen concentration. The deterioration of combustion results in increased unburned hydrocarbons and carbon monoxide (CO) emissions.⁷

Mixtures of fuels with lower cetane numbers (CN) and high volatility, such as natural gas and gasoline, may aid in efforts to reduce nitrogen oxides (NO_x) and particulate matter emission from internal combustion engines.^{8–11} A blend that might aid in decreasing emissions is gasoline + diesel fuel, a mixture that has been called dieseline. Gasoline is currently the main output from crude oil refining (though this is subject to market forces) making the blend of gasoline and diesel fuel an obvious choice to lower CN and raise volatility. The resistance

to autoignition of low CN fuels can provide sufficient ignition delay for air-fuel mixing, whereas faster vaporization (due to a higher volatility) can potentially increase the mixing rate.¹² Indeed, such properties have been considered beneficial, and extensive research has been carried out that includes combining these fuels in a dual injection mode.^{12,13} Blends, however, would be easier to transport, store, and deliver and would not require complex injection and valve actuation.^{12,13} In addition, it has been suggested that dieseline may have additional benefits such as lowered misfire limit, increased engine stability, and reduced peak cylinder pressures in moderately high compression ratios and complex direct injection strategies.¹⁴

Unfortunately, the presence of additives in both gasoline and diesel fuel could lead to decreased miscibility of the fuels.^{15–20} Additionally, the use of fuels with gasoline proportions higher than 20% (v/v) may cause increasing combustion instability.²¹ Gasoline at higher proportions might be possible and even favorable when using systems that utilize supercritical (SC) fluid technology. Injecting fuels and fuel mixtures into the cylinders as supercritical fluids has been suggested as one way to increase engine efficiency and decrease emissions. In these systems, gasoline could serve an additional function as an anticoking agent.^{22–28} Also, dieseline blends were shown to be beneficial for use in partially premixed compression ignition engines. At 50% gasoline, dieseline emitted fewer particles and lower levels of NO_x than diesel fuel.^{29,30}

The rational design of complex fuel mixtures such as dieseline requires reliable descriptions of the thermodynamic and kinetic properties, typically determined by models and simulations.

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Table 1. Table of the Aliphatic Hydrocarbon Family Types Resulting from the ASTM D-2789 Analysis Performed on the Neat Samples of the Fuels and Fuel Blends

sample	paraffins (%)	monocycloparaffins (%)	dicycloparaffins (%)	alkylbenzenes (%)	indanes and tetralins (%)	naphthalene (%)
diesel fuel	37.0	36.0	12.5	7.7	3.9	2.8
90% diesel fuel/10% gasoline	28.1	29.3	14.8	15.7	9.3	2.9
80% diesel fuel/20% gasoline	27.5	29.3	13.6	18.5	9.1	1.9
70% diesel fuel/30% gasoline	30.2	29.7	12.3	18.2	7.6	1.8
50% diesel fuel/50% gasoline	29.3	26.4	10.7	24.1	7.4	2.1
30% diesel fuel/70% gasoline	32.7	23.7	8.2	27.1	6.3	2.0
20% diesel fuel/80% gasoline	29.3	22.1	7.3	34.0	5.9	1.4
10% diesel fuel/90% gasoline	25.0	16.5	3.1	50.2	4.4	0.8
gasoline	22.1	10.4	0.2	63.1	4.1	0.1

Modeling diesel fuel blend behavior requires reliable fuel property data such as volatility, heat capacity, density, diffusivity, critical point, thermal conductivity, and viscosity. Fuel volatility can be studied comprehensively by the advanced distillation curve (ADC) method.^{31–33} The distillation (or boiling) curve of a complex fuel such as diesel is a critically important indicator of the bulk behavior of the fuel.^{34–42}

In earlier work, the volatility of diesel blends was determined by the advanced distillation curve method.⁴² Distillation curves were constructed for blends of 10, 30, 50, 70, and 90% (v/v) and compared to those of automotive gasoline with octane number 97 and diesel fuel No. 2. The results showed that diesel volatility is close to that of gasoline at the start of distillation and approaches that of diesel fuel at the end of the process. Experiments on the thermal stability of diesel in a batch reactor showed no significant thermal decomposition at 400 °C for one hour. This reactivity-inhibition of the thermally labile compounds was attributed to the lighter, less reactive fuel components. These authors also showed that this fuel substantially improved the phase transition from liquid to SC states, with the more chemically stable gasoline acting as an antiknock agent for heated diesel fuel.

Additional research has been performed to determine the energy content and the hydrocarbon classification of distillate fractions. These studies were not possible earlier due to logistical problems but are reported herein. Five diesel samples of different compositions and two separate commercial samples of automotive gasoline and diesel fuel no. 2 were analyzed with the advanced distillation curve method. Our purpose in performing these measurements is the same as in earlier work; we seek to develop structure–property relationships in terms of the complex mixture equation of state.^{43,44} Equations of state are the best means of economically predicting the thermodynamic and transport properties of fuels.

■ EXPERIMENTAL SECTION

Materials. A supply of unleaded, unoxxygenated gasoline was obtained from a commercial source. Unoxxygenated conventional gasoline is available in limited geographical areas and does not contain ethanol or other oxygenates such as ethers. This fuel had an antiknock index (average of the research octane number (RON) and the motor octane number (MON)) of 91, with the RON reported by the supplier as 97. The supply of diesel fuel was obtained from a commercial distributor, free of oxygenate additives or cetane boosters. The fuel was a winter grade, low wax, ultra low sulfur diesel fuel that incorporated a red dye (specifying off-road use). It was refined locally from petroleum from the Denver-Julesburg field. Both fuels were used with no purification or modification.

We note that diesel fuel and gasoline are commodity fluids with seasonal and regional variations, (although the degree of variability is

typically greater for gasoline). We have discussed the variability in detail in previous work, and have presented measurements that are descriptive of the experience base encountered by the liquid fuel industry. The diesel fuel and gasoline that we have used in the work presented herein are representative of that experience base.^{45–48} More importantly, we have used the same fuels throughout our work on these fuels, and thus they serve as a prototype fluids of known pedigree that can be used for comparison. This allows general conclusions to be drawn regarding the fluid behavior of mixtures of diesel fuel and gasoline.

The solvent used in this work, *n*-hexane, was obtained from a commercial source. It was analyzed by gas chromatography (30 m capillary column of 5% phenyl-95% dimethyl polysiloxane having a thickness of 1 μ m, temperature program from 50 to 170 °C, 5 °C per minute) using flame ionization detection and mass spectrometric detection.^{49,50} These analyses revealed the purity to be approximately 99.9%, and the solvent was used without further purification.

ADC Sampling. The ADC apparatus and procedure have been described in previous papers;^{51–58} thus, only a brief description, as it applies to this study, will be given here. For each measurement, 200 mL of diesel fuel was placed in a boiling flask. The thermocouples were then inserted into the proper locations to monitor (a) the kettle temperature (T_k), the temperature in the fluid, and (b) the head temperature (T_h), the temperature of the vapor at the bottom of the takeoff position in the distillation head. In terms of significance, T_k is a thermodynamically consistent bubble point temperature, whereas T_h approximates what might be obtained from the classical distillation measurement procedure. Enclosure heating was then commenced with a model-predictive temperature controller.⁵⁸ The heating profile was designed to be of similar shape to that of the distillation curve, but it leads the distillation curve by approximately 20 °C. As heating progressed, the volume of the distilled liquid was measured in a level-stabilized receiver. Measurements of the temperature data grid were reported previously;⁴² here we focus on extracting information from the composition data channel of the ADC. For distillate fraction sample analysis, approximately 7 μ L sample aliquots were collected at the receiver adapter hammock.

The general composition of each distillate volume fraction of fuel or fuel blend was studied by a gas chromatographic method (30 m capillary column of 5% phenyl/95% dimethyl polysiloxane, with a thickness of 0.25 μ m) with mass spectrometric (MS) detection and flame ion detection (FID).^{49,50} The GC analysis of all samples was performed with helium carrier gas at 55.2 kPa (8 psi, gauge), and column temperature programming (two min at 40 °C, increased to 250 °C at 10 °C/min, and 14 min at 250 °C to ensure complete removal of the solvent, and trace contaminants). MS was used with the aid of the NIST/EPA mass spectral database following column separation to provide compositional information by identification of peaks in the resulting chromatogram.^{49,50,59} These analytical results (compositions and relative quantities of components) are consistent with our knowledge of each fuel.

Distillate Composition. Whereas the gross examination of the distillation curves is instructive and valuable for many design purposes, the composition channel of ADC can provide additional information. One can sample and examine the individual fractions as they emerge

from the condenser. Sampling was performed by withdrawing approximately 7 μL aliquots of distillate (at various distillate volume fractions) and diluting the aliquot in a known mass ($\sim 1\text{ mL}$) of hexane as a solvent. This fluid was chosen as a solvent because it had a short retention time and did not interfere with the majority of the GC peaks of the distillate fractions. We note that the solvent choice with the diesel line mixture is somewhat challenging because gasoline in fact contains some fraction of C6 species. The use of *n*-hexane represented the best

compromise because when necessary this peak could be removed electronically from any calculation. Each of these fractions was analyzed by GC with FID and MS method using the same column and oven temperature program as described above. To quantify the compositional mole fractions in the distillate cuts, calibration on the FID was performed with octane.

Hydrocarbon Classification. An analytical technique that complements the above detailed analyses examines the diesel line

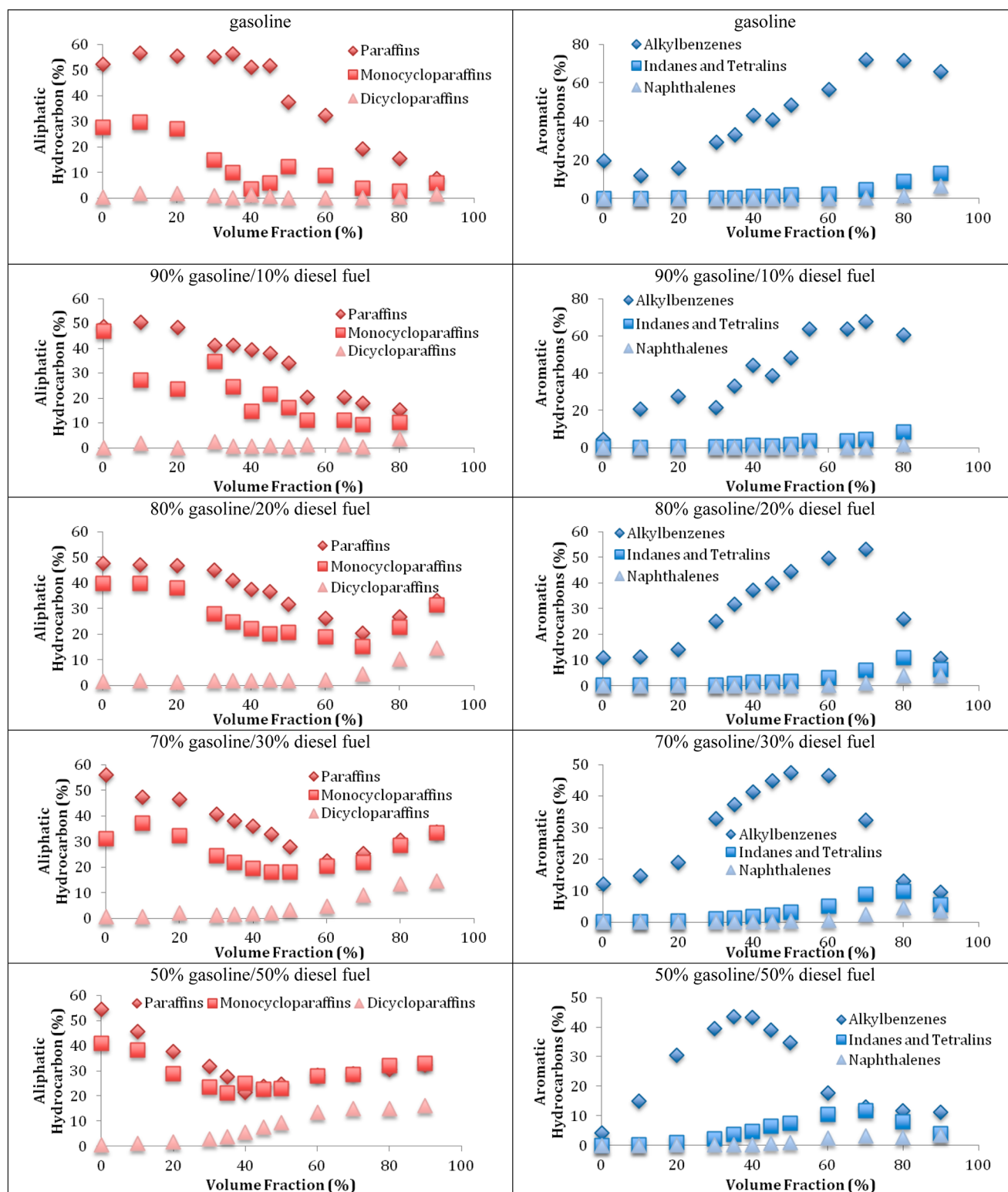


Figure 1. continued

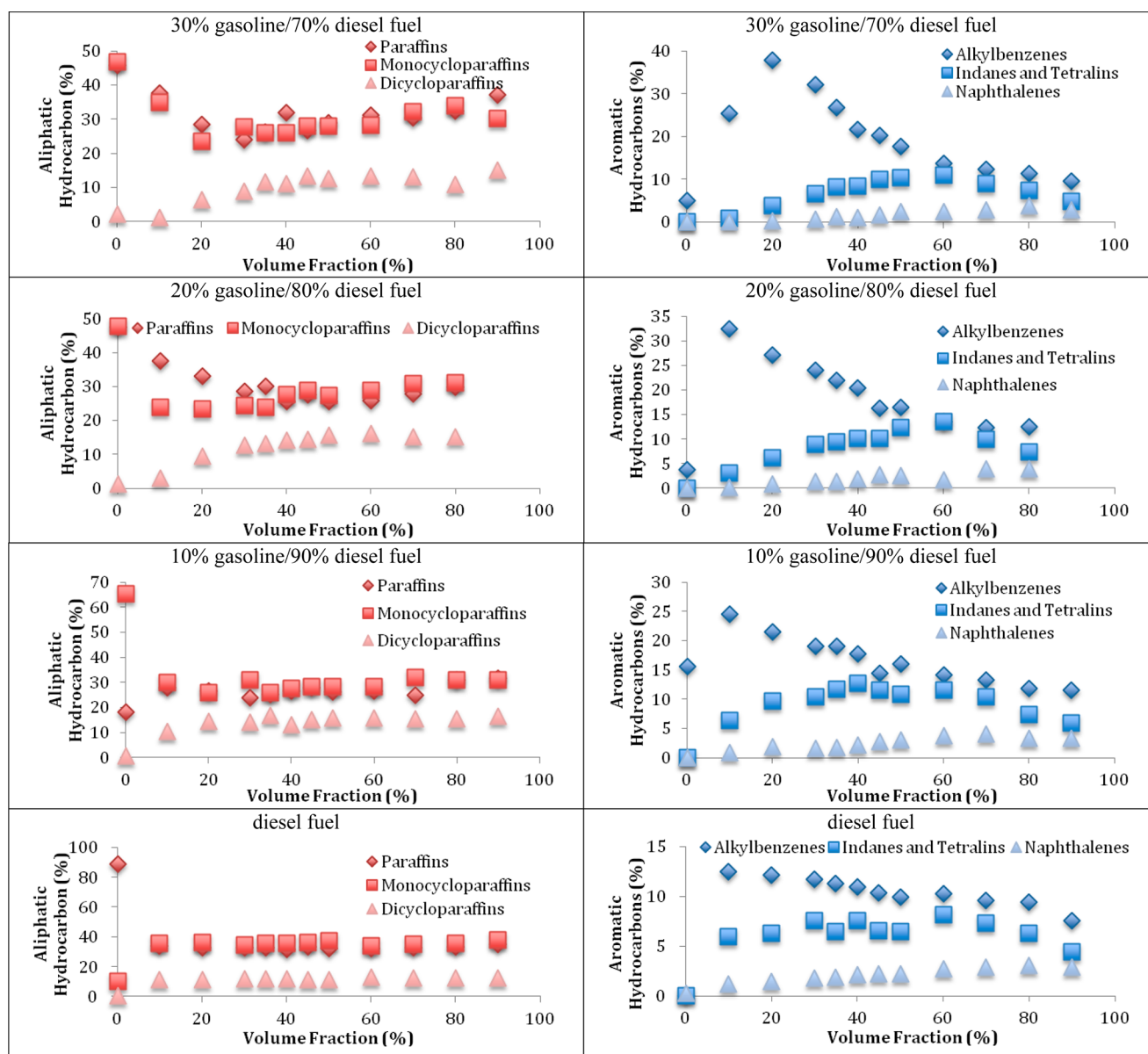


Figure 1. Plots of the hydrocarbon family types resulting from the moiety family analysis performed on diesel line blends. The uncertainty is discussed in the text.

samples for hydrocarbon types by use of a mass spectrometric classification method similar to that summarized in ASTM D-2789.⁶⁰ In this method, one uses MS (or GC-MS) to characterize hydrocarbon samples by grouping the compounds into six types. The six types or families include the following: paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes. Although the method is specified only for application to low olefinic gasoline and has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, rocket propellants, and missile fuels.⁶¹ The uncertainty of this method and the potential pitfalls were discussed earlier.⁵⁴ Once again, the sample solutions were prepared from $\sim 7 \mu\text{L}$ aliquots of emergent distillate that were withdrawn from the sampling adapter at specified volume fractions and added to a vial containing a known mass of solvent (*n*-hexane). For the hydrocarbon-type analysis of the distillate fraction samples, $1 \mu\text{L}$ of these solutions was injected into the GC-MS. Because of this consistent injection volume, no corrections were needed for sample volume. The integrations of the total ion chromatograms, required to establish the moiety fractions, specifically avoided the solvent area.

Distillate Fraction Energy Content. As we have demonstrated previously, it is possible to add thermochemical information to the distillation curve when the composition channel of data is used to provide quantitative analysis on specific distillate fractions.^{53,54,56} This is done by calculating a composite enthalpy of combustion based on the enthalpy of combustion of individual (pure) components of a distillate fraction and the measured mole fractions of those components. The enthalpy of combustion of the individual (pure) components is taken from a reliable database compilation.⁶² Uncertainty in this calculation has been attributed to a number of sources^{53,54} including (1) the neglect of the enthalpy of mixing, (2) the uncertainty in the individual (pure component) enthalpy of combustion as tabulated in the database, (3) the uncertainty in the measured mole fraction, (4) the uncertainty posed by very closely related isomers that cannot be resolved by the analytical protocol, (5) the uncertainty introduced by neglecting components present at very low concentrations (that is, uncertainty associated with the chosen area cutoff), (6) the uncertainty introduced by a complete misidentification of a component, (7) the uncertainty in quantitation introduced by eluting peaks that are poorly resolved, and (8) the uncertainty introduced when

experimental data for the pure component enthalpy of combustion are unavailable (and the Cardozo equivalent chain model must be used).⁶³ On the basis of the uncertainty sources listed above and the samples being investigated, a 5% uncertainty was ascribed to the molar enthalpy calculations reported in this work.

RESULTS AND DISCUSSION

The results of the hydrocarbon classification for the neat fuels can be seen in Table 1, and the graphical results of the hydrocarbon classification for the fuels are presented in Figure 1. In the gasoline and the diesel blends with a high percentage of gasoline, the alkylbenzenes increase throughout the distillation. As the percent of diesel fuel increases in the blends, the alkylbenzenes reach a maximum during the distillation. This is consistent with our earlier work on gasoline and mixtures of gasoline with oxygenate fluids. This maximum appears earlier in the distillation as the percent of diesel fuel increases, until the maximum disappears entirely and the fraction of alkylbenzenes then decreases throughout the distillation. Again, this is consistent with our earlier observations with diesel fuel and mixtures of diesel fuel with oxygenate additives. The percent of indanes and tetralins, and naphthalenes remains below 15% for all fractions sampled. The percent of paraffins decreases throughout the distillations of gasoline and 90% gasoline/10% diesel fuel blend. Then, we observe that minima develop as the fraction of diesel fuel increases. The minimum is observed at 70% distillate volume fraction for the 70% gasoline/30% diesel fuel mixture, and as the fraction of diesel fuel increases, the minimum shifts to earlier distillate volume fractions. Indeed, when the diesel fuel fraction is increased to 90%, the minimum is observed at the 30% distillate volume fraction, after which it becomes relatively constant.

Figures 2 and 3 show the overall trends with the paraffinic hydrocarbons being the sum of the paraffins, monocycloparaffins, and dicyclopaffins, and the aromatic hydrocarbons being the sum of the alkylbenzenes, indanes and tetralins, and naphthalenes. The lines are provided only as a guide to the reader and are not best-fit lines. It can clearly be seen that the maximum of the aromatic hydrocarbons increases with an increasing percent of gasoline. Also, this maximum shifts to later distillate fractions as the percent of gasoline increases and there is also an increase of lighter components that come out earlier in the distillation. Fuels containing a higher percent paraffins of appropriate properties have shorter ignition delays because oxidation and decomposition reactions proceed faster through mechanisms involving free radicals. Fuels with higher aromatics content have longer ignition delays due to their more stable ring structures, thus requiring higher temperatures and pressures to ignite. This frequently leads to increased soot production and less desirable fuel operability characteristics. As mentioned in the introduction, however, ignition delay caused by addition of such fluids can result in improved mixing prior to reaction.

Figures 4, 5, and 6 show the molar enthalpy of combustion as a function of the distillate fraction for each of the diesel line samples. The enthalpies with their uncertainties are provided in Tables 2, 3, and 4. The molar enthalpy of combustion (Table 2, Figure 4) increases with distillate fraction as the concentration of longer *n*-alkanes increases in the later distillate fractions and roughly corresponds to the variation in distillation curves reported in the earlier work on diesel line. Also, the enthalpy tended to increase proportionally with diesel fuel content, from the first drop of gasoline (2982.7 kJ/mol) to diesel fuel's 80%

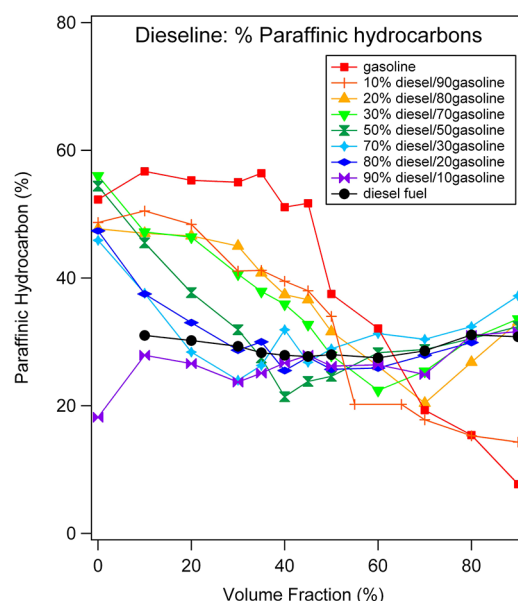


Figure 2. Plot of the sum of the paraffinic hydrocarbon family resulting from the moiety family analysis performed on diesel line blends. Lines are drawn to guide the eyes of the viewer, and do not represent a fit. The uncertainty is discussed in the text.

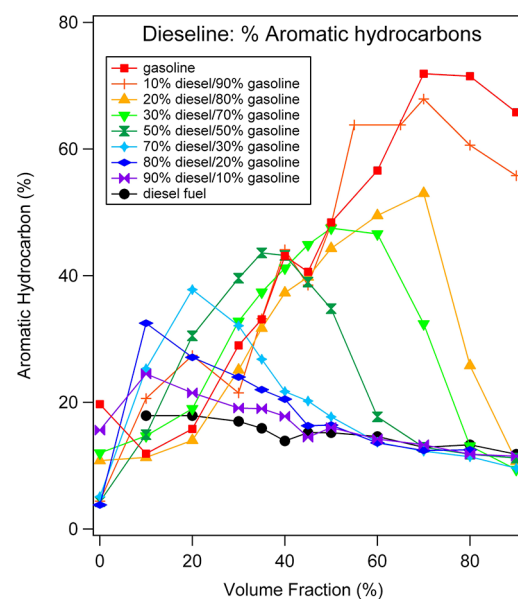


Figure 3. Plot of the sum of the aromatic hydrocarbon family resulting from the ASTM D-2789 analysis performed on the diesel line blends. Lines are drawn to guide the eyes of the viewer, and do not represent a fit. The uncertainty is discussed in the text.

fraction (10746.5 kJ/mol). As shown in Tables 3 and 4, the enthalpies by mass and volume for all distillate cuts and fuels are very similar.

Previous research on commercial gas turbine fuels by use of the ADC method showed significant variability in composition and energetics.⁶⁴ It is likely that there is similar variability in both diesel fuel and gasoline, although this has not yet been studied by the ADC method. The variability of commercial fuels will cause variation in distillate fraction energy content and percent of hydrocarbon family types between batches of diesel line. Therefore, a thermophysical property model based on a single set of samples will not be sufficient to represent the variability in any commercial

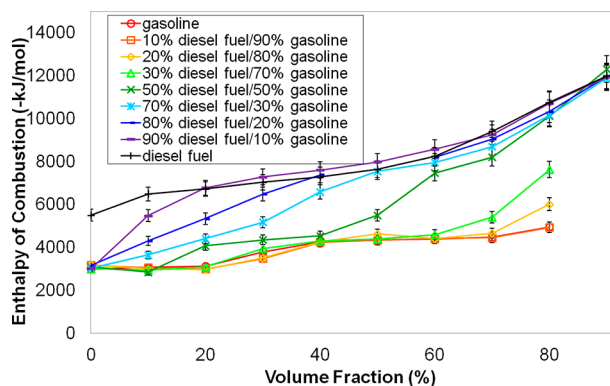


Figure 4. Energy content, presented as the composite enthalpy of combustion, $-\Delta H_c$ (kJ/mol), as a function of the distillate volume fraction for dieseline fuels. The uncertainties are discussed in the text. Lines are drawn to guide the eyes of the viewer and do not represent a fit.

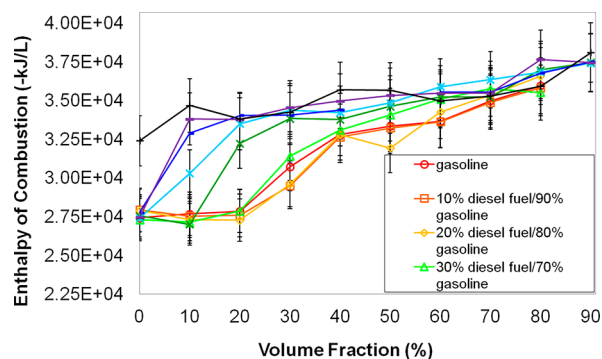


Figure 5. Energy content, presented as the composite enthalpy of combustion, $-\Delta H_c$ (kJ/L), as a function of the distillate volume fraction for dieseline fuels. The uncertainties are discussed in the text. Lines are drawn to guide the eyes of the viewer and do not represent a fit.

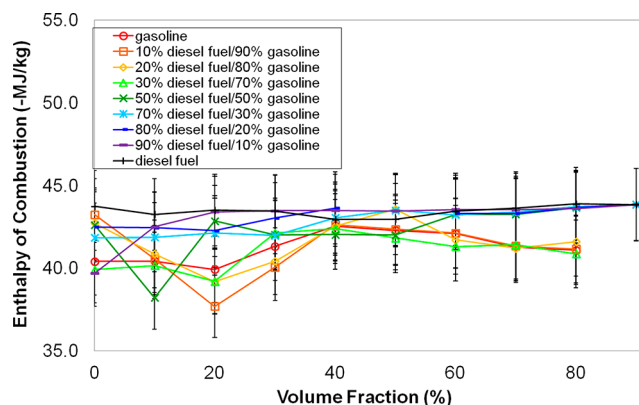


Figure 6. Energy content, presented as the composite enthalpy of combustion, $-\Delta H_c$ (MJ/kg), as a function of the distillate volume fraction for dieseline fuels. The uncertainties are discussed in the text. Lines are drawn to guide the eyes of the viewer, and do not represent a fit.

production of dieseline, and a tunable model is needed for fuel blends. Nevertheless, the fuels used in these experiments are prototypes that have been extensively characterized, and the data presented here provides trends that should be applicable in any dieseline blend using commercial fuels.

Table 2. Energy Content, Presented As the Composite Enthalpy of Combustion $-\Delta H_c$ (kJ/mol), As a Function of the Distillate Fraction for Dieseline Fuels, the Uncertainties Are Discussed in the Text and Are Provided in Parentheses

Distillate Volume Fraction (%)	0.03%	10%	20%	30%	40%	50%	60%	70%	80%
diesel fuel									
90% diesel fuel/10% gasoline	5497.6 (274.9)	6481.1 (324.1)	6718.0 (335.9)	7024.8 (351.2)	7271.6 (363.6)	7637.5 (381.9)	8246.2 (412.3)	9403.4 (470.2)	10746.5 (537.3)
80% diesel fuel/20% gasoline	3010.1 (150.5)	5471.4 (273.6)	6769.8 (338.5)	7273.9 (363.7)	7598.9 (379.9)	7973.8 (398.7)	8573.0 (428.7)	9247.2 (462.4)	10706.0 (535.3)
70% diesel fuel/30% gasoline	3152.1 (157.6)	4295.5 (214.8)	5333.6 (266.7)	6482.9 (324.1)	7372.9 (368.6)	7579.0 (329.0)	8201.9 (410.1)	9081.6 (454.1)	10330.8 (516.5)
50% diesel fuel/50% gasoline	3027.9 (151.4)	3641.0 (182.1)	4397.4 (219.9)	5165.6 (258.3)	6579.0 (329.0)	7544.3 (377.2)	7954.3 (397.7)	8691.0 (434.6)	10165.2 (508.3)
30% diesel fuel/70% gasoline	3080.8 (154.0)	2835.9 (141.8)	4071.7 (203.6)	4349.3 (217.5)	4533.4 (226.7)	5487.6 (274.4)	7468.3 (373.4)	8198.2 (409.9)	10118.6 (505.9)
20% diesel fuel/80% gasoline	2994.4 (149.7)	2935.6 (154.5)	3090.3 (154.5)	4291.9 (214.6)	4291.9 (214.6)	4391.0 (219.6)	4586.6 (229.3)	5401.5 (270.1)	7620.9 (381.0)
10% diesel fuel/90% gasoline	3171.2 (158.6)	2997.5 (149.9)	2962.4 (148.1)	3505.3 (175.3)	4251.4 (212.6)	4618.3 (230.9)	4396.7 (219.8)	4658.3 (222.3)	6010.1 (246.4)
gasoline	3164.7 (158.2)	3049.2 (152.5)	2980.6 (149.0)	3476.6 (173.8)	4229.3 (211.5)	4332.3 (216.6)	4395.6 (219.8)	4446.7 (222.3)	4928.2 (246.4)
	2982.7 (149.1)	3068.6 (153.4)	3117.7 (155.9)	3784.3 (189.2)	4245.9 (212.3)	4346.6 (217.3)	4384.9 (219.2)	4464.9 (223.2)	4951.9 (247.6)

Table 3. Energy Content on a Mass Basis, Presented As the Composite Enthalpy of Combustion – ΔH_c (kJ/g), As a Function of the Distillate Fraction for Dieseline Fuels, the Uncertainties Are Discussed in the Text and Are Provided in Parentheses

Distillate Volume Fraction (%)	Composite Enthalpy of Combustion (kJ/g)								
	0.03%	10%	20%	30%	40%	50%	60%	70%	80%
diesel fuel	43.7 (2.2)	43.3 (2.2)	43.5 (2.2)	43.5 (2.2)	43.0 (2.2)	43.0 (2.2)	43.5 (2.2)	43.6 (2.2)	43.9 (2.2)
90% diesel fuel/10% gasoline	39.7 (2.0)	42.5 (2.1)	43.4 (2.2)	43.5 (2.2)	43.5 (2.2)	43.5 (2.2)	43.6 (2.2)	43.6 (2.2)	43.6 (2.2)
80% diesel fuel/20% gasoline	42.5 (2.1)	42.5 (2.1)	42.3 (2.1)	43.0 (2.2)	43.6 (2.2)		43.3 (2.2)	43.3 (2.2)	43.7 (2.2)
70% diesel fuel/30% gasoline	41.8 (2.1)	41.9 (2.1)	42.1 (2.1)	42.0 (2.1)	43.1 (2.2)	43.5 (2.2)	43.2 (2.2)	43.4 (2.2)	43.7 (2.2)
50% diesel fuel/50% gasoline	42.6 (2.1)	38.2 (1.9)	42.9 (2.1)	42.0 (2.1)	42.0 (2.1)	42.0 (2.1)	43.3 (2.2)	43.3 (2.2)	43.7 (2.2)
30% diesel fuel/70% gasoline	39.9 (2.0)	40.2 (2.0)	39.2 (2.0)	42.1 (2.1)	42.4 (2.1)	41.8 (2.1)	41.3 (2.1)	41.4 (2.1)	40.9 (2.0)
20% diesel fuel/80% gasoline	42.7 (2.1)	40.9 (2.0)	39.2 (2.0)	40.4 (2.0)	42.6 (2.1)	43.6 (2.2)	41.7 (2.1)	41.2 (2.1)	41.6 (2.1)
10% diesel fuel/90% gasoline	43.2 (2.2)	40.6 (2.0)	37.7 (1.9)	40.1 (2.0)	42.6 (2.1)	42.4 (2.1)	42.1 (2.1)	42.3 (2.1)	41.2 (2.1)
gasoline	40.4 (2.0)	40.4 (2.0)	39.9 (2.0)	41.3 (2.1)	42.6 (2.1)	42.3 (2.1)	42.1 (2.1)	41.3 (2.1)	41.1 (2.1)

Table 4. Energy Content on a Volume Basis, Presented As the Composite Enthalpy of Combustion – ΔH_c (kJ/mL), As a Function of the Distillate Fraction for Dieseline Fuels, the Uncertainties Are Discussed in the Text and Are Provided in Parentheses

Distillate Volume Fraction (%)	Composite Enthalpy of Combustion (kJ/mL)								
	0.03%	10%	20%	30%	40%	50%	60%	70%	80%
diesel fuel	32.4 (1.6)	34.7 (1.7)	33.8 (1.7)	34.2 (1.7)	35.7 (1.8)	35.7 (1.8)	35.0 (1.8)	35.3 (1.8)	35.9 (1.8)
90% diesel fuel/10% gasoline	27.5 (1.4)	33.8 (1.7)	33.8 (1.7)	34.5 (1.7)	35.0 (1.8)	35.3 (1.8)	35.5 (1.8)	35.5 (1.8)	37.7 (1.9)
80% diesel fuel/20% gasoline	27.8 (1.4)	33.0 (1.7)	34.1 (1.7)	34.1 (1.7)	34.4 (1.7)		35.6 (1.8)	35.6 (1.8)	36.8 (1.8)
70% diesel fuel/30% gasoline	27.4 (1.4)	30.3 (1.5)	33.5 (1.7)	34.4 (1.7)	34.2 (1.7)	34.8 (1.7)	35.9 (1.8)	36.3 (1.8)	36.3 (1.8)
50% diesel fuel/50% gasoline	27.6 (1.4)	27.0 (1.4)	32.2 (1.6)	33.8 (1.7)	33.8 (1.7)	34.6 (1.7)	35.2 (1.8)	35.2 (1.8)	37.0 (1.9)
30% diesel fuel/70% gasoline	27.3 (1.4)	27.1 (1.4)	27.9 (1.4)	31.4 (1.6)	33.1 (1.7)	34.0 (1.7)	35.0 (1.8)	35.8 (1.8)	35.5 (1.8)
20% diesel fuel/80% gasoline	27.9 (1.4)	27.3 (1.4)	27.3 (1.4)	29.6 (1.5)	32.8 (1.6)	31.9 (1.6)	34.3 (1.7)	35.4 (1.8)	36.6 (1.8)
10% diesel fuel/90% gasoline	28.0 (1.4)	27.6 (1.4)	27.6 (1.4)	29.5 (1.5)	32.6 (1.6)	33.2 (1.7)	33.3 (1.7)	34.8 (1.7)	35.8 (1.8)
gasoline	27.4 (1.4)	27.7 (1.4)	27.9 (1.4)	30.8 (1.5)	32.8 (1.6)	33.4 (1.7)	33.7 (1.7)	35.0 (1.8)	36.0 (1.8)

CONCLUSIONS

The volatility of dieseline blends, as measured with the ADC method, was previously reported and observed to be in the range spanned by automotive gasoline and diesel fuel. The distillation curves of the unmixed gasoline and diesel fuels exhibit similar shapes (that is, a subtle sigmoidal shape), with the gasoline curve lower by approximately 150 °C compared to that of diesel fuel. In this work, we measured blends of 10, 20, 30, 50, 70, 80, and 90% (v/v) gasoline in diesel fuel in the composition channel of information to determine the hydrocarbon classifications in the various volume fractions. This allows us to track the hydrocarbon families throughout the distillation process, and, most importantly, observe changes in the aromatic content of the distillate cuts. In addition, we have shown how the composition explicit data channel allows the addition of thermochemical information to the data temperature grid of the distillation curves reported earlier. This provides an explicit measure of the energy content of each fraction. The addition of gasoline to diesel fuel increases the amount of light paraffins in early distillate cuts and increases the amount of aromatics in later distillate cuts. In some blends, the benefit of light paraffins may outweigh the disadvantages of the additional aromatics. Also, the addition of gasoline to diesel fuel decreases the enthalpy of combustion especially in early distillate cuts on a molar, mass, and volume basis. A comparison of a number of dieseline blend samples allows us to better understand properties of fuel blends, which can lead to a more efficient and clean combustion of SC fluid dieseline. Future work will utilize the data presented here and additional data to determine compositional and energetic variability in order to develop a methodology to model the fuel blends.

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The authors declare no competing financial interest.

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