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## Measurements and Modeling Study on a High-Aromatic Diesel Fuel

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**ABSTRACT:** The increasing cost of diesel fuel, potential for supply disruptions, and environmental concerns have resulted in a great deal of research to improve the performance and efficiency of diesel engines. This includes significant efforts in the reformulation of conventional diesel fuels and the development of renewable diesel fuels. An integral part of work on diesel fuels has been the measurement and modeling of the thermophysical properties of the fuels; this knowledge is critical to effective design and application. In this paper, we present the development of a model for thermodynamic and transport properties for a conventional diesel fuel based on our measurements of chemical composition, density, viscosity, and volatility. This information, along with the cetane number and heat of combustion, was used to develop surrogate mixture models. The models contain constituent fluids representative of those found in the fuel and were designed to represent thermophysical properties (density, viscosity, and volatility) and also the heat of combustion and cetane number. Comparisons (calculated with the surrogate models) to limited density and viscosity experimental data are within 0.6 and 2%, respectively. The model represents the cetane number of the fuel to within 2 cetane numbers and the heat of combustion to within 5%. The volatility behavior, indicated by the temperatures obtained from the advanced distillation curve method, is reproduced to within 0.5%.

### INTRODUCTION

Diesel engine designers have come under increasing pressure to improve the efficiency, operation, and environmental performance of compression ignition (CI) engines.<sup>1-6</sup> These demands stem from anxiety over the supply of economical liquid fuels for transportation. The many reasons for this anxiety include potential supply disruptions, the dependence upon foreign sources of petroleum, and the vulnerability of large centralized refineries (to both weather events and terrorist acts), all of which contribute to dwindling supply and rising costs of current fuel streams. The environmental issues are also significant. Although very efficient, diesel engines have had difficulties achieving desirable emission targets, especially for soot and NO<sub>x</sub> formation.<sup>7,8</sup> Over the years, improvements have been made in the design of fuel systems, combustion chambers, and engine control. Indeed, catalytic after-treatment of diesel exhaust has become common on large diesel power plants.

Research on new engine technologies and new fuels is ongoing, to address the concerns listed above. Progress in these areas strongly depends upon the availability of an adequate knowledge base that includes a wide range of material properties. Among the most important factors are the thermophysical properties of the liquid fuels, including the volatility, density, heat capacity, transport properties, etc.<sup>9</sup> Of these properties, the volatility is especially critical because it is very sensitive to compositional variability and is crucial for engine operation.<sup>10–14</sup> We use for the measurement of this property the composition-explicit or advanced distillation curve method.<sup>15–17</sup> This technique allows for the measurement of volatility of the complex fluid and, in addition, allows for the temperature data grid to be related to the fluid composition. Moreover, all characteristics that can be determined from the fractional composition are accessible as well, including thermochemical properties.  $^{18}\,$ 

Advanced Distillation Curve Measurement. In earlier work, we described a method and apparatus for an advanced (or composition-explicit) distillation curve (ADC) measurement that is especially applicable to the characterization of fuels.<sup>19-23</sup> This method is a significant improvement over earlier approaches, featuring (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) a corrosivity assessment of each distillate fraction. The very significant advantage offered by the approach discussed in this paper is the ability to model the distillation curve, resulting from our metrology with equation-of-state-based models.<sup>19-28</sup> Such thermodynamic model development is simply impossible with the classical approach to the distillation curve measurement or with any of the other techniques that are used to assess fuel volatility or vapor liquid equilibrium. We have applied the ADC metrology to azeotropes, gasolines, diesel fuels, aviation fuels, rocket propellants, and crude oils.

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#### EXPERIMENTAL SECTION

The high-aromatic diesel (HAD) fuel used in this work was a type 2D grade fluid used for laboratory studies (that is, a noncommercial sample). The aromatic content was in fact significantly higher than that of the base diesel fuel that has been used in our previous work. This aspect of the composition and the ramifications that result will be discussed in more detail throughout this paper. The aromatic content had been measured with American Society for Testing and Materials (ASTM) method D5186<sup>29</sup> and was found to be 30% (mass/mass), which included 4.8% (mass/mass) polycyclic aromatics. The uncertainty of this measurement, performed with supercritical fluid

chromatography, is estimated to be 0.3% (mass/mass). The cetane number of the diesel fuel had been measured with ASTM method D613<sup>30</sup> and was found to be 40.9, with an uncertainty of 0.8. We note that this is at the lower range of diesel fuels that are considered typical in the United States market. In addition to these diagnostic tests, the composition was studied in more detail in our laboratory with a gas chromatographic method (30 m capillary column of 5% phenyl/95% dimethyl polysiloxane, having a thickness of 1  $\mu$ m and temperature program from 90 to 275 °C, at 9 °C/min) by use of flame ionization detection (GC–FID) and mass spectrometric detection (GC–MS).<sup>31,32</sup> The major components that were identified are listed in Table 1. This detailed analysis showed an aromatic content of approximately 12% on

Table 1. Listing of the Major Components in the HAD Fuel Examined in This Work, Listed by Increasing Retention Times  $(RTs)^a$ 

RT (min)	compound	area (%)	RT (min)	compound	area (%)
8.59	1-methyl-3-propyl benzene	0.60	17.25	2,6,10-trimethyldodecane	1.75
8.76	2-ethyl-1,4-dimethyl benzene	0.66	17.40	3-methyltetradecane	1.06
9.22	1-ethyl-2,4-dimethyl benzene	1.28	17.59	2-methyltetradecane	0.56
9.37	4-ethyl-1,2-dimethyl benzene	1.60	17.76	1-pentadecene	1.12
9.70	<i>n</i> -undecane	1.23	17.95	<i>n</i> -pentadecane	3.02
9.86	1-ethyl-3,5-dimethyl benzene	0.87	18.10	1-pentyl-2-propylcyclopentane	1.55
10.07	1,2,4,5-tetramethyl benzene	1.47	18.32	1,4,5-trimethylnaphthalene	0.52
10.17	1,2,3,5-tetramethyl benzene	1.88	18.50	1,4,6-trimethylnaphthalene	0.96
10.59	2,3-dihydro-4-methyl-1 <i>H</i> -indene	1.08	18.59	1,2,5-trimethylnaphthalene	1.02
10.74	1-methyl-4-methylpropyl benzene	0.87	18.78	7-methylpentadecane	1.18
10.84	2,3-dihydro-7-methyl-1 <i>H</i> -indene	1.05	18.90	decylcyclopentane	1.31
10.90	2,4-diethyl-1-methyl benzene	1.15	19.09	2-methylpentadecane	0.99
11.14	2-methylundecane	1.13	19.22	3-methylpentadecane	1.25
11.60	naphthalene	1.73	19.54	1,6,7-trimethylnaphthalene	0.61
11.93	<i>n</i> -dodecane	1.61	19.60	2,3,6-trimethylnaphthalene	0.54
12.24	2,6-dimethylundecane	0.53	19.74	n-hexadecane	2.51
12.71	pentylcyclohexane	0.51	19.85	1-propenylnaphthalene	0.89
13.04	2,3-dihydro-4,7-dimethyl indene	1.08	20.00	1-pentyl-2-propylcyclopentane	0.76
13.21	4-methyldodecane	0.61	20.19	2,6-dimethyl-1-phenylmethyl benzene	0.62
13.31	2-methyldodecane	0.86	20.33	1,2-dimethyl-4-phenylmethyl benzene	0.74
13.49	3,9-dimethylundecane	1.25	20.57	7-methylhexadecane	1.56
13.69	pentamethylbenzene	0.86	20.71	cyclohexadecane	0.87
13.98	<i>n</i> -tridecane	3.16	20.81	5-methylhexadecane	0.75
14.06	2-methylnaphthalene	2.29	20.94	4-methylhexadecane	0.85
14.34	1-methylnaphthalene	2.85	21.06	3-methylhexadecane	0.74
14.94	heptylcyclohexane	1.13	21.19	1,4,5,8-tetramethylnaphthalene	0.67
15.08	6-methyltridecane	0.54	21.43	n-heptadecane	2.03
15.15	5-methyltridecane	0.60	21.52	2-methylhexadecane	1.18
15.23	4-methyltridecane	0.92	21.62	1,2-dimethyl-3-pentyl-4-propylcyclohexane	0.80
15.34	3-methyltridecane	1.28	21.72	w,x-dimethyl-y-pentyl-z-propylcyclohexane	0.85
15.48	2-methyltridecane	0.92	22.00	decylcyclopentane	0.59
15.60	4,6-dimethyldodecane	1.41	22.14	6-methylheptadecane	1.10
15.72	2-ethenyl naphthalene	0.62	22.28	5-methylheptadecane	0.59
15.91	2-methyl-1-(cyclohexylmethyl) cyclohexane	0.70	22.44	4-methylheptadecane	1.28
15.99	1-tetradecene	0.72	22.58	3-methylheptadecane	0.93
16.06	<i>n</i> -tetradecane	1.78	22.79	1-octadecene	0.77
16.21	2,6-dimethylnaphthalene	1.53	23.04	<i>n</i> -octadecane	1.88
16.36	2,7-dimethylnaphthalene	0.70	23.19	2-methylheptadecane	1.42
16.50	1,7-dimethylnaphthalene	1.16	23.43	5-methyloctadecane	0.93
16.57	1,4-dimethylnaphthalene	1.14	23.70	4-methyloctadecane	0.86
16.70	2,3-dimethylnaphthalene	0.62	24.02	2-methyloctadecane	0.75
16.78	1,5-dimethylnaphthalene	0.64	24.58	<i>n</i> -nonadecane	1.06
16.88	1,8-dimethylnaphthalene	0.68	24.75	x-methylnonadecane	0.75
16.98	cyclotetradecane	1.28	25.19	x-methylnonadecane	0.57
17.07	5-methyltetradecane	0.54	25.79	x-methylnonadecane	0.56
17.17	4-methyltetradecane	0.78	26.04	n-eicosane	0.77

"The analysis was performed with gas chromatography with detection by mass spectrometry. Note that, in some cases, the substitution is ambiguous (as determinable from mass spectrometry) and is thus indicated by the letters *w*, *x*, *y*, and *z*.

a molar basis, which is consistent with the observation made with ASTM D5186. The fluid was clear and transparent (containing no dye) and was stored before measurement at 7  $^\circ$ C to preserve any volatile components. No phase separation was observed as a result of this storage procedure.

For comparison, we also present volatility measurements on a more typical commercial ultralow-sulfur diesel fuel, used as a base fuel in our previous measurements.<sup>33–38</sup> This fuel was fully compliant with the requisite specifications in ASTM D975.<sup>39</sup> This was also stored at 7 °C to preserve any volatile components. No phase separation was observed as a result of this storage procedure. The fuel was a wintergrade, low-wax, ultralow-sulfur diesel fuel that incorporated a red dye (specifying off-road use) and was refined locally from petroleum of the Denver-Julesburg field.<sup>33</sup> This fluid is referred to herein as the low-aromatic diesel (LAD) fuel.

We note inter alia that the aromatic content of the diesel fuels that we have studied in the past ranges from 18 to 20% (mass/mass, via ASTM D5186)<sup>33-38,40,41</sup> These lower aromatic fuels also typically had cetane numbers ranging between 51 and 52. As a further comparison, we present in Figure 1 representative chromatograms measured with gas chromatography (mass spectrometric detection) for a representative sample of the (a) LAD fuel and (b) higher aromatic diesel fuel. The low-aromatic fuel shows the classical pattern of strong *n*-alkane peaks among smaller branched alkane peaks. Indeed, this chromatogram is similar to those presented for diesel fuels in the Ignitable Liquids Reference Collection<sup>42</sup> sample reference numbers 0050, 0051, 0114, and 0108. Remarkable is the greater multiplicity of peaks in the high-aromatic fluid compared to the low-aromatic fuel. Both the highand low-aromatic fluids show the classical kerosene hump, while the high-aromatic fluid has (in addition) an atypical cluster of peaks (corresponding to numerous substituted aromatics) superimposed at the beginning of the hump.

*n*-Hexane used as a solvent in this work was obtained from a commercial supplier and was analyzed by gas chromatography (30 m capillary column of 5% phenyl/95% dimethyl polysiloxane, having a thickness of 1  $\mu$ m and temperature program from 50 to 170 °C, at 5 °C/min) using flame ionization detection and mass spectrometric

detection. These analyses revealed the purity to be approximately 99.9%, and the fluid was used without further purification.

The method and apparatus for the distillation curve measurement has been reviewed in a number of sources; <sup>19,43,44</sup> therefore, an additional general description will not be provided here. The required volume of fluid for the distillation curve measurement (in each case, 200 mL) was placed into the boiling flask with a 200 mL volumetric pipet. The thermocouples were then inserted into the proper locations to monitor  $T_k$  (signifying placement in the kettle; the temperature in the fluid) and  $T_h$  (the temperature at the bottom of the takeoff position in the distillation head). Enclosure heating was then commenced with a four-step program based on a previously measured distillation curve. Volume measurements were made in the levelstabilized receiver, and sample aliquots were collected at the receiver adapter hammock. In the course of this work, we performed between four and six complete distillation curve measurements for each of the fluid samples.

Because the measurements of the distillation curves were performed at ambient atmospheric pressure (measured with an electronic barometer), temperature readings were corrected for what should be obtained at standard atmospheric pressure (1 atm = 101.325 kPa). This adjustment was performed with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000 109.45,46 This value corresponds to a carbon chain of 12. In the chemical analysis of the diesel fuel sample (see above), as well as in previous work on diesel fuel, 33-38 it was found that *n*-dodecane can indeed represent the fluid as a very rough surrogate. The magnitude of the correction is of course dependent upon the extent of departure from standard atmospheric pressure. The location of the laboratory in which the volatility measurements reported herein were performed is approximately 1655 m above sea level, resulting in a typical temperature adjustment of 8 °C. The actual measured temperatures are easily recovered from the Sydney Young equation at each measured atmospheric pressure.



Figure 1. Chromatograms measured with GC-MS for the (a) HAD fuel studied here and, for comparison, (b) LAD fuel studied previously.

#### RESULTS AND DISCUSSION

Diesel fuel is a commodity fluid with seasonal and regional variations (or recipes), although the degree of variability is not as great as that of gasoline. This variability naturally limits the conclusions that may be drawn from any one sample; however, in this case, measurements have been performed on a research fuel that is well-characterized.

Density and Viscosity. The density of the diesel fuel was measured at atmospheric pressure with a commercial vibrating tube densimeter that had been calibrated with water and air. The laboratory in which density measurements were made is located at an elevation of 298 m (879 ft) above sea level, although the local atmospheric pressure is typically 100 kPa. The uncertainty in the measured sample temperature (during the density measurement) was 1 °C, because of the readability of the thermometer used. The actual uncertainty in temperature control was lower, at 0.5 °C. The combined propagated uncertainty of the density was 0.015%. The viscosity of the diesel fuel was measured at local atmospheric pressure (100 kPa) with a commercial tuning-fork-type viscometer that was calibrated with pure water. The uncertainty in the sample temperature was 0.05 °C, and the overall propagated uncertainty of the measured viscosity was 0.000 05 Pa s. The measured values for the density and viscosity at three temperatures are provided in Table 2.

 Table 2. Density and Viscosity Measured for the HAD Fuel

 Examined in This Work<sup>a</sup>

temperature (°C)	density (g/mL)	viscosity (Pa s)
5.1	0.8650	
14.0	0.8586	
24.7		0.00203
25.3	0.8504	
29.3		0.00185
33.9		0.00168

 $^{a}$ These measurements were made at 101 kPa. The uncertainties are discussed in the text.

Volatility: Initial Boiling Temperatures. During the initial heating of each sample in the distillation flask, the behavior of the fluid was carefully observed. Direct observation through the flask window or through the bore scope allowed for measurement of the onset of boiling for each of the mixtures (measured with  $T_k$ ). Typically, to characterize the initial boiling behavior, we measure the onset of bubbling, the temperature at which bubbling is sustained, and the temperature at which the vapor rises into the distillation head. This can be noted visually or by the rapid increase in the temperature of the thermocouple that monitors  $T_{\rm h}$ . We have shown that this last temperature is actually the initial boiling temperature (IBT; an approximation of the bubble point temperature at ambient pressure) of the initial fluid. This measurement is significant for a mixture because it can be modeled with an equation of state. Vapor rise is accompanied by a sharp increase in  $T_{\rm h\prime}$  is therefore far less subjective to ascertain, and thus, is less uncertain than the onset of bubbling. Experience with previous mixtures, including *n*-alkane standard mixtures that were prepared gravimetrically, indicates that the uncertainty in the onset of the bubbling temperature is approximately 1 °C. The uncertainty in the vapor rise temperature is 0.3  $^{\circ}C.^{19,20}$ 

In Table 3, we present the initial temperature observations for mixtures of the HAD fuel. These values have been adjusted

 Table 3. Summary of the Initial Boiling Behavior of the HAD
 Fuel with That of a LAD Fuel Provided for Comparison<sup>a</sup>

	HAD (°C, at 83.1 kPa)	LAD (°C, at 83.9 kPa)
onset	204.1	197.0
sustained	216.3	209.7
vapor rise	229.3	217.6

"The vapor rise temperature is that at which vapor is observed to rise into the distillation head, considered to be the IBT of the fluid. These temperatures have been adjusted to standard atmospheric pressure with the modified Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text.

to atmospheric pressure with the Sydney Young equation, as mentioned earlier. For comparison, we include the initial temperature observations for the LAD fuel sample. This fuel is low in aromatic content (as discussed earlier) and has been the basis of our prior work on diesel fuels with oxygenate additives.<sup>33–38</sup> We note that the HAD fuel that is the subject of the present study has an IBT that is 12 °C higher than that of the low-aromatic fluid. Likewise, the onset and sustained temperatures are also higher for the high-aromatic fuel.

**Volatility: Distillation Curves.** Representative distillation curve data (presented as  $T_k$ , measured directly in the fluid, and  $T_h$ , measured at the bottom of the head take off) for the HAD fuel are presented in Table 4. For comparison, data for the LAD

Table 4. Representative Distillation Curve Data (Given as the Average between Four and Six Distillation Curves) for the HAD Fuel with That of a LAD Fuel Provided for Comparison<sup>a</sup>

	HAD (83.1 kPa)		LAD (8	3.9 kPa)
distillate volume fraction (%)	$T_k$ (°C)	$T_{\rm h}$ (°C)	$T_k$ (°C)	$T_{\rm h}$ (°C)
0.025	229.7	209.1	217.9	181.6
5	233.3	220.3	225.5	206.8
10	237.2	225.6	230.1	212.4
15	240.9	229.3	235.4	219.3
20	245.1	233.4	240.9	224.3
25	249.2	237.6	245.9	229.2
30	253.7	242.1	251.2	235.2
35	258.2	246.8	256.5	241.0
40	263.2	251.8	261.9	246.1
45	268.3	256.8	268.2	252.0
50	273.7	262.1	273.8	257.4
55	279.0	267.5	280.2	264.6
60	285.0	274.3	287.1	271.7
65	291.0	280.8	294.3	279.0
70	296.8	287.0	301.6	285.4
75	303.2	293.6	310.0	294.7
80	311.1	301.3	319.2	303.5
85	319.5	309.6	328.9	312.6
90	329.4	320.1		

"The uncertainties are discussed in the text. These temperatures have been adjusted to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures.

fuel described above are also provided. The estimated uncertainty (with a coverage factor k = 2) in the temperatures is 0.3 °C. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case.

The uncertainty in the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) is 0.001 kPa. The relatively low uncertainties in the measured quantities facilitate modeling the results, for example, with an equation of state. We note from the data that there is always an appreciable difference in the temperatures measured at the  $T_{\rm h}$  and  $T_{\rm k}$  positions. This difference ranges from approximately 10 to 40 °C and averages approximately 12 °C for the HAD fuel and 15 °C for the LAD fuel. These observations indicate the absence of azeotropy between the major constituents of both diesel fuels, an observations with related fluids.<sup>47</sup>

The  $T_k$  data in Table 4 (for both fluids) are presented graphically in Figure 2, where the volatility characteristics are



**Figure 2.** Measured distillation curves  $(T_k)$  for the HAD fuel studied in this work. For comparison, the curve for the LAD fuel is also provided. Both curves are averages of three separate measurements. All of the temperatures were adjusted to a pressure of standard atmospheric pressure using the modified Sydney Young equation. Uncertainties are discussed in the text.

apparent. We note that the initial boiling temperature is presented as a hatch mark on the temperature axis. The LAD fuel shows higher volatility than the high-aromatic fluid, up to the 45% distillate volume fraction. This is consistent with our analyses in Figure 1. We also note a crossover after the 45% distillate volume fraction, subsequent to which the high-aromatic fluid becomes more volatile. This is also consistent with the measured composition presented earlier. We note from Figure 1 that the LAD fuel has more light normal and branched alkanes compared to the high-aromatic fuel (early in the chromatogram), while later, we note that the high-aromatic fuel is richer in heavier components (late in the chromatogram).

**Composition Channel Information.** While the gross examination of the distillation curves is instructive and valuable for many design purposes, the composition channel of the ADC approach can provide an even greater understanding and information content. One can sample and examine the individual fractions as they emerge from the condenser. Chemical analyses of each fraction, collected during distillation, were performed by GC–FID and GC–MS (on two separate instruments). In Figure 3, we provide chromatograms (performed by use of GC–MS) of the first drop and then 10, 50, and 80% distillate volume fractions. Here, one can see the progression from a large quantity of aromatic constituents (up to 10% distillate

volume fraction), then the disappearance of the aromatics, until finally only the heavy linear and branched aliphatics remain. These observations are consistent with the distillation curves of Figure 2 and, indeed, help explain the structure of those curves.

While a detailed peak-by-peak comparison can be made for each fuel as a function of the distillate fraction, a survey comparison can be performed with an analysis method that is based on ASTM method D2789.48-50 In this method, one uses GC-MS to classify hydrocarbon samples into six different types (moiety families) entirely based on the fragmentation behavior observed in mass spectra. The six different moieties are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (or aromatics), indanes and tetralins, and naphthalenes. While this method has many limitations and sources of uncertainty (we have reviewed the pitfalls elsewhere<sup>21,22</sup>) and is only specified for use on low-olefinnic gasoline samples, it is routinely used for all types of liquid fuel. Interpretation of these results should primarily emphasize fuel-to-fuel comparisons and secondarily emphasize detailed comparisons among the moieties in a given fuel. Thus, a comparison of the paraffinic content from two different fuels is very informative, while the comparison of the paraffinic content to the tetralin content in a given fuel should be approached with more caution. In Figure 4, we present the results of this analysis for the distillate volume fractions of the HAD fuel. We observe during the distillation an increase in the paraffins, monocyclopraffins, and dicycloparaffins in Figure 4a. Correspondingly, we observe in Figure 4b a slight decrease in indanes and tetralins and a gentle rise and fall in naphthalenes that crests at the 50% distillate volume fraction. The behavior of the alkylbenzenes is more striking; here, we observe a dramatic decline from 34% (v/v), leveling to approximately 12% (v/v). The change in the slope of this plot occurs at a distillate volume fraction of between 45 and 50% (v/v), consistent with the expectation from the distillation data.

**Enthalpy of Combustion.** The composition-explicit data channel of the ADC allows for the inclusion of thermochemical data, such as the enthalpy of combustion, to the distillation curve. The total enthalpy of combustion (which we represent as  $-\Delta H_c$ ) can be approximated by multiplying the enthalpy of combustion of each of the pure (or individual) components by the mole fraction of that component and then adding the contributions of the individual components to obtain the total enthalpy of combustion

$$-\Delta H_{\rm c} = \sum x_i (-\Delta H_i) \tag{1}$$

where the subscript i refers to the individual components that have been identified or selected.

We have discussed the contributions to the overall uncertainty of the total enthalpy of combustion elsewhere.<sup>51</sup> The main sources of uncertainty in the enthalpy of combustion calculation here are due to (1) uncertainty in the values tabulated for the individual enthalpy of combustion values for each component, (2) uncertainty in the measured mole fraction, and (3) uncertainty arising from the absence of data for experimental enthalpy of combustion for some of the constituents. There is also uncertainty in neglecting the enthalpy of mixing; however, this value has been shown previously to be less than 0.01% of the enthalpy of combustion for hydrocarbon species. Additionally, there may be uncertainty in the enthalpy of combustion because of the inability to resolve very closely related isomers via the analytical protocol, the complete misidentification of a component, and neglecting components



Figure 3. Chromatograms measured by GC-MS of the first drop and then the 10, 50, and 80% distillate volume fractions of the HAD fuel studied in this work. Details of the separation method are provided in the text.

present at very low concentrations. In past work, we determined that neglecting peaks with total uncalibrated area percentages of up to 4% increased the uncertainty of the calculated enthalpy by only 1.5%. Here, however, we included peaks that were 0.5% or larger; therefore, this source of uncertainty is very small. In view of these sources of uncertainty, the overall combined uncertainty in our total enthalpy of combustion calculations (with a coverage factor k = 2) was less than 3%.



**Figure 4.** (a and b) Results of the moiety family analysis performed on the HAD fuel with a modification of ASTM method D2789.

The uncertainty, as usual, is dominated by the analytical measurement and determination of the component mole fractions.

In Table 5, we provide the enthalpy of combustion of selected distillate volume fractions on a molar, mass, and volume

Table 5. Enthalpy of Combustion for Selected Distillate Fractions of the HAD Fuel Studied in This Work<sup>a</sup>

distillate volume fraction (%)	$-\Delta H_{\rm c}$ (-kJ/mol)	$-\Delta H_{\rm c}$ $(-{\rm kJ/g})$	$-\Delta H_{\rm c} \ (-{\rm kJ/L})$
0.025	5909 (295)	42 (2)	36045 (1802)
10	6284 (314)	42 (2)	36900 (1845)
50	7533 (377)	42 (2)	38373 (1919)
80	10042 (502)	46 (2)	41764 (2088)
composite	7888 (394)	43 (2)	38610 (1931)
<sup><i>a</i></sup> These data are provided	on a molar.	mass. and vol	ume basis. The

uncertainties, provided in parentheses, are discussed in the text.

basis. We note that the enthalpy of combustion on a molar basis increases as a function of the distillate cut. This is expected because the heavier compounds that distill at higher temperatures have higher molar enthalpies of combustion. We also provide the enthalpy of combustion for the composite fuel (starting fluid).

**Modeling.** From the analysis by GC–MS of the HAD fuel sample described earlier, we compiled a list of potential candidate fluids for the surrogate model. These fluids are listed in

Table 6 along with their normal boiling point and their boiling points at an atmospheric pressure of 83 kPa (the typical local pressure of our laboratory, located at 1655 m above sea level), their cetane numbers, and heats of combustion. Factors involved in the selection of the candidate fluids were the chemical types (straight and branched paraffins, cycloparaffins, aromatics, etc.), the boiling points (to span the temperature range observed over the course of the distillation curve), and the availability of experimental data (especially density, viscosity, vapor pressure, and cetane number). The exact fluids may not be present in the fuel, but the intent was to be representative of the chemical class. For each possible constituent fluid, we searched the literature and the DIPPR52 and NIST-TDE53 databases for experimental physical property data. For some of the fluids, the data were sparse and were supplemented with predicted values from the NIST-TDE and DIPPR programs.

Because our modeling approach<sup>25,26,28</sup> requires thermophysical property models for all pure constituent fluids, it was necessary to have available equations of state and a correlation for the viscosity for all of the potential constituent pure fluids. Details of the modeling procedure are available in other work;<sup>25,26,28</sup> therefore, we provide only a brief summary here. With the available experimental data supplemented with predictions obtained from the TDE program, we developed Helmholtz-form equations of state (similar to the form developed by Span and Wagner<sup>54</sup>). One may also use any equation of state that can adequately represent the target properties; for example, a volume-translated Peng-Robinson equation of state could also be used, although with some deterioration in the ability to model the density and distillation curve. For viscosity, we primarily used an extended corresponding states model,  $^{55,56}$  with *n*-dodecane or propane as a reference fluid.  $^{57,58}$ When sufficient data were available, the representation of the viscosity was improved by fitting the data to correction functions for the shape factors.<sup>56</sup> In the absence of experimental data, we used the predictive method by Van Velzen for viscosity, as implemented in the DIPPR DIADEM program.<sup>52</sup>

For calculations of the thermodynamic properties of mix-tures, we used the mixture model<sup>59-61</sup> incorporated into the REFPROP program.<sup>62</sup> This model includes an algorithm for estimating binary interaction parameters when data are unavailable for a particular fluid pair. The model for calculating the transport properties of a mixture is an extended corresponding states method.  $^{56,63-67}$  In addition, we used an algorithm developed in earlier work<sup>25</sup> to compute the distillation curve; this procedure incorporates data from the ADC metrology.<sup>18-22,43,44,68</sup> Cetane numbers for individual pure fluids were obtained from the work by Murphy et al.69<sup>+</sup> and Heyne et al.<sup>70</sup> or estimated by use of the work by Ghosh.<sup>71</sup> According to Murphy et al.,<sup>69</sup> the repeatability of the pure fluid cetane numbers in their compendium varies from 7.9 to 8.6%. The cetane number for a mixture was estimated by a linear volume fraction mixing rule,<sup>69,72</sup> as is common in the literature. The heats of combustion for components were obtained from the DIPPR DIADEM program, and a linear mole fraction average is used for mixtures, ignoring the enthalpy of mixing.<sup>51,73,74</sup>

The property measurements discussed earlier (density, viscosity, initial boiling point, and the ADC) and, additionally, the cetane number and heat of combustion reported for this fuel formed the basis of the experimental data set used to obtain the surrogate models. We used a multi-property, nonlinear regression procedure to minimize the differences between the experimental data and the predictions of the model to determine the Table 6. Potential Constituent Fluids for the Surrogate Fuel Mixtures

compound	CAS number	class <sup>a</sup>	number of carbon atoms	boiling point at 83 kPa (°C)	normal boiling point at 101.3 kPa (°C)	cetane number	enthalpy of combustion (-kJ/mol)	
1,2,4-trimethylbenzene	95-63-6	MA	9	161.7	169.4	7.7	4931	
<i>cis</i> -decalin	493-01-6	DP	10	187.3	195.8	42	5892	
trans-decalin	493-02-7	DP	10	178.9	187.3	31.8	5881	
tetralin	119-64-2	MA	10	199.2	207.7	8.9	5358	
1-methylnaphthalene	90-12-0	DA	11	235.8	244.8	6.9	5596	
<i>n</i> -dodecane	112-40-3	LP	12	208.1	216.3	88	7514	
n-hexylcyclohexane	4292-75-5	MP	12	216.6	225.3	65	7312	
1,3- diisopropylbenzene	99-62-7	MA	12	195.6	203.9	-7	6770	
2,6- dimethylnaphthalene	933-98-2	DA	12	252.8	261.9	-13	6168	
2-methyldodecane	1560-97-0	BP	13	222.2	230.6	50	8118	
n-heptylcyclohexane	5617-41-4	MP	13	236.1	244.8	79	7922	
n-tetradecane	629-59-4	LP	14	245.0	253.6	95	8733	
2-methyltetradecane	1560-95-8	BP	15	244.3	253.5	52	9337	
1,3,5- triisopropylbenzene	717-74-8	MA	15	235.6	244.7	2	8580	
n-hexadecane	544-76-3	LP	16	277.9	287.0	100	9951	
2-methylhexadecane	1560-92-5	BP	17	288.4	297.6	60	10556	
n-octadecane	593-45-3	LP	18	307.5	316.8	116	11172	
2-methyloctadecane	1560-88-9	BP	19	313.6	323.1	71	11775	
<i>n</i> -eicosane	112-95-8	LP	20	334.3	343.8	120	12391	
<sup>4</sup> BP, branched paraffin; MA, monoaromatic; DA, diaromatic; DP, dicyclic paraffin; LP, linear paraffin; MP, monocyclic paraffin.								

components and their compositions to define the surrogate fluid mixtures for the diesel fuel sample. The objective function was the weighted sum of the squared percentage differences between the experimental data and the predicted values.

$$F = W_{\rm IBP}F_{\rm IBP}^{2} + \sum_{i=1}^{N_{\rm dis}} W_{i,\rm dis}F_{i,\rm dis}^{2} + \sum_{i=1}^{N_{\rm p}} W_{i,\rho}F_{i,\rho}^{2} + \sum_{i=1}^{N_{\rm \eta}} W_{i,\eta}F_{i,\eta}^{2} + W_{\rm CN}F_{\rm CN}^{2} + W_{\Delta H}F_{\Delta H}^{2}$$
(2)

In eq 2, the weights for each data point are denoted by  $W_{\nu}$  the objective function is *F*, and the subscripts IBP, dis,  $\rho$ ,  $\eta$ , CN, and  $\Delta H$  refer to the data type (initial boiling point, distillation, density, viscosity, cetane number, and heat of combustion, respectively). Other types of information, such as the C/H ratio, could also be easily added to eq 2 if desired. The objective function components are defined as the percent deviations between the calculated value and the experimental value for each type

$$F_{\rm IBP} = 100 \times (T_{\rm IBP,calc} - T_{\rm IBP,exp}) / T_{\rm IBP,exp}$$
(3)

$$F_{\rm dis} = 100 \times (T_{\rm calc} - T_{\rm exp}) / T_{\rm exp}$$
<sup>(4)</sup>

$$F_{\rho} = 100 \times (\rho_{calc} - \rho_{exp}) / \rho_{exp}$$
<sup>(5)</sup>

$$F_{\eta} = 100 \times (\eta_{calc} - \eta_{exp}) / \eta_{exp}$$
<sup>(6)</sup>

$$F_{\rm CN} = 100 \times (\rm CN_{calc} - \rm CN_{exp})/\rm CN_{exp}$$
<sup>(7)</sup>

$$F_{\Delta H} = 100 \times (\Delta H_{\text{calc}} - \Delta H_{\text{exp}}) / \Delta H_{\text{calc}}$$
(8)

where T is an absolute temperature on the distillation curve, in kelvins. The weighting factors for each type of property data are found by trial and error based on the desired results.

For example, in this work, we place a major emphasis on the ADC; therefore, the weighting factors on the distillation points were increased until the distillation curve was matched to within one-half percent. The goals for additional properties are to represent the density to within 1%, the viscosity to within 10%, the heat of combustion to within 5%, and the cetane number to within 2 cetane numbers.

The process was initiated by assuming equal compositions of all of the components in Table 6. Successive calculations gave very small concentrations of some components, and these were removed from the mixture. The minimization process was repeated until further reductions in the number of components resulted in unacceptably large deviations from the experimental data. The minimization algorithm proceeded until a minimum was located, and because of the complex nature of the search space, this may not be the absolute minimum. Runs from different starting points were tried to investigate alternative solutions. The values of the final weights used in eq 2 and details on the numbers of points of the different types of data used are given in Table 7.

Table 7. Summary of Details from the Regression

		surrogate 1	surrogate 2
property	number of points	weight factor $(W_i)$	weight factor $(W_i)$
initial boiling point	1	2000	2000
distillation curve	17	800	800
density	3	100	1500
viscosity	3	1000	1000
cetane number	1	50	50
heat of combustion	1	200	200

Two models were selected to represent the fuel. Their compositions are given in Table 8. The first model has six components and represents the experimental data to within the

Table 8. Compositions of the Surrogate Mixture

Article

	surrogate 1 (si	ix component)	surrogate 2 (ni	ne component)
fluid	composition (mole fraction)	composition (mass fraction)	composition (mole fraction)	composition (mass fraction)
<i>n</i> -hexadecane	0.153	0.192	0	0
2-methylhexadecane	0	0	0.085	0.114
n-octadecane	0	0	0.067	0.095
2-methyloctadecane	0.153	0.228	0.054	0.081
n-eicosane	0.006	0.009	0.032	0.050
n-hexylcyclohexane	0	0	0.149	0.140
trans-decalin	0.061	0.047	0.053	0.041
1,3-diisopropylbenzene	0.276	0.248	0.188	0.170
1-methylnaphthalene	0.351	0.276	0.186	0.147
2,6-dimethylnaphthalene	0	0	0.186	0.162

desired targets. The calculated and experimental distillation curves are shown in Figure 5. Note that the curves shown in



Figure 5. ADCs of the HAD fuel sample, at 83 kPa. The experimental error bars are smaller than the plot symbols on the figure.

Figure 5 have not been adjusted with the Sydney Young equation; they are raw values at 83 kPa. In the regression process, the unadjusted temperatures are used. The highest temperature observed in the experimental distillation curve (at 83 kPa) was 320.5 °C; the only constituent fluid in Table 6 that has a temperature higher than this is n-eicosane. Therefore, it is impossible to attain the highest points in the curve without neicosane. A five-component model (with the same components as the six-component model, except without *n*-eicosane) was also tried, but we found that it could not represent the hightemperature end of the distillation curve; therefore, it was not selected here. The second model was chosen because, in addition to representing the data within the targeted ranges, it also contains representative fluids from all of the constituent chemical families identified in the chemical analysis (the sixcomponent model lacks single-ring paraffins). This model may be used if it is important to have all chemical families represented in the surrogate; otherwise, the two models are equivalent in their ability to model the properties of the fuel, as indicated in Table 9. In Table 9, we define the percent deviation  $P = 100 \times (X_{calc} - X_{exp})/X_{exp}$ , where  $X_{exp}$  is the experimental value of the property of interest and  $X_{calc}$  is the

Table 9. Comparisons to Experimental Data

		surrogate model 1 (six component)		surrogate model 2 (nine component)			
property	п	AAD	AVG	STDEV	AAD	AVG	STDEV
density	3	0.3	-0.3	0.003	0.6	-0.6	0.017
viscosity	3	1.6	1.6	1.07	1.0	0.0	1.1
IBT	1	0.1	-0.1	0	0.3	0.3	0
distillation curve	17	0.4	0.2	0.4	0.2	0.2	0.2
cetane number	1	1.4	1.4	0	0.05	-0.05	0
enthalpy of combustion	1	3.8	-3.8	0	4.4	-4.4	0

value calculated from the surrogate model. The average absolute percent deviation (AAD) is found with the expression AAD =  $(\sum |P|)/n$ , where the summation is over all *n* points. The average percent deviation is AVG =  $(\sum P)/n$ , and the standard deviation is STDEV =  $([n\sum P^2 - (\sum P)^2]/n^2)^{1/2}$ . Both models represent the density to within the target value of 1% and the viscosity to within 2%, which is well within the target of 10%. The initial boiling point behavior is captured well by both models, achieving agreement to generally within 0.3% (about 1.5 °C). The cetane number of both surrogates is within 2 cetane numbers of the experimental value, and the heat of combustion is modeled to within 5%.

The surrogate compositions in this study have not been optimized to represent cold-flow properties. Preliminary calculations comparing the experimental HAD cloud point to the calculated cloud point show that surrogate 1 predicts a cloud point that is 13 K too high and surrogate 2 predicts a cloud point 57 K too high. These preliminary comparisons demonstrate that the cloud point is an additional property that must be considered in the future when developing surrogate compositions. Future work will discuss incorporation of coldflow properties into surrogate compositions.

#### CONCLUSION

Determination of the best surrogate model depends upon the intended application. The surrogate models in this work were designed for the simultaneous representation of thermody-namic (density and volatility) and transport (viscosity) properties. In addition, we also modeled the cetane number and the heat of combustion. Comparisons to limited density and viscosity experimental data to the values calculated with the surrogate models are within 0.6 and 2%, respectively. The model represents the cetane number of the fuel to within 2 cetane numbers and the heat of combustion to within 5%.

The volatility behavior, indicated by the temperatures obtained from the ADCs, is reproduced to within 0.5%. The current work does not include the optimization of cold-flow properties.

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#### Notes

The authors declare no competing financial interest.

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