

Enthalpy of Combustion of Fuels as a Function of Distillate Cut: Application of an Advanced Distillation Curve Method[†]

Thomas J. Bruno* and Beverly L. Smith

Physical and Chemical Properties Division, National Institute of Standards and Technology,
Boulder, Colorado 80305-3328

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In previous work, several significant improvements in the measurement of distillation curves for complex fluids were introduced. The modifications to the classical measurement provide for (1) temperature and volume measurements of low uncertainty, (2) temperature control based upon fluid behavior with a model predictive temperature controller, and, most important, (3) a composition-explicit data channel in addition to the temperature–volume relationship that usually comprises the measurement. This latter modification was achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, during the measurement of the distillation curve. In this paper, we utilize the composition-explicit information to characterize distillate cuts in terms of available energy content. This is critical information in the study of real fuels. The measure we use for the fluid energy content is the composite enthalpy of combustion for each component selected for identification in each distillate fraction. As a test system, we present the distillation cuts of two prepared mixtures of *n*-decane + *n*-tetradecane. Then, as a further illustration of the approach, we present an analysis of distillate fractions of a 91 antiknock index (AI) gasoline and a 91 AI gasoline with 15% methanol (vol/vol) added.

Introduction

One of the most important and informative engineering properties that is measured for complex fluid mixtures is the distillation (or boiling) curve.¹ Simply stated, the distillation curve is a graphical depiction of the boiling temperature of a fluid mixture plotted against the volume fraction distilled. One most often thinks of distillation curves in the context of petrochemicals and petroleum refining, but such curves are of great value in assessing the properties of any complex fluid mixture.² For crude petroleum, the distillation curve can be divided into distinct regions that contain: butanes and lighter, gasoline, naphtha, kerosene, gas-oil, and residue. The temperature at each of these cuts or regions provides an idea of the volatility of each cut. Products resulting from petroleum crude as multicomponent mixtures, such as gasoline, diesel fuel, jet fuel, kerosene, rocket propellant, and missile fuel are also characterized by their respective distillation curves as a function of component volatility.¹

The information that can be inferred from the distillation curve extends well beyond the rough description in terms of fluid mixture volatility.^{3–8} For example, it has been possible in recent years to relate the distillation curve to operational

parameters of complex liquid fuels. These parameters include engine starting ability, vehicle drivability, fuel system icing and vapor lock, the fuel injection schedule, fuel autoignition, etc.^{9–12} The front end (low temperature region) of the distillation curve of gasoline (up to approximately 70 °C) is used to assess and optimize ease of starting and the potential for hot weather vapor lock in engines. The midrange of the gasoline curve (up to a temperature of approximately 100 °C) is used to assess and optimize cold weather performance, the operational readiness of a hot engine, and the acceleration behavior of a hot engine under load. The top range of the distillation curve is used to assess and optimize fuel economy in a hot engine. In addition to these applications to performance optimization and design, the distillation curve provides an avenue to long term trend analysis of fuel performance, since changes in the distillation curve are related to changes in fuel performance.^{9,13} Beyond these operational and design applications, distillation curves are

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* To whom correspondence should be addressed. E-mail: bruno@boulder.nist.gov.

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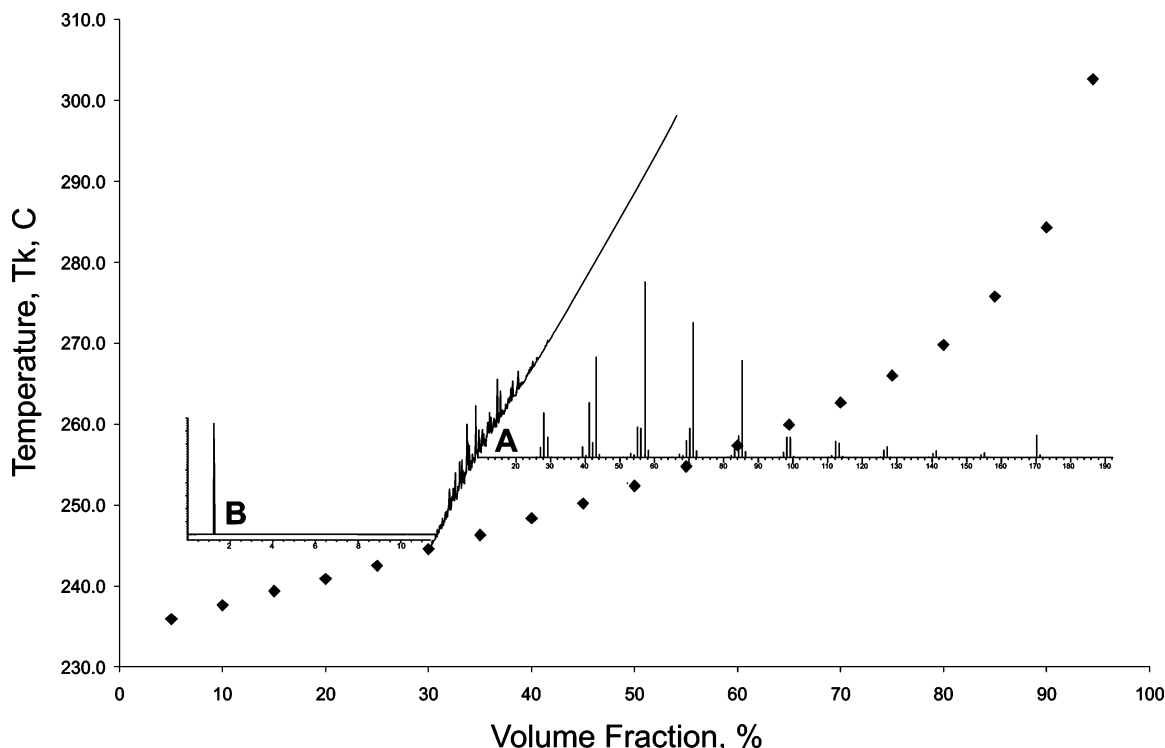


Figure 1. Distillation curve for RP-1, in which the chromatogram for the volume fraction at 30% is shown. Analytical samples were routed into a mass selective detector (inset A) and a sulfur chemiluminescence detector (inset B). The mass spectrum of the largest peak allows the identification of *n*-dodecane. The sulfur detector shows the total sulfur budget of the fraction.

important in evaluating the environmental impact of the use of complex liquid fuels and the reclamation of waste.^{14–17}

The most common presentation of the distillation curve is a plot of boiling temperature (at ambient pressure) against volume fraction. The ASTM D-86 standard test method provides the usual approach to the measurement, in which the data obtained are the initial boiling temperature (IBT), the temperature at volume fractions of 10, 20, 30, 40, 50, 60, 70, 80, and 90%, and then the final boiling temperature (FBT).¹⁸ The method historically suffers from major disadvantages, and recently, we have developed several improvements to the metrology. These improvements are discussed in detail elsewhere, so only a very brief summary will be provided here.^{19–22}

Our modifications to the classical measurement provide for (1) temperature and volume measurement(s) of low uncertainty, (2) temperature control based upon fluid behavior (with a model-

predictive temperature controller), and, most important, (3), a composition-explicit data channel in addition to the temperature–volume relationship that usually is measured. This latter modification was achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, during the measurement of the distillation curve. Thus, for the typical distillation curve presented as temperature against volume fraction, we can also perform (for each fraction) a quantitative and qualitative chemical analysis. An example of such information is presented in Figure 1, in which a distillation curve of the rocket fuel RP-1 is shown.²¹ Here, the plot shows the temperature–distillate volume fraction pairs as is typical for a distillation curve. For the 30% distillate volume fraction, a chromatogram of the fraction is illustrated. This chromatogram resulted from sampling the 30% fraction during the measurement of the distillation curve. For that chromatogram, the mass spectrum of the most intense chromatographic peak is displayed (allowing the identification of *n*-dodecane). Moreover, a total sulfur analysis, measured with a sulfur chemiluminescence detector, has also been obtained for this fraction and is provided. These serve as examples of the information that becomes available upon the application of any appropriate analytical technique. The usefulness of such information for process design and optimization is clear.

For the advanced distillation curve approach, the uncertainty in temperature measurement is 0.05 °C and the uncertainty in the volume measurement is 0.05 mL (coverage factor $k = 2$). In addition to the lower uncertainty, the temperature measured with the advanced approach is an actual fluid state point that can be modeled theoretically. The temperature measured with

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the traditional approach has no such basis in theory; its only importance comes from the fact that the method is standardized (that is, everyone performs the test in the same way).

The uncertainty in quantitative composition measurements in the advanced approach is dependent upon the individual calibration and the specific analytical method that is employed. The uncertainty in the qualitative identification of components is also dependent on the analytical technique that is chosen and the information content of the resulting signal.

The chemical analysis made possible by the advanced distillation curve approach provides an avenue to extend the descriptive chemistry applications and add thermochemical data to the distillation curve. In the case of fuels, it is clear that knowledge of, for example, the enthalpy of combustion of each fraction of the distillation curve would be invaluable. Fortunately, the enthalpy of combustion is a well-known thermochemical quantity, tabulated in several reliable databases.^{23,24} Thus, for a mixture, even a complex mixture, knowledge of the identities of the chemical components and their relative concentrations allows access to the composite enthalpy of combustion of the mixture. In this way, the composition-explicit data channel of the advanced distillation curve approach allows determination of the composite enthalpy of combustion of each distillate fraction.

As an example, in this paper, we present the composite, fraction by fraction enthalpy of combustion for two test systems. The first system consists of test mixtures of *n*-decane + *n*-tetradecane (mixtures having initial mole fractions of 50/50 and 75/25). The second system consists of two real gasoline mixtures. One is a straight premium grade 91 antiknock index (AI) fuel, and the other, a 15% (vol/vol) mixture of this gasoline with methanol, as an example of an oxygenate gasoline. The antiknock index cited above is the average of the research octane number and the motor octane number.

Theory

The enthalpy of combustion is the heat released when a given amount of a combustible pure substance is burned (in oxygen) to form incombustible products (e.g., water and carbon dioxide). For example, the combustion reaction of *n*-octane is



which results in an enthalpy of combustion of -5074 kJ/mol.²³ This thermochemical quantity is a characteristic of the substance. Enthalpies of combustion are routinely used as a basis for comparing the heating value of fuels, since the fuel that produces the greater amount of heat for a given cost is often the more economical. Enthalpies of combustion of pure substances are also used in comparing the stabilities of chemical compounds. One must be explicit in terms of the definition of the enthalpy of combustion, since it is possible to define the water produced in terms of vapor or liquid.²⁵ If the enthalpy is specified in terms of $H_2O(g)$, then the enthalpy is called the net heat or net enthalpy of combustion. If the enthalpy is specified in terms of $H_2O(l)$, then the result is called the gross heat or gross enthalpy of

Table 1. Composite Enthalpy of Combustion, ΔH_c , for the Distillation Curve Data of a 50/50 Mol Fraction Mixture of *n*-Decane + *n*-Tetradecane (Actual Starting Composition: 0.499/0.501)^a

distillate vol fraction, %	temp, °C	<i>x</i> , C ₁₄	$-\Delta H_c$, comp, kJ/mol	uncertainty, kJ/mol
0.025	196.5	0.034	6376.9	14
15	197.7	0.082	6494.0	15
25	204.3	0.104	6547.6	16
35	213.8	0.125	6598.9	17
50	236.7	0.584	7718.3	51
65	244.0	0.951	8613.3	83
75	244.4	1	8732.8	87
85	244.4	1	8732.8	87
98	244.4	1	8732.8	87

^a The temperature listed is that of the emergent distillate fraction.

combustion. The difference between the two values is the enthalpy of vaporization of water. Throughout this paper, we will use the net enthalpy of combustion, in which the product specification is for $H_2O(g)$.²³

In the case of mixtures, the situation is complicated slightly by the enthalpy of mixing, although in most practical situations this is not a concern.²⁶ The enthalpy of combustion is much larger than the enthalpy of mixing for hydrocarbon species. For example, a typical enthalpy of mixing, that of *n*-hexane + toluene, is 0.8–0.9 kJ/mol. Since this is in the range of 0.02% of the enthalpy of combustion and most tabulated enthalpies of combustion (for hydrocarbons) report uncertainties between 0.2 and 3%, we will neglect this effect. Ignoring the enthalpy of mixing, the composite enthalpy of combustion, which we will represent as $-\Delta H_c$, can be found 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 individual components to obtain the composite result:

$$-\Delta H_c = \sum x_i (-\Delta H_i) \quad (2)$$

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

Experimental Section

The apparatus used for advanced distillation curve measurements has been described above in brief. More details are to be found in refs 19–22.

The research grade *n*-decane and *n*-tetradecane were obtained from a commercial supplier. The purity was checked with gas chromatography (with a 30 m capillary column of 5% phenyl polydimethyl siloxane having a thickness of 1 μ m and a temperature program from 90 to 225 °C at 7 °C/min) using flame ionization detection and mass spectrometric detection. The purity was found to be better than 99.99% (mass/mass), and the fluids were used as received. The mixtures (at a nominal 50/50 and 75/25 mole percent; actual compositions are provided in Tables 1 and 2) were prepared gravimetrically as stock solutions. The uncertainty of the mass measurement was 0.0002 g, based on replicate measurements. The methanol used in this work was HPLC grade, with a purity listed at 99.9% and a moisture content of 0.001 percent. The purity was checked with gas chromatography (with a 30 m capillary column of 5% phenyl polydimethyl siloxane having a thickness of 1 μ m and a temperature program from 40 to 110 °C at 5 °C/min) using flame ionization detection and mass spectrometric detection. The purity was found to be better than 99.9% (mass/mass), and the fluid was used as received. Care was taken to minimize the exposure of

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Table 2. Composite Enthalpy of Combustion, ΔH_c , for the Distillation Curve Data of a 75/25 Mol Fraction Mixture of *n*-Decane + *n*-Tetradecane (Actual Starting Composition: 0.747/0.253)^a

distillate vol fraction, %	temp, °C	<i>x</i> , C ₁₄	$-\Delta H_c$, comp, kJ/mol	uncertainty, kJ/mol
0.025	184.6	0.014	6328.1	14.0
20	188.0	0.031	6369.6	14.0
30	190.5	0.042	6396.4	14.1
40	194.2	0.05	6409.6	14.1
50	199.5	0.071	6467.2	14.6
60	209.4	0.125	6598.9	16.6
65	217.7	0.152	6664.7	18.0
70	228.7	0.227	6847.6	22.8
80	249.3	0.827	8310.9	72.2
95	265.1	1	8732.8	87
98	265.1	1	8732.8	87

^a The temperature listed is that of the emergent distillate fraction.

the fluids to the atmosphere, so that water uptake by the mixtures could be minimized.

The premium grade gasoline used in this work was obtained from a commercial supplier and had an antiknock index (AI) rating of 91 listed on the specification. This fluid was analyzed by gas chromatography (with a 30 m capillary column of 5% phenyl dimethylpolysiloxane having a thickness of 1 μ m and a temperature program from 50 to 170 °C at 7 °C/min) using flame ionization detection and mass spectrometric detection. When the mass spectrometer was used for identification, spectra were recorded by scanning from a relative molecular mass of 15 to 550, with the mass spectra presented as ion abundance plotted against *m/z* (defined as the ratio of ion mass to ion charge). This analysis showed a large fraction of aromatic constituents, consistent with the relatively high antiknock index number.

Distillation curves for the two mixtures of *n*-decane + *n*-tetradecane and for the gasoline and the gasoline + methanol blend were measured with the apparatus described in the Introduction. For the *n*-decane + *n*-tetradecane mixtures, aliquots of 7 μ L of emergent distillate were withdrawn at specified volume fractions (shown in Tables 1 and 2) and added to a vial containing a known mass of solvent (*n*-hexane). Samples were taken to correspond to temperature–volume fraction data pairs, thus providing a composition channel of data to accompany the temperature-explicit distillation curve. Distillate cut samples, in *n*-hexane, were then analyzed with a gas chromatographic method (with a 30 m capillary column, 0.250 mm o.d., coated with 1 μ m of dimethyl polysiloxane, and temperature programmed from 90 to 250 °C at 8 °C/min, autosampler injection into a split injector set at 100:1, and flame ionization detection). Calibration was provided by external standards (a mixture of *n*-alkanes from C₉ to C₁₅) measured before and after each solution cut. The uncertainty in mole fraction of the compositions so determined was approximately 0.0005.

For the gasoline mixtures, the same procedure was used for the measurement of the distillation curves. Since gasoline is a complex multicomponent mixture, a different approach was needed for the composition channel. Here, aliquots of 7 μ L of emergent fluid fractions were withdrawn at specified fractions and added to a vial containing a known mass of solvent (*n*-dodecane). The use of *n*-dodecane as the solvent stabilized the samples in that the resulting mixture was less prone to the loss of the more volatile constituents. In this way, the *n*-dodecane serves as a solvent and as a “keeper” (much the same way as a drop of mineral oil is used when concentrating analytical samples in a Danish Kuderna concentrator tube during a nitrogen blowdown).²⁷ The *n*-dodecane elutes well after all of the gasoline peaks have eluted and poses no chromatographic interference. For the gasoline samples, a gas chromatographic method was used with mass spectrometric detection. This allowed the qualitative identification of the components of each

fraction, in addition to the quantitative determination. Because of the complexity of the mixtures, it was not practical to calibrate for each component, and instead, measured response factors were applied to extract ions that constitute the total ion chromatograms obtained from the mass spectrometer. The aromatic hydrocarbons were standardized with mixtures of toluene + ethyl benzene and the xylenes. The aliphatic hydrocarbons were standardized with mixtures of toluene + hexane, toluene + heptane, and toluene + 2,3-dimethyl hexane. Several mixtures of toluene + methanol were used to standardize the mixtures that contained methanol. This approach to standardization was checked with several binary mixtures (*n*-heptane + *n*-octane, *n*-octane + ethylbenzene), that were gravimetrically prepared. The uncertainty in the mole fraction determinations was approximately 10%, on the basis of replicate measurements. All of the measurements and checks that were performed indicate a lower uncertainty, between 6 and 8%, but we have chosen to be more conservative with a claim of 10%. While this uncertainty is much higher than that obtained for the binary *n*-decane + *n*-tetradecane solutions, this is to be expected considering the complexity of the gasoline fractions. A more detailed discussion of the total overall uncertainty will be provided in the next section.

The choice to measure a methanol blend as a representative oxygenate gasoline requires some discussion. Although gasoline + methanol blends have been used commercially as oxygenates, the more common commercial alcohol oxygenate is, of course, made with ethanol. Methanol was chosen as the oxygenate in this work because it causes a far more pronounced azeotropic inflection in the distillation curve than does ethanol. The azeotropic inflection is a pronounced flattening of the distillation curve, making the curve resemble that of a pure fluid. For this reason, the mixtures with methanol pose a much greater challenge in the measurement when a model-predictive temperature controller is employed.²² We therefore chose to focus on methanol mixtures in the development of the advanced distillation curve approach, since the test of the temperature control of the advanced approach would be more stringent.

Results and Discussion

***n*-Decane + *n*-Tetradecane Mixtures.** The composite enthalpy of combustion, $-\Delta H_c$, as a function of distillation volume fraction for the 50/50 mol % starting mixture of *n*-decane + *n*-tetradecane is provided in Table 1. Also provided is the temperature associated with the emergence of the fraction. Thus, for the 50/50 (mole/mole) mixture, the 35% volume fraction emerges at 213.8 °C. The uncertainties in the composite enthalpies of combustion arise from the uncertainty in the mixture composition (taken as 0.0005 in mole fraction) and the published uncertainty of the enthalpy of combustion of *n*-decane (−6294 kJ/mol, uncertainty 0.2%) and *n*-tetradecane (−8732.8 kJ/mol, uncertainty 1%). More significant figures than are warranted by the uncertainty are provided here in order to be consistent with the presentation in the databases.

Some comments about the uncertainties listed in the database are in order. The actual uncertainty listed for the *n*-tetradecane was “>1%”. Indeed, the original measurement indicates that an uncertainty closer to 0.1% would be appropriate.²⁸ In this paper, we adopt a more conservative approach and apply the (perhaps unrealistically) larger uncertainties given in the database, since we require the more extensive data collection of these database²³ in order to treat the more complex gasoline mixtures.

At volume fractions above 75%, no *n*-decane can be detected in the distillate by chromatographic analysis. Because of this,

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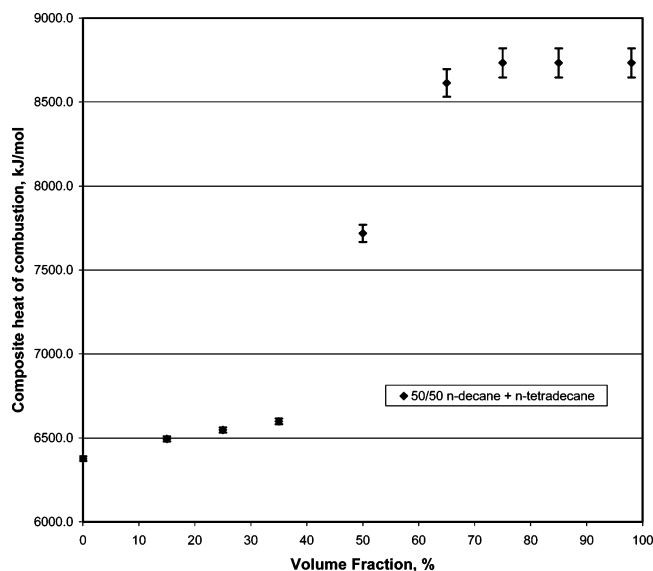


Figure 2. Plot of the composite enthalpy of combustion, $-\Delta H_c$, of the distillate volume fractions from a starting mixture of 50/50 (mol/mol) *n*-decane + *n*-tetradecane. The uncertainty bars represent a coverage factor $k = 2$.

the mole fraction of *n*-tetradecane is listed as 1. This is not strictly the result of a mole fraction determination, which would be subject to the usual uncertainties inherent in the chemical analysis. It is merely noting the absence of one peak. For this reason, the uncertainty of these points is simply the uncertainty in the enthalpy of combustion of *n*-tetradecane, with no contribution from the analytical measurement. We note that more significant digits are listed for the composite enthalpies of combustion than are actually warranted based on the uncertainty. As with the pure components discussed above, this is done to maintain consistency with the practice of thermo-physical property databases and to facilitate calculations done with the composite enthalpies of combustion.

A plot of the composite enthalpy of combustion against volume fraction is provided in Figure 2. The uncertainty, presented with a coverage factor $k = 2$ (that is, two standard deviations), increases with volume fraction as the mixture becomes richer in *n*-tetradecane. The plot is sigmoidal in shape, due to the effect of the binary mixture of components with different molecular sizes. Reflected in this plot is the leveling off of the composite enthalpy of combustion at volume fractions above 75%. One can infer from the plot that, for the mixture, the composite enthalpy of combustion increases moderately up to a volume fraction of approximately 45%, whereupon it increases sharply and ultimately becomes constant.

For the 75/25 mol % starting mixture of *n*-decane + *n*-tetradecane, the composite enthalpy of combustion as a function of distillation volume fraction is provided in Table 2 and plotted in Figure 3. Again, the listed uncertainty reflects the uncertainty in composition and the enthalpy of combustion of the pure components, except for volume fractions above 95%. Here, the uncertainty is only due to the uncertainty in the enthalpy of combustion of *n*-tetradecane. For this mixture, richer in *n*-decane, the moderate increase in enthalpy of combustion is observed until a volume fraction of approximately 60% is reached, whereupon it increases sharply as the distillate fluid becomes pure *n*-tetradecane.

Gasoline Mixtures. Assessing the uncertainty in the composite enthalpy of combustion for a more complex mixture such as a gasoline fraction is somewhat more complex than was the uncertainty analysis for the *n*-decane + *n*-tetradecane mixtures.

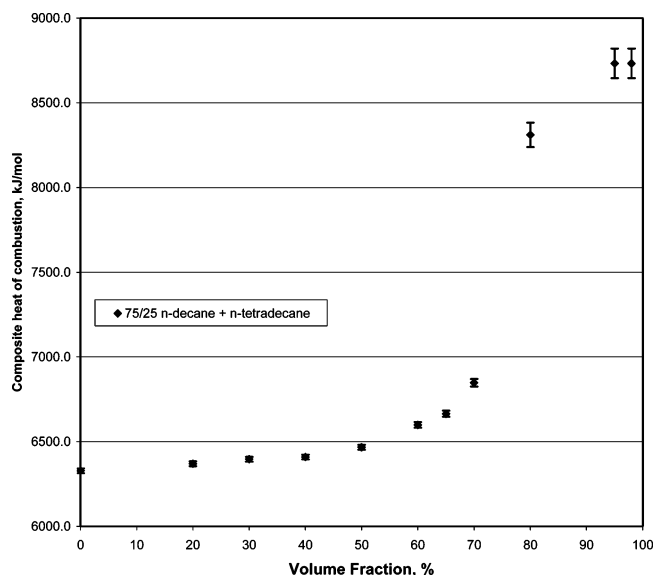


Figure 3. Plot of the composite enthalpy of combustion, $-\Delta H_c$, of the distillate volume fractions from a starting mixture of 75/25 (mol/mol) *n*-decane + *n*-tetradecane. The uncertainty bars represent a coverage factor $k = 2$.

For the gasoline samples, there are four major contributions to the uncertainty that must be considered: the uncertainty in the pure component enthalpy of combustion, the random uncertainty in the quantitative analytical determination, the systematic uncertainty that can potentially be introduced by a complete misidentification of a component, and the effect of neglecting minor peaks. We will discuss all four of these contributions.

The uncertainty in the pure component enthalpy of combustion is typically provided in reliable databases as a percentage.²³ The uncertainty commonly varies between 0.2 and 3%, depending upon the original source. All of the enthalpies of combustion that have been used in this work are experimental values rather than predictions; predictions may be expected to have a larger uncertainty. The experimental uncertainty for each enthalpy of combustion listed in the database was used directly in the uncertainty propagation.

The next source of uncertainty in the composite enthalpy of combustion to be considered lies in the measured molar composition of the distillate fraction. The area counts that are obtained directly from the total ion chromatogram cannot be used for a quantitative determination. Standardization is required, and this is done on the basis of extracted ions (sometimes called single ion monitoring or selected ion monitoring, SIM).²⁹ Several mixtures of toluene + methanol were used to standardize the mixtures that contained methanol. The methanol mole fractions are therefore known to within 1%. We note that methanol co-elutes with butane (always noted as a dissolved gas present in gasoline) on the stationary phase used in this work. Choosing another stationary phase is not practical, since a 5% phenyl polydimethyl siloxane is generally the best for a mixture of aliphatic and aromatic hydrocarbons. A consequence of this co-elution is that the analysis of the gasoline mixtures cannot be done with flame ionization detection. We therefore had to use extracted ions at $m/z = 30-33$ for the methanol determination. The aromatic hydrocarbons were standardized with mixtures of toluene + ethyl benzene and the xylenes. The aliphatic hydrocarbons were standardized with mixtures of toluene + hexane, toluene + heptane, and toluene + 2,3-dimethyl hexane.

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Table 3. Major Components Determined by Gas Chromatographic Mass Spectrometric Analysis of the First Drop (0.025% Volume Fraction) of Distillate from the Advanced Distillation Curve Measurement of (A) 91 AI Gasoline and (B) 91 AI Gasoline + 15% (vol/vol) Methanol^a

(A) 91 AI Gasoline		
compound	enthalpy of combustion, $-\Delta H$, kJ/mol	% molar composition
2-methyl butane	3239.5	23.4
2-methyl pentane	3849.2	17.6
<i>n</i> -hexane	3855	7.7
benzene	3136	5.1
methyl cyclopentane	3674	16.1
2,2,3,3-tetramethyl butane	5063.9	3.8
<i>n</i> -heptane	4464.7	2.4
2,3,3-trimethyl butene	4329.9	0.7
toluene	3734	18.6
ethyl benzene	4345	1.0
1,4-dimethyl benzene	4333	3.8
1,2-dimethyl benzene	4333	0.9
(B) 91 AI Gasoline + 15% Methanol		
compound	enthalpy of combustion, $-\Delta H$, kJ/mol	% molar composition
methanol	638.2	39.5
2-methyl butane	3239.5	6.1
<i>n</i> -pentane	3239.5	4.7
2-methyl pentane	3849.2	5.9
3-methyl pentane	3851.4	2.7
<i>n</i> -hexane	3855.1	3.7
methyl cyclopentane	3674.1	1.4
benzene	3136	7.1
3-methyl hexane	4462.7	1.9
2,2,4-trimethyl pentane	5065.3	2.4
toluene	3734	18.7
1,4-dimethyl benzene	4333	4.6
ethylbenzene	4345	1.3

^a The uncertainties in the enthalpies of combustion are between 0.2 and 3%; the uncertainty in the composition is 10%.

The standardization was checked with binary mixtures containing other aliphatic hydrocarbons. Since we were unable to standardize for each component (due to the multiplicity of components found in gasoline), we assign an uncertainty in our measured composition of each component in the individual gasoline fractions to be 10%.

The next source of uncertainty that we will consider is the possibility of a complete misidentification of the component. This would, of course, lead to the application of the incorrect pure component enthalpy of combustion. To minimize the potential of a misidentification, a stringent procedure was followed in the analysis of each component.

For each chromatographic peak, mass spectra were examined at the leading edge, trailing edge, and apex of the peak. This was done to ensure mass spectral purity. When two peaks closely elute, for example, there is inevitably some chemical impurity of the overlapping tails of the peak. Examining the chromatographic peak for mass spectral purity ensures that the most reliable region will be chosen for the identification. In some cases, an average over the entire peak is the most appropriate basis for examination.

For each chosen mass spectrum, a background spectrum was subtracted that included traces of nitrogen and water. This simplified subsequent analysis by removing extraneous *m/z* peaks. The parent ion was identified independent of software, approximate molecular mass and isotopic calculations were done as a guide, and fragmentation patterns were noted.^{30,31} The peak

Table 4. Composite Enthalpies of Combustion as a Function of Distillate Fraction for the Two Gasoline Mixtures^a

distillate vol fraction, %	$-\Delta H_c$, composite, kJ/mol, gasoline	$-\Delta H_c$, composite, kJ/mol, gasoline + 15% methanol	% diff
0.025	3708.5 (152)	2510.2 (93)	33.1
45	4523.1 (185)	3869.7 (158)	14.4
80	4937.8 (202)	4929.9 (202)	0.2

^a The uncertainties (also in kilojoules per mole) for each composite enthalpy are provided in parentheses. The percent difference between the two gasoline mixtures is included as well.

apex and the leading and following edges were checked for consistency. A search of the NIST-EPA mass spectral database was then performed.³² In most cases, the results from the database search were consistent with what was expected on the basis of the initial examination of the mass spectrum. Difficulties arose in differentiating closely related isomers of species that were found in relatively low concentrations (that is, with small peaks). In some cases, only the parent ion and one fragment ion *m/z* peak was available for up to three components. These could only be identified as an isomeric family (for example, the *x,y*-diethyl benzenes). In these cases, the order of the isomers was determined by published retention indices or by past experience with the stationary phase characteristics. The difference in the enthalpy of combustion between these kinds of closely related isomers is very small, typically far less than the experimental uncertainty in the measurement. As a conservative position, however, we adjusted the contribution to the overall uncertainty when, in these cases, the identity of the component was somewhat uncertain. Here, we used a coverage factor of 2.5 instead of 2 in the uncertainty propagation of the mole fraction to obtain the uncertainty of the composite enthalpy of combustion. The combined effects of these three major sources of uncertainty were considered in determining the overall uncertainty of the composite enthalpy of combustion for the gasoline fractions. This resulted in an overall 4.1% uncertainty.

It is interesting to note that if all of the pure component enthalpies of combustion listed in the database²³ are assumed to have an uncertainty of 3% (the highest uncertainty given for any of the values required in this work), the overall propagated uncertainty in the composite enthalpy of combustion only rises to 4.2%.

The final source of uncertainty that we will treat concerns the minor or trace constituents that are not included in the integration of the total ion chromatogram of each of the distillate volume fractions. It is important to note that although a gasoline sample can be expected to have several hundred components, individual distillate fractions typically have far fewer, with the total number close to 50–60 constituents per fraction. Often, these peaks appear as shoulders on larger peaks and simply cannot be reliably identified as individual peaks. In such cases, the integrated area of these shoulders is included with the main peak. In other instances, the peaks are simply too small (that is, the signal is too low) to allow reliable identification and quantitation, even if they are baseline-resolved. Our approach is to consider a “quorum” of compounds having peak areas in excess of 1% of the total uncalibrated peak area. Indeed, in related work on gas turbine fuel, we determined the effect of setting the analytical cutoff at increasing levels. This was done by only considering peaks with area percentages of 1, 2, 3, and

(31) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Fundamental Spectroscopic Correlation Charts*; Taylor and Francis CRC Press: Boca Raton, FL, 2005.

(32) NIST/EPA/NIH Mass Spectral Database, S. R. D., SRD Program, National Institute of Standards and Technology: Gaithersburg, MD, 2005.

(30) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Basic Tables for Chemical Analysis*, 2nd. ed., CRC Press: Boca Raton, FL, 2004.

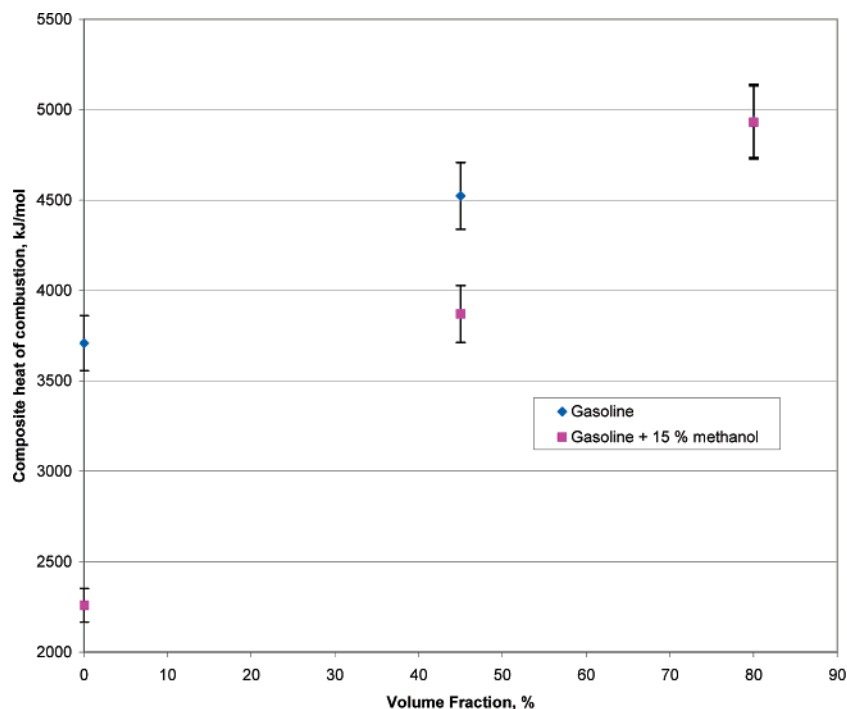


Figure 4. Plot showing the composite enthalpy of combustion, $-\Delta H_c$, for selected distillate volume fractions of 91 AI gasoline and the same gasoline with 15% methanol (vol/vol). The uncertainty bars represent a coverage factor $k = 2$. The plotting symbols at the 80% distillate volume fraction overlap.

4%. We found that this increased the uncertainty modestly, increasing the uncertainty only by 1.5% at a cutoff in area of 4%. We therefore expect the neglect of minor components to be a minor source of uncertainty that will not affect the uncertainty of the composite enthalpy in a significant way.

In Table 3a and b, we present the analytical results of the first drop of distillate to emerge from the advanced distillation curve instrument for the 91 AI gasoline and the 15% (vol/vol) methanol mixture. We have included the major components only (mole percentages in excess of 1%) for this analysis. Also provided are the pure component enthalpies of combustion. The compositions are consistent with what is expected for a relatively high octane number motor gasoline, with a relatively high percentage of aromatic constituents, even at the first drop of distillate. Similar analyses were done for the 45 and 80% distillate volume fractions, although the results of these analyses are not shown.

In Table 4, we present the composite enthalpy of formation as a function of several distillate volume fractions for the two gasoline mixtures. The uncertainty for each composite enthalpy is provided in parentheses, as well as the difference that is observed between the straight gasoline and the 15% methanol blend (expressed as a percent). These results are plotted in Figure 4.

Although it is often reported from many sources that gasoline oxygenates have a lower energy content (and therefore result in lower vehicle mileage), it is often difficult to quantitate these kinds of differences. While an overall analysis and composite enthalpy calculation for the fuel is valuable, it is clear that coupling such information with the distillation curve is far more informative. There is a dramatic difference in the energy content of the two fluids in the early part of the distillation curve. For the 0.025 distillate volume fraction, this difference is approximately 33%. Recall that this part of the distillation curve of gasoline motor fuels is indicative of ease of starting and the potential for hot weather vapor lock in engines. At the midrange of the distillation curve, the difference is still very large at 14%.

This region of the curve is indicative of cold weather performance, the operational readiness of a hot engine, and the acceleration behavior of a hot engine under load. We note that, at the latter part of the curve, the composite enthalpies of combustion of the two mixtures begin to approach one another. Indeed, by the 80% distillate volume fraction, they are the same, within experimental error.

We note that in this work we have chosen to present the thermochemical information in terms of kilojoules per mole. This presentation is especially useful for design and modeling studies, since thermochemical information presented in this way are fundamental values. A practical alternative would be a presentation in terms of volume expressed as kilojoules per liter. This is a simple change, requiring only the density of each identified compound at a particular temperature of interest. Thus, for the data in Table 3a and b, one can find the liquid molar volumes (or densities) of each constituent at 25 °C and calculate the composite enthalpy of combustion for the 91 AI gasoline as 30 751 kJ/L and that of the 91 AI gasoline + 15% methanol as 25 680 kJ/L. On a volume basis, the difference is 16.5% at 25 °C. While enthalpies of combustion presented in kilojoules per mole have very little temperature dependence, those presented in kilojoules per liter may be expected to have a significant temperature dependence. Still another practical alternative would be to present the thermochemical parameters on a mass basis. While the database can provide a variety of mass-based units, it is a simple matter to convert the molar-based units to joules per gram. On this basis, again for the fraction presented in Table 3a and b, the composite enthalpy of combustion for the 91 AI gasoline will be 43 815 J/g and that of the 91 AI gasoline + 15% methanol will be 33 574 J/g. The difference on a mass basis is therefore approximately 23%.

Conclusions

In this paper, we have demonstrated that it is possible to couple thermochemical information with the descriptive infor-

mation that becomes available upon the application of an advanced method to measure the distillation curve. The resulting composite enthalpies of combustion are statistically significant measures of the energy content of distillate fractions of fuels. This information can be coupled with the volatility information of the distillation curve of fuels to better design and program operational parameters such as fuel injection schedules and vehicle operability. It can also be used in the optimization of turbine and rocket fuels, since the specification of these fluids is also dependent upon the distillation curve.

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