
Danny R. Sprinkle, Sushil K. Chaturvedi, and Ali Kheireddine

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Danny R. Sprinkle
Langley Research Center • Hampton, Virginia

Sushil K. Chaturvedi and Ali Kheireddine
Old Dominion University • Norfolk, Virginia

National Aeronautics and Space Administration
Langley Research Center • Hampton, Virginia 23681-0001

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Abstract

A method for the on-line measurement of the heat of combustion of gaseous hydrocarbon fuel mixtures has been developed and tested. The method involves combustion of a test gas with a measured quantity of air to achieve a preset concentration of oxygen in the combustion products. This method involves using a controller which maintains the fuel (gas) volumetric flow rate at a level consistent with the desired oxygen concentration in the combustion products. The heat of combustion is determined from a known correlation with the fuel flow rate. An on-line computer accesses the fuel flow data and displays the heat of combustion measurement at desired time intervals. This technique appears to be especially applicable for measuring heats of combustion of hydrocarbon mixtures of unknown composition such as natural gas.

Introduction

Several well-known techniques are available currently for the measurement of heat of combustion of hydrocarbon fuels. Constant-volume bomb calorimeters are commonly used for determining heat of combustion of liquid fuels (refs. 1 and 2). Similarly, constant-pressure flame calorimeters are employed for measuring the heat of combustion of gaseous fuels (refs. 3 and 4). Singh et al. (ref. 5) have developed an on-line technique which requires injection of pure oxygen prior to combustion for measuring the heat of combustion of gaseous fuels. The injection is necessary to maintain the required 21-percent oxygen concentration in the combustion products. Singh et al. have also developed a simplified method that eliminates the need for the addition of pure oxygen and uses a computational algorithm that is valid only for a prescribed air flow rate and combustion-product oxygen concentration (ref. 6). The present technique offers an improvement over this latter method by using a computational algorithm that is valid over a wide range of flow rates and oxygen concentrations. Development of the present measurement system satisfies the need for accurate, on-line measurement of heat of combustion of gaseous fuel mixtures with methane as the dominant component. This fuel has been used in the combustor of the Langley 8 Foot High-Temperature Tunnel (8-Ft HTT) to produce temperature levels approaching 2000 K.

In the present study, an on-line gas calorimeter was developed and tested for high-precision measurement of heat of combustion of gaseous hydrocarbon mixtures. The method described herein involves the measurement of the concentration of oxygen in the combustion products and its correlation with the heat of combustion of the fuel.

Symbols

\[ A = 4 \sum_{i=1}^{m} f_i x_i + (1 + P) \sum_{i=1}^{m} f_i x_i - 4P \]

\( C_f \) fuel flow rate correction factor
\( C_{CH} \) hydrocarbon
\( E \) optical encoder data
\( f \) total hydrocarbon mole fraction
\( f_i \) mole fraction of ith hydrocarbon species
\( I \) inert fraction of fuel
\( l \) air volumetric flow rate
\( m \) number of hydrocarbon species
\( n \) fuel volumetric flow rate
\( P \) combustion-product oxygen mole fraction
\( P_o \) mole fraction of oxygen in air
\( R^2 \) coefficient of determination
\( \alpha, \beta \) regression coefficients
\( \Delta H \) heat of combustion

Experimental Setup

The prototype gas calorimeter is shown schematically in figure 1 and photographically in figure 2. The fuel gas is mixed with air and fed into a specially designed burner. The fuel flow rate is measured by a volumetric flowmeter with an optical encoder mounted on its shaft. The flow rate is determined by measuring the counts/min of the etched lines on the encoder disk. Each revolution of the shaft, which is nominally equivalent to 1000 cc, produces 1200 counts.

A burner that is fabricated with an internal honeycomb structure was used to ensure a stable flame over a range of air and fuel flow rates. The burner was enclosed in a vented glass container which prevented atmospheric contamination of the combustion products.

The oxygen concentration in the combustion products was measured by pumping the combustion products through a yttrium-stabilized zirconium oxide oxygen sensor that produces a voltage related to the concentration of oxygen in the environment to which it is exposed (ref. 7). The oxygen sensor output was directed to a
controller that maintained the desired concentration of oxygen in the combustion products by varying the fuel flow rate. This technique requires a sufficient quantity of oxygen (>0.1 percent) in the combustion products to be measurable by the oxygen sensor. A set point concentration of 3-percent oxygen was used throughout this study.

Because of the precision uncertainties of the volumetric flowmeter, the oxygen sensor, and the air flowmeter, and because of the inherent unsteadiness of the combustion process, the oxygen concentration in the product gases exhibited small fluctuations about the 3-percent set point. To account for the random fluctuations in the oxygen concentration, the mean and the standard deviation (of heat of combustion) were obtained for a set of data points at several time intervals.

**Experimental Procedure**

The oxygen sensor was calibrated with mixtures of known oxygen concentrations so that a sensor output (in mV) versus oxygen-concentration calibration curve could be obtained. Subsequently, the system was flushed with air for several minutes to scavenge any fuel that was left inside the system from the previous experiment. Air from a pressurized cylinder was used for combustion, and its oxygen concentration was measured with the oxygen sensor prior to the experiment. The fuel flowmeter was also calibrated so that the number of counts/min from the optical encoder could be converted readily into flow rate in standard cubic centimeters per minute (scm).

A given air flow rate from the pressurized cylinder was initiated, and the fuel flow rate was gradually increased to a level at which a stable flame was established. The 3-percent oxygen concentration was dialed as a set point in the controller, and the controller was activated to maintain the fuel flow rate. The fuel flow rate data in counts/min were recorded at regular intervals and were used in a correlation (described in the “Test Results” section) to obtain the value of heat of combustion. Over a time period, several data points were recorded, and the mean and the standard deviation were computed for the period.

**Theoretical Principles**

The heat of combustion \( \Delta H_{\text{mix}} \) of a gaseous mixture that has several saturated hydrocarbons and a noncombustible inert gas may be expressed as

\[
\Delta H_{\text{mix}} = \sum_{i=1}^{m} f_i \Delta H_i
\]

where \( f \) is the total hydrocarbon mole fraction, \( m \) is the number of hydrocarbon species, \( f_i \) is the mole fraction of the \( i \)th hydrocarbon species \((\sum f_i = 1)\), and \( \Delta H_i \) is the heat of combustion of the \( i \)th hydrocarbon species.

The combustion of this mixture with air\(^1 \) may be expressed as

\[
\begin{align*}
1 + n[f&(f_1 C_n H_{2n} + f_2 C_{2n} H_{2n} + \ldots + f_m C_{m n} H_{m n})] + (1 - f)I \\
\text{Heat} &- nf(f_1 x_1 + f_2 x_2 + \ldots + f_m x_m)CO_2 \\
&+ \frac{n f}{2}(f_1 y_1 + f_2 y_2 + \ldots + f_m y_m)H_2O \\
&+ [n(P_o - n[f(f_1 r_1 + \ldots + f_m r_m)]) - \frac{n f}{4}(f_1 y_1 + \ldots + f_m y_m)]O_2 \\
&+ [(1 - P_o)]N_2 + n(1 - f)I
\end{align*}
\]

where \( I \) is the volumetric flow rate of air, \( n \) is the volumetric flow rate of the gaseous fuel mixture, \( f \) is the noncombustible inert fraction of the test gas, and \( P_o \) is the mole fraction of oxygen in the air.

The mole fraction of oxygen in the combustion products \( P \) can be expressed as

\[
P = \frac{4IP_o - 4nf \sum_{i=1}^{m} f_i x_i - nf \sum_{i=1}^{m} f_i y_i}{nf \sum_{i=1}^{m} f_i y_i + 4n - 4nf + 4I}
\]

Solving for \( f \),

\[
f = \frac{4I(P_o - P) - 4nP}{n} \left[ 4 \sum_{i=1}^{m} f_i x_i + (1 + P) \sum_{i=1}^{m} f_i y_i - 4P \right]
\]

Substitution for \( f \) in equation (1) yields the following expression:

\[
\Delta H_{\text{mix}} = \frac{[4IP_o - 4P]}{n} \sum_{i=1}^{m} f_i \Delta H_i - 4P \left[ 4 \sum_{i=1}^{m} f_i x_i + (1 + P) \sum_{i=1}^{m} f_i y_i - 4P \right]
\]

Let

\[
A = \sum_{i=1}^{m} f_i x_i + (1 + P) \sum_{i=1}^{m} f_i y_i - 4P
\]

\( A \) is a measure of the effective hydrocarbon content of the combustible component. Note that for saturated

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\(^1\) Air is assumed to be composed of nitrogen and oxygen.
hydrocarbons, \( A \) can be further simplified since \( y_i = 2x_i + 2 \).

The \( \Delta H_{mix} \) may now be expressed as

\[
\Delta H_{mix} = \left[ \frac{4l(P_o - P)}{n} - 4P \right] \sum_{i=1}^{m} \frac{f_i \Delta H_i}{A} \tag{6}
\]

For a binary mixture of a single pure hydrocarbon species (\( m = 1 \)) and an inert gas, the above equation reduces to

\[
\Delta H_{mix} = \left[ \frac{4l(P_o - P)}{n} - 4P \right] \Delta H \tag{7}
\]

where \( A = 4x + (1 + P)y - 4P \), and \( \Delta H \) is the heat of combustion of the hydrocarbon species. Note that for methane (\( y = 4 \)), \( A \) is independent of \( P \).

For a mixture of unknown composition, the value of \( \Sigma f_i \Delta H_i / A \) to be used in equation (6) is not known since \( f_i \) and \( A \) are unknown. Table I shows values of \( \Delta H \) (ref. 8), \( A \), and \( \Delta H / A \) for various saturated hydrocarbons. (When more than one form of a hydrocarbon exists, such as n-butane and isobutane, the average value of \( \Delta H \) is given.) A value of 0.03 for \( P \) is used in the calculation of \( A \) in each case. In the present technique, the adoption of a universal value of the \( \Sigma f_i \Delta H_i / A \) coefficient in equation (6) is crucial for measuring the heat of combustion of a gaseous mixture of unknown composition. However, as noted from table I, \( \Delta H / A \) varies from 25.94 for hexane to 26.6 for methane. For the present technique it is sufficient to adopt a value of this coefficient that will minimize the error in the prediction of the \( \Delta H_{mix} \) for the domain of samples to be tested. Thus, for the domain of samples where all species occur with equal probability, the mean value of 26.27 is the appropriate choice for \( \Sigma f_i \Delta H_i / A \) in equation (6).

In nature, however, hydrocarbons are not distributed uniformly. Methane makes up the bulk of the hydrocarbon component in most natural gas samples. Figure 3 shows the variation of \( \Sigma f_i \Delta H_i / A \) with the methane mole fraction of the hydrocarbon component for 265 well samples that were analyzed in a 1982 Bureau of Mines survey of natural gases (ref. 9). Figure 4 shows the variation of \( \Sigma f_i \Delta H_i / A \) for these samples. Although the value of \( \Sigma f_i \Delta H_i / A \) varies significantly from sample to sample, the value of \( \Sigma f_i \Delta H_i / A \) varies in a narrower range. Figure 5 presents a frequency distribution plot of \( \Sigma f_i \Delta H_i / A \) for these samples. More than 90 percent of these well samples have a \( \Sigma f_i \Delta H_i / A \) between 26.5 and 26.6. Thus, the mean value of 26.55 is the appropriate choice for \( \Sigma f_i \Delta H_i / A \) for a wide range of natural gas samples.

Table II shows values of \( \Sigma f_i \Delta H_i / A \) for six natural gas pipeline samples from the Bureau of Mines survey. Although values of \( \Sigma f_i \Delta H_i / A \) vary significantly from sample to sample, the value of \( \Sigma f_i \Delta H_i / A \) is constricted to a narrow band from 26.53 to 26.59, in agreement with the mean value cited previously. Thus, although the adoption of a universal value for the \( \Sigma f_i \Delta H_i / A \) coefficient inevitably introduces an error in the calculated value of \( \Delta H \), this error will be negligible in the overwhelming majority of samples from natural gas sources.
Test Results

In the present study, \( I = 7000 \text{ sccm} \) and \( P = 0.03 \). For these values equation (6) reduces to

\[
\Delta H_{\text{mix}} = \left[ \frac{28000(P_o - 0.03)}{n} - 0.12 \right] \sum_{i=1}^{m} \frac{f_i \Delta H_i}{A} \quad (8)
\]

Equation (8) forms the basis for calculation of the \( \Delta H_{\text{mix}} \) from the volumetric fuel flow rate measurements.

The present technique was first applied to two pure gas samples: methane and ethane. Since heats of combustion of these gases were already known, the results were used to determine the precision error of the method, and to this end a correction factor \( C_f \) was introduced in the calculation of volumetric flow rate from the optical encoder data \( E \) to correct for bias in the system. Table III shows the experimental data for methane that involves optical encoder data \( E \) in counts/3 min intervals, the fuel flow rate \( n \) in sccm calculated from the optical encoder data \( (n = E/3 \text{ min} * 1000 \text{ cc}/1200 * C_f) \), and the heat of combustion \( (\Delta H) \) in kcal/mol calculated from equation (8); \( P_o \) was measured at 0.209. The mean value of the heat-of-combustion data is 212.80 \( \pm 1.22 \) for methane.

Table IV shows the data for ethane; \( P_o \) was measured at 0.210. Readings were taken at 5-min intervals. The mean value of the heat-of-combustion data for ethane is 372.82 \( \pm 2.60 \). These two cases indicate that a precision approaching 0.6 percent can be achieved for pure saturated hydrocarbon fuels such as methane and ethane.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{E}, counts/3 min & \textbf{Fuel flow rate, } \textbf{n, sccm} & \textbf{\( \Delta H \), kcal/mol} \\
\hline
2122 & 356.2 & 370.9 \\
2119 & 355.7 & 371.4 \\
2121 & 356.0 & 371.1 \\
2122 & 356.2 & 370.9 \\
2117 & 355.4 & 371.8 \\
2112 & 354.5 & 372.7 \\
2113 & 354.7 & 372.5 \\
2112 & 354.5 & 372.7 \\
2107 & 353.7 & 373.5 \\
2102 & 352.8 & 374.4 \\
2108 & 353.8 & 373.4 \\
2103 & 353.0 & 374.3 \\
2103 & 353.0 & 374.3 \\
2101 & 352.7 & 374.6 \\
2104 & 353.2 & 374.1 \\
\hline
\end{tabular}
\caption{Ethane Data}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{E}, counts/3 min & \textbf{Fuel flow rate, } \textbf{n, sccm} & \textbf{\( \Delta H \), kcal/mol} \\
\hline
2297 & 672.8 & 195.0 \\
2265 & 663.4 & 197.8 \\
2284 & 669.0 & 196.1 \\
2288 & 670.1 & 195.8 \\
2260 & 661.9 & 198.2 \\
2246 & 657.8 & 199.5 \\
2262 & 662.5 & 198.0 \\
2301 & 673.9 & 194.6 \\
2280 & 667.8 & 196.4 \\
\hline
\end{tabular}
\caption{Data for 92.49 Percent CH\(_4\) Plus 7.51 Percent N\(_2\)}
\end{table}
Table VI. Summary of Data for Methane, Ethane, and Methane Plus Nitrogen

\[
\Delta H_{\text{est}} = 48.6 + \frac{3.42 \times 10^5}{E}
\]

Regression output: \( \alpha = 48.5844 \); Standard error of \( \Delta H_{\text{est}} \): 2.005064; \( R^2 \): 0.999463; Number of observations, 33; Degrees of freedom, 31; \( \beta \), 342320.7; Standard error of \( \beta \), 1425.077

<table>
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<th>Calibration gas</th>
<th>Flow data (( E )), counts/3 min</th>
<th>( \Delta H ), kcal/mol</th>
<th>( \Delta H_{\text{est}} ), kcal/mol</th>
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<td>2280.0</td>
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</tr>
</tbody>
</table>

equation (4). A value of 212.80 for \( \Delta H \) and a value of 8 for \( \beta \) were used since methane was the only hydrocarbon involved. The mean value of the heat-of-combustion data is \( 196.82 \pm 3.10 \). The mean value of the fuel mole fraction data is \( 0.9249 \pm 0.0145 \).

**Numerical Approach**

The heat of combustion may also be expressed as

\[
\Delta H = \alpha + \frac{\beta}{E} \tag{9}
\]

where \( E \) is flow data, either in the form of flow units or directly in optical encoder counts, and \( \alpha \) and \( \beta \) are constants determined from a least-squares regression analysis of flow data and heat of combustion for gases of various heat content, assuming constant values for \( I, P_0 \), and \( P \). Equation (9) allows calibration of \( \Delta H \) directly in terms of optical encoder counts using calorimetric gas standards, thus obviating the intermediate steps of quantifying the flow rate and oxygen concentration of the combustion air, calibrating fuel flow rate from optical encoder counts, and calibrating oxygen concentration from oxygen sensor voltage. This regression algorithm
was applied to optical encoder readings for the methane, ethane, and methane-plus-nitrogen data presented above and effectively provides a 3-point calibration of $\Delta H$ in terms of $E$ (optical encoder data for ethane were normalized for 3-min intervals). Table VI summarizes these data and presents results of the regression analysis. A graphical plot of the data, the least-squares regression curve fit $\Delta H_{est}$, and the $\pm 2$ standard error of $\Delta H_{est}$ (SEE) band, which approximates the 95-percent confidence interval about the curve fit (ref. 10), are shown in figure 6.

Conclusions

An experimental technique has been developed and tested to measure the heat of combustion of a saturated hydrocarbon and inert gas mixture. The technique is especially attractive for applications in which an on-line measurement of the heat of combustion of natural gas is required. The system worked reasonably well during the course of laboratory investigation and thus validated the technique. Preliminary test results indicate that this technique can determine the heat of combustion of a gas of unknown composition with an uncertainty on the order of 2 percent.

References


Figure 1. System diagram.
Figure 2. Experimental setup.
Figure 3. Variation in calculated heat of combustion $\sum f_i \Delta H_i$ with methane mole fraction of hydrocarbon component for 265 natural gas well samples.
Figure 4. Variation of $\Sigma f_i \Delta H_f / A$ with methane mole fraction of hydrocarbon component for 265 natural gas well samples.
Figure 5. Distribution of $\Sigma f_i \Delta H_i / A$ for 265 natural gas well samples. Mean = 26.55; Standard deviation = 0.06.
Figure 6. Summary of experimental data and regression results.

\[ \Delta H_{\text{est}} = 48.6 + 3.42 \times 10^5 \frac{1}{E} \]

- Ethane data (15 pts.)
- Methane data (9 pts.)
- 92.49-percent CH\(_4\) +7.51-percent N\(_2\) (9 pts.)

±2 (SEE)
A method for the on-line measurement of the heat of combustion of gaseous hydrocarbon fuel mixtures has been developed and tested. The method involves combustion of a test gas with a measured quantity of air to achieve a preset concentration of oxygen in the combustion products. This method involves using a controller which maintains the fuel (gas) volumetric flow rate at a level consistent with the desired oxygen concentration in the combustion products. The heat of combustion is determined from a known correlation with the fuel flow rate. An on-line computer accesses the fuel flow data and displays the heat of combustion measurement at desired time intervals. This technique appears to be especially applicable for measuring heats of combustion of hydrocarbon mixtures of unknown composition such as natural gas.