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# A Simplified Method for Determining Heat of Combustion of Natural Gas

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## Abstract

A simplified technique for determination of the heat of combustion of natural gas has been developed. It is a variation of the previously developed technique wherein the carrier air, in which the test sample was burnt, was oxygen enriched to adjust the mole fraction of oxygen in the combustion product gases up to that in the carrier air. The new technique eliminates the need for oxygen enrichment of the carrier air without affecting the sensitivity of the technique. It has been tested on a number of experimental mixtures and natural gas samples and has been found to predict their heats of combustion to an uncertainty of the order of 1 percent.

## Introduction

Natural gas heats of combustion are determined by direct combustion calorimetry or calculated from the known heats of combustion of the experimentally measured components of the natural gas test samples. Both types of techniques depend on the accuracy of the calibration standards and require tedious secondary measurements. We had previously developed an on-line technique for determining heats of combustion of mixtures of gaseous hydrocarbons and inert gases (ref. 1). The technique was based on measuring the ratio  $m/n$ , where  $m$  is the volumetric flowrate of oxygen required to enrich the carrier air in which the test gas flowing at the rate  $n$  is burnt, such that the mole fraction of oxygen in the combustion product gases equals that in the carrier air. The ratio  $m/n$  is directly related of the heat of combustion of the test gas.

It now appears that the previous technique can be further simplified by eliminating the need for oxygen used for carrier air enrichment. A measurement of the test gas flowrate alone can be used to determine the heat of combustion of the test gas. The theoretical principles, computational procedure, test calculations, and comparisons with previously reported results are described in the following sections.

## Symbols

|        |                                                                           |
|--------|---------------------------------------------------------------------------|
| $A$    | calibration constant (eq. (9))                                            |
| $H$    | heat of combustion                                                        |
| $\ell$ | volumetric flowrate of air (set at 4000 sccm)                             |
| $m$    | volumetric flowrate of oxygen                                             |
| $n$    | volumetric flowrate of test gas                                           |
| $X_c$  | mole fraction of oxygen in combustion product gases (selected to be 0.10) |

$X_o$  mole fraction of oxygen in air (assumed to be 0.2095 in calculations)

$\alpha$  calibration constant (eq. (9))

$\beta$  calibration constant (eq. (9))

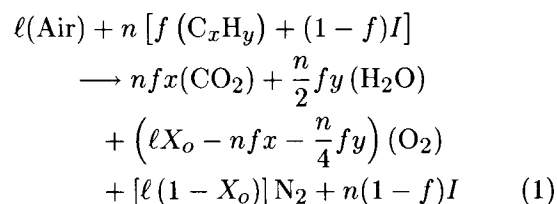
$\gamma$  calibration constant (eq. (9))

Abbreviation:

sccm standard cubic centimeters per minute; values listed are for 20°C and 101.3 kPa

## Theoretical Principles

The test gas combustion process can be written as follows:



where

$\ell$  volumetric flowrate of air

$n$  volumetric flowrate of test gas

$f$  hydrocarbon fraction of the test gas

$I$  noncombustible content of the test gas

$X_o(\text{O}_2)$  mole fraction of oxygen in the carrier air (assumed to be 0.2095 in later calculations)

From equation (1), one obtains

$$X_c(\text{O}_2) = \frac{\ell X_o - nf \left( \frac{4x+Y}{4} \right)}{\ell + n + nf \left( \frac{y-4}{4} \right)} \quad (2)$$

where  $X_c(\text{O}_2)$  is the mole fraction of oxygen in the combustion product gases. Suppose we now assume<sup>1</sup> that  $\ell = 4000$  sccm and  $X_c(\text{O}_2) = 0.10$ . Equation (2) is then simplified as follows:

$$0.10 = \frac{838 - nf \left( \frac{4x+Y}{4} \right)}{4000 + n + nf \left( \frac{y-4}{4} \right)} \quad (3)$$

<sup>1</sup> The value of the carrier air flowrate ( $\ell$ ) was chosen to be 4000 sccm to ensure that the test gas flowrate ( $n$ ) is not too low to measure accurately. The  $X_c(\text{O}_2) = 0.10$  value was selected because the ZrO<sub>2</sub>-oxygen sensor output is a reasonably strong function of the oxygen partial pressure around this value (ref. 2).

This gives  $n$  as a function of  $f$ ,  $x$ , and  $y$  as follows:

$$n = \frac{438}{0.025f(40x + 11y - 4) + 0.1} \quad (4)$$

Calculated values of  $n$  for various pure saturated hydrocarbons are summarized in table I.

The test gas flowrate ( $n$ ) is directly related to its gross (high) heat of combustion ( $H$ ). By using  $n$  versus  $H$  graphs for pure saturated hydrocarbons (or mixtures thereof) whose heats of combustion are well known (refs. 3-5), one can easily determine the calibration constants that enable a computation of  $H$  from the measured value of  $n$ .

Thus a measurement of  $n$  can be used to determine the heat of combustion of the test gas, in much the same way as  $m/n$  was used previously (ref. 1). The sensitivities of the two techniques are the same since they are both subject to the same limitations—namely, the accuracies of the constituent saturated hydrocarbon heats of combustion and the test gas flowrates.

Table I. Summary of Saturated Hydrocarbon Flowrates

[ $\ell = 4000$  sccm;  $X_c(O_2) = 0.10$ ;  $X_o(O_2) = 0.2095$ ]

| Hydrocarbon,<br>$C_xH_y$       | Flowrate required,<br>$n$ , sccm |
|--------------------------------|----------------------------------|
| CH <sub>4</sub>                | 208.6                            |
| C <sub>2</sub> H <sub>6</sub>  | 120.0                            |
| C <sub>3</sub> H <sub>8</sub>  | 84.2                             |
| C <sub>4</sub> H <sub>10</sub> | 64.9                             |
| C <sub>5</sub> H <sub>12</sub> | 52.8                             |
| C <sub>6</sub> H <sub>14</sub> | 44.5                             |

## Computational Procedure

As is apparent from equation (4), the test gas flowrate is a function of its combustible and noncombustible fractions. It does not depend on the nature of the noncombustible components, but is a very sensitive function of the character and composition of the combustible fraction.

A calibration procedure involving well-characterized test gas mixtures is first developed. These mixtures include various combinations of saturated hydrocarbons, saturated hydrocarbons and inert gases, and pure hydrocarbon ranging from methane (CH<sub>4</sub>) to hexane (C<sub>6</sub>H<sub>14</sub>). The compositions of representative mixtures and their calculated heats of combustion are summarized in table II. Also included in this table are the hydrocarbon mixture flowrates ( $n$ ) required to make  $X_c(O_2) = 0.10$  in the combustion product gases.

The heats of combustion of the various mixtures were calculated by two methods. The first was the method of mixtures:

$$H(\text{Mixture}) = \sum_i f_i H_i \quad (5)$$

where  $H_i$  refers to the gross heat of combustion of the  $i$ th hydrocarbon and  $f_i$  is its corresponding mole fraction. (The inert components do not contribute to  $H(\text{Mixture})$ .) The second method, which has been explained fully in reference 1, is based on the ratio  $m/n$ :

$$H(\text{Mixture}) = \sum_{i=0}^4 a_i \left(\frac{m}{n}\right)^i \quad (6)$$

where  $a_i$  are calibration constants and  $m/n$  is the ratio of the oxygen-enrichment flowrate to the test gas flowrate.

From an examination of the data summarized in table II and illustrated in figure 1, it is apparent that  $n$  can be related to  $H$  by an expression of the following form:<sup>2</sup>

$$H = Ae^{-\alpha n} \quad (7)$$

where  $A$  and  $\alpha$  are constants to be determined from calibration data analysis.

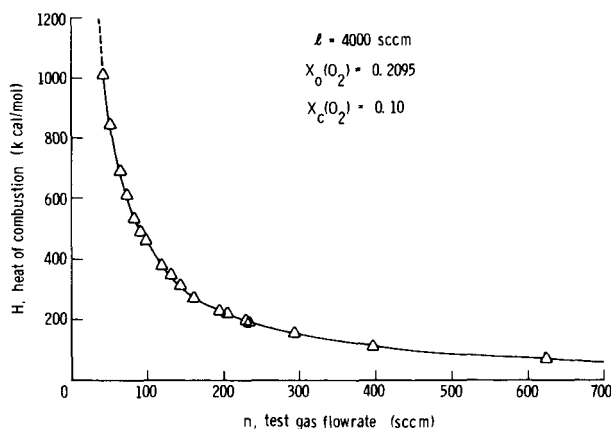


Figure 1. Heat of combustion of the test gas as a function of its flowrate.

Comparison of the calculated values of heats of combustion and the values computed from equation (7) indicated that the dependence of  $H$  on  $n$  is

<sup>2</sup> An alternate expression relating  $n$  and  $H$  could be of the following form:

$$H = \frac{A}{n} + B$$

where  $A$  and  $B$  are constants.

Table II. Summary of Gas Mixtures and Their Heats of Combustion

[ $\ell = 4000$  sccm;  $X_c(O_2) = 0.10$ ;  $X_o(O_2) = 0.2095$ ]

| Test mixture                                                           | Calculated <sup>a</sup><br>test gas<br>flowrate,<br>$n$ , sccm | Calculated, <sup>b</sup><br>$m/n$ | $H$ , kcal/mol                  |                             |                                 |
|------------------------------------------------------------------------|----------------------------------------------------------------|-----------------------------------|---------------------------------|-----------------------------|---------------------------------|
|                                                                        |                                                                |                                   | Method of<br>mixtures (eq. (5)) | Based on $m/n$<br>(eq. (6)) | Calculated<br>from equation (8) |
| C <sub>6</sub> H <sub>14</sub>                                         | 44.5                                                           | 12.945                            | 1002.55                         | 1002.68                     | 1032.16                         |
| C <sub>5</sub> H <sub>12</sub>                                         | 52.8                                                           | 10.915                            | 845.10                          | 844.70                      | 868.06                          |
| C <sub>4</sub> H <sub>10</sub>                                         | 64.9                                                           | 8.885                             | 687.65                          | 687.76                      | 703.08                          |
| 50% C <sub>3</sub> H <sub>8</sub> + 50% C <sub>4</sub> H <sub>10</sub> | 73.3                                                           | 7.870                             | 609.13                          | 609.38                      | 620.35                          |
| C <sub>3</sub> H <sub>8</sub>                                          | 84.2                                                           | 6.855                             | 530.61                          | 530.84                      | 537.56                          |
| 30% C <sub>2</sub> H <sub>6</sub> + 70% C <sub>3</sub> H <sub>8</sub>  | 92.5                                                           | 6.246                             | 483.27                          | 483.54                      | 487.83                          |
| 50% C <sub>2</sub> H <sub>6</sub> + 50% C <sub>3</sub> H <sub>8</sub>  | 99.0                                                           | 5.840                             | 451.72                          | 451.92                      | 454.67                          |
| C <sub>2</sub> H <sub>6</sub>                                          | 120.0                                                          | 4.825                             | 372.82                          | 372.38                      | 371.78                          |
| 20% CH <sub>4</sub> + 80% C <sub>2</sub> H <sub>6</sub>                | 131.1                                                          | 4.419                             | 340.82                          | 340.33                      | 338.66                          |
| 40% CH <sub>4</sub> + 60% C <sub>2</sub> H <sub>6</sub>                | 144.6                                                          | 4.013                             | 308.81                          | 308.12                      | 305.60                          |
| 60% CH <sub>4</sub> + 40% C <sub>2</sub> H <sub>6</sub>                | 161.0                                                          | 3.607                             | 276.81                          | 275.73                      | 272.57                          |
| 60% C <sub>2</sub> H <sub>6</sub> + 40% N <sub>2</sub>                 | 196.4                                                          | 3.001                             | 223.69                          | 227.00                      | 220.57                          |
| CH <sub>4</sub>                                                        | 208.6                                                          | 2.795                             | 212.80                          | 210.33                      | 206.82                          |
| 90% CH <sub>4</sub> + 10% N <sub>2</sub>                               | 230.5                                                          | 2.542                             | 191.52                          | 189.79                      | 185.72                          |
| 50% C <sub>2</sub> H <sub>6</sub> + 50% N <sub>2</sub>                 | 233.6                                                          | 2.545                             | 186.41                          | 190.00                      | 183.10                          |
| 70% CH <sub>4</sub> + 30% N <sub>2</sub>                               | 292.0                                                          | 2.036                             | 148.96                          | 148.30                      | 143.81                          |
| 50% CH <sub>4</sub> + 50% N <sub>2</sub>                               | 398.2                                                          | 1.530                             | 106.40                          | 106.40                      | 102.43                          |
| 30% CH <sub>4</sub> + 70% N <sub>2</sub>                               | 625.7                                                          | 1.024                             | 63.84                           | 63.99                       | 62.00                           |
| 10% CH <sub>4</sub> + 90% N <sub>2</sub>                               | 1460.0                                                         | 0.518                             | 21.28                           | 21.04                       | 23.60                           |

<sup>a</sup>The values of  $n$  were calculated from equation (4) using composition-weighted values for  $x$  and  $y$ .<sup>b</sup>The values of  $m/n$  were calculated in the manner detailed in reference 1. They were used to determine the heats of combustion listed in the next to last column, using equation (6).

stronger than implied by this expression. The equation was then modified as follows:

$$H = Ae^{-\alpha(n)^\beta} \quad (8)$$

where  $\beta$  is a constant less than 1.

Calculations made using various empirical values of  $\beta$  indicated that  $\beta = 0.04$  gave the closest fit for various mixtures. In general, however, equation (8) overestimates the true value of  $H$  for  $n$  up to about 100 sccm and thereafter it underestimates it as can be seen from the data in the last column of table II. This implies a slight dependence of  $A$  on  $n$ , leading to an expression given by the following equation:

$$H = \frac{A}{n^\gamma} e^{-\alpha(n)^\beta} \quad (9)$$

where  $\gamma$  is a constant to be determined. However, extensive series of calculations made using equation (9) made it plain that a universal equation giving equally good fits for all values of  $n$  was not possible. It was therefore decided to develop two expressions—one valid for low values of  $n$  ( $n \leq 175$  sccm) and the other valid for high values of  $n$  ( $n > 175$  sccm). Appropriate constants in equation (9) for  $H$  versus  $n$  expressions, based on an *extensive* set of  $n$  versus  $H$  data, are summarized below:

For  $n \leq 175$  sccm,

$$\left. \begin{aligned} A &= (41.915 \pm 0.872)10^{10} \\ \alpha &= 16.154 \pm 0.019 \\ \beta &= 0.025 \\ \gamma &= 0.550 \end{aligned} \right\} \quad (10a)$$

For  $n > 175$  sccm,

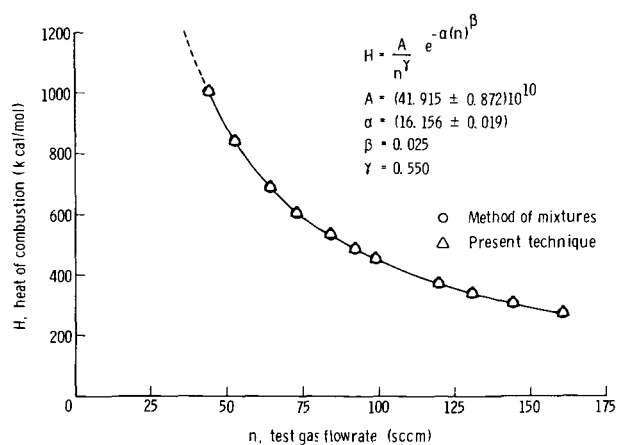
$$\left. \begin{aligned} A &= (26.557 \pm 0.694)10^3 \\ \alpha &= 0.498 \pm 0.007 \\ \beta &= 0.250 \\ \gamma &= 0.550 \end{aligned} \right\} \quad (10b)$$

Heats of combustion of various gas mixtures calculated by the method of mixtures and from equations (9) and (10) are compared in table III.

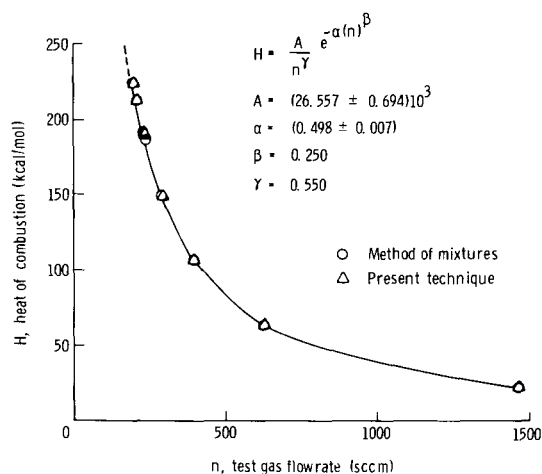
As indicated by the data in table III, and illustrated in figure 2, the agreement between the values calculated by the method of mixtures and the values predicted by the expressions developed in this paper is very good.

### Comparison With Other Techniques

Appropriate expressions developed in this paper have been used to predict the heats of combustion



(a)  $n \leq 175$  sccm.



(b)  $n > 175$  sccm.

Figure 2. Heats of combustion calculated by the method of mixtures and the present technique.

of various mixtures studied by other authors (refs. 1 and 6).

**Comparison with the results of the previously reported technique.** Heats of combustion of multicomponent mixtures calculated with the previously reported (ref. 1) technique are compared with values computed from the present technique in table IV. The agreement appears to be reasonably good. The errors on the results reflect the uncertainty in the mixture compositions. The agreement between the results of the two techniques is better for binary mixtures mainly because of lesser uncertainty about their composition. Figure 3 illustrates the comparison between results of the present and previously reported technique.

Table III. Comparison Between Calculated Heats of Combustion of Various Test Mixtures

| Test mixture                                                           | Calculated <sup>a</sup><br>test gas flowrate,<br><i>n</i> , sccm | <i>H</i> , kcal/mol             |                                 |
|------------------------------------------------------------------------|------------------------------------------------------------------|---------------------------------|---------------------------------|
|                                                                        |                                                                  | Method of<br>mixtures (eq. (5)) | Calculated from<br>equation (9) |
| <i>n</i> ≤ 175 sccm; calibration constants in equation (10a)           |                                                                  |                                 |                                 |
| C <sub>6</sub> H <sub>14</sub>                                         | 44.5                                                             | 1002.55                         | 1002.31                         |
| C <sub>5</sub> H <sub>12</sub>                                         | 52.8                                                             | 845.10                          | 845.38                          |
| C <sub>4</sub> H <sub>10</sub>                                         | 64.9                                                             | 687.65                          | 687.88                          |
| 50% C <sub>3</sub> H <sub>8</sub> + 50% C <sub>4</sub> H <sub>10</sub> | 73.3                                                             | 609.13                          | 608.95                          |
| C <sub>3</sub> H <sub>8</sub>                                          | 84.2                                                             | 530.61                          | 529.97                          |
| 30% C <sub>2</sub> H <sub>6</sub> + 70% C <sub>3</sub> H <sub>8</sub>  | 92.5                                                             | 483.27                          | 482.51                          |
| 50% C <sub>2</sub> H <sub>6</sub> + 50% C <sub>3</sub> H <sub>8</sub>  | 99.0                                                             | 451.72                          | 450.83                          |
| C <sub>2</sub> H <sub>6</sub>                                          | 120.0                                                            | 372.82                          | 371.56                          |
| 20% CH <sub>4</sub> + 80% C <sub>2</sub> H <sub>6</sub>                | 131.1                                                            | 340.82                          | 339.83                          |
| 40% CH <sub>4</sub> + 60% C <sub>2</sub> H <sub>6</sub>                | 144.6                                                            | 308.81                          | 308.10                          |
| 60% CH <sub>4</sub> + 40% C <sub>2</sub> H <sub>6</sub>                | 161.0                                                            | 276.81                          | 276.33                          |
| <i>n</i> > 175 sccm; calibration constants in equation (10b)           |                                                                  |                                 |                                 |
| 60% C <sub>2</sub> H <sub>6</sub> + 40% N <sub>2</sub>                 | 196.4                                                            | 223.69                          | 225.25                          |
| CH <sub>4</sub>                                                        | 208.6                                                            | 212.80                          | 211.82                          |
| 90% CH <sub>4</sub> + 10% N <sub>2</sub>                               | 230.5                                                            | 191.52                          | 191.13                          |
| 50% C <sub>2</sub> H <sub>6</sub> + 50% N <sub>2</sub>                 | 233.6                                                            | 186.41                          | 188.50                          |
| 70% CH <sub>4</sub> + 30% N <sub>2</sub>                               | 292.0                                                            | 148.96                          | 149.10                          |
| 50% CH <sub>4</sub> + 50% N <sub>2</sub>                               | 398.2                                                            | 106.40                          | 106.47                          |
| 30% CH <sub>4</sub> + 70% N <sub>2</sub>                               | 625.7                                                            | 63.84                           | 63.63                           |
| 10% CH <sub>4</sub> + 90% N <sub>2</sub>                               | 1460.0                                                           | 21.28                           | 22.17                           |

<sup>a</sup>The values of *n* were calculated from equation (4) using composition-weighted values for *x* and *y*.

Table IV. Comparison Between Results From Previously Reported Technique (Ref. 1) and Present Technique

| Test mixture                                                                                                                                                              | Calculated <sup>a</sup><br>test gas flowrate,<br><i>n</i> , sccm | <i>H</i> , kcal/mol                             |                                                  |                                   |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|-------------------------------------------------|--------------------------------------------------|-----------------------------------|
|                                                                                                                                                                           |                                                                  | Method of<br>mixtures <sup>a</sup><br>(eq. (5)) | Based on<br><sup>b</sup> <i>m/n</i><br>(eq. (6)) | Present<br>technique <sup>c</sup> |
| Complex mixtures                                                                                                                                                          |                                                                  |                                                 |                                                  |                                   |
| 44.63% C <sub>2</sub> H <sub>6</sub> + 25.88% C <sub>3</sub> H <sub>8</sub><br>+ 10.81% C <sub>4</sub> H <sub>10</sub> + 5.09% CO <sub>2</sub><br>+ 13.59% N <sub>2</sub> | 117.6 ± 1.6                                                      | 378.1 ± 3.7                                     | 388.8 ± 11.7                                     | 379.2 ± 5.2                       |
| 51.51% CH <sub>4</sub> + 21.24% C <sub>2</sub> H <sub>6</sub><br>+ 23.82% C <sub>3</sub> H <sub>8</sub> + 1.74% CO <sub>2</sub><br>+ 1.69% N <sub>2</sub>                 | 141.3 ± 1.3                                                      | 315.2 ± 3.0                                     | 312.3 ± 8.0                                      | 315.2 ± 2.9                       |
| 53.04% CH <sub>4</sub> + 26.09% C <sub>2</sub> H <sub>6</sub><br>+ 18.42% C <sub>3</sub> H <sub>8</sub> + 1.43% CO <sub>2</sub><br>+ 1.01% N <sub>2</sub>                 | 144.7 ± 1.2                                                      | 307.9 ± 2.8                                     | 305.3 ± 7.8                                      | 307.8 ± 2.6                       |
| 50.84% CH <sub>4</sub> + 17.12% C <sub>2</sub> H <sub>6</sub><br>+ 24.87% C <sub>3</sub> H <sub>8</sub> + 3.34% CO <sub>2</sub><br>+ 3.83% N <sub>2</sub>                 | 146.3 ± 1.3                                                      | 304.0 ± 3.1                                     | 294.8 ± 5.6                                      | 304.4 ± 2.7                       |
| Binary mixtures                                                                                                                                                           |                                                                  |                                                 |                                                  |                                   |
| 50.40% CH <sub>4</sub> + 49.60% C <sub>4</sub> H <sub>10</sub>                                                                                                            | 99.4 ± 1.0                                                       | 448.3 ± 4.7                                     | 450.2 ± 7.4                                      | 448.9 ± 4.5                       |
| 50.19% CH <sub>4</sub> + 49.81% C <sub>3</sub> H <sub>8</sub>                                                                                                             | 120.2 ± 1.0                                                      | 371.1 ± 3.2                                     | 370.4 ± 5.2                                      | 370.9 ± 3.1                       |
| 50.10% CH <sub>4</sub> + 49.90% C <sub>2</sub> H <sub>6</sub>                                                                                                             | 152.4 ± 1.2                                                      | 292.7 ± 2.9                                     | 289.5 ± 3.4                                      | 292.1 ± 2.3                       |
| 49.96% C <sub>3</sub> H <sub>8</sub> + 50.04% N <sub>2</sub>                                                                                                              | 165.4 ± 3.1                                                      | 265.1 ± 5.3                                     | 269.7 ± 3.8                                      | 269.0 ± 5.0                       |
| 49.91% C <sub>3</sub> H <sub>8</sub> + 50.09% CO <sub>2</sub>                                                                                                             | 165.6 ± 3.1                                                      | 264.8 ± 5.3                                     | 269.4 ± 3.0                                      | 268.6 ± 4.9                       |
| 49.92% C <sub>2</sub> H <sub>6</sub> + 50.08% N <sub>2</sub>                                                                                                              | 234.0 ± 4.4                                                      | 186.1 ± 3.7                                     | 188.0 ± 3.1                                      | 188.2 ± 3.7                       |
| 49.87% C <sub>2</sub> H <sub>6</sub> + 50.13% CO <sub>2</sub>                                                                                                             | 234.2 ± 4.4                                                      | 185.9 ± 3.8                                     | 187.9 ± 2.6                                      | 188.0 ± 3.7                       |
| 50.13% CH <sub>4</sub> + 49.87% N <sub>2</sub>                                                                                                                            | 397.2 ± 7.1                                                      | 106.7 ± 2.1                                     | 105.9 ± 2.2                                      | 106.8 ± 2.1                       |
| 50.08% CH <sub>4</sub> + 49.92% CO <sub>2</sub>                                                                                                                           | 397.6 ± 7.1                                                      | 106.6 ± 2.1                                     | 105.8 ± 2.2                                      | 106.6 ± 2.1                       |

<sup>a</sup>The errors on the values of *n* and *H* (method of mixtures) result from an assumed error of ±1% of the reported concentrations of the various mixture components.

<sup>b</sup>The values of heat of combustion listed in this column are based on the measured values of *m/n* reported in reference 1. However, these values of *H* were calculated using a more extensive (*m/n* vs. *H*) calibration data base than was used in reference 1.

<sup>c</sup>The errors on the values of *H* (present technique) result from the errors on the values of the test gas flowrates, *n*.



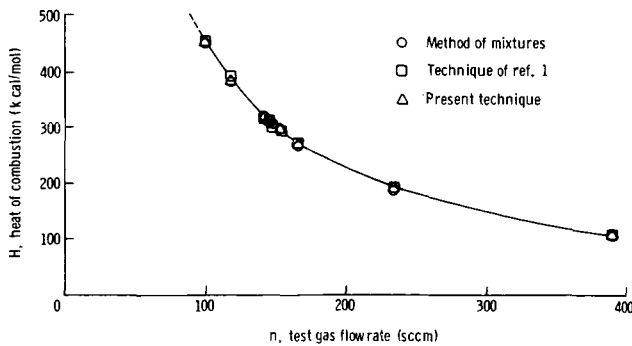


Figure 3. Heats of combustion computed by previously reported technique and the present technique.

#### Comparison with the Bureau of Mines results.

The Bureau of Mines (BOM) has reported (ref. 6) heats of combustion of 271 natural gas samples, from 22 states, collected during 1982. The samples were analyzed by mass spectrometry and gas chromatography. The results are summarized in table V, along with the corresponding values predicted with the present technique. No errors were cited on the Bureau of Mines values. The agreement appears to be satisfactory. Figure 4 illustrates the comparison.

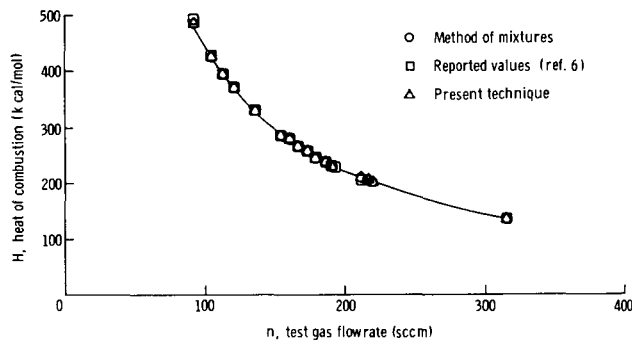


Figure 4. Heats of combustion reported by BOM and calculated by the present technique.

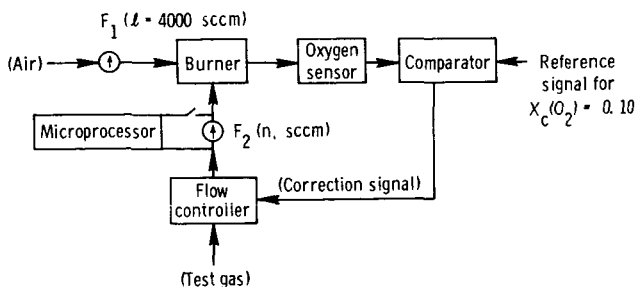


Figure 5. Recommended experimental procedure for determining heats of combustion of test gas samples.

## Recommended Experimental Procedure

Figure 5 illustrates the procedure recommended for determining the heats of combustion of the test gas samples. The test gas is burnt in an airstream flowing at the rate of 4000 sccm. Combustion product gases are sampled for oxygen mole fraction by means of  $ZrO_2$ -oxygen sensor. The sensor output is fed into a comparator circuit referenced at an analog voltage signal corresponding to  $X_c(O_2) = 0.10$ . The comparator provides a correction signal for the test gas flow controller to ensure that the oxygen mole fraction in the combustion product gases equals 0.10. The test gas flowrate that gives  $X_c(O_2) = 0.10$  is noted and converted into a corresponding heat of combustion value by means of an on-line microprocessor.

## Conclusions

A new simplified technique for determining heats of combustion of natural gas samples has been developed. It is based on measuring the flowrate of the test gas required to maintain a preset value the mole fraction of oxygen in the products of combustion in an airstream flowing at a preselected rate. This flowrate is directly related to the heat of combustion of the test gas.

Calibration relationships were obtained for an airstream flowrate of 4000 sccm and the oxygen mole fraction of 0.10 for a number of well-characterized test mixtures. Using these calibration data, heats of combustion of various types of gas mixtures were calculated and compared with their reported values in the literature. The agreement between the values calculated by the present technique and the values reported in the literature is very good. The accuracy of the present technique is limited only by the accuracy of the test gas flowrates and the reported values of heats of combustion of the pure saturated hydrocarbons.

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February 25, 1987

Table V. Comparison Between the Values Reported by the Bureau of Mines (Ref. 6) and the Calculations of the Present Technique

(a)  $n \leq 175$  sccm

| Test mixture                                                                                                                                                                                                                                                                                                        | Calculated <sup>a</sup> test gas flowrate, $n$ , sccm | $H$ , kcal/mol     |                                      |                                |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------|--------------------|--------------------------------------|--------------------------------|
|                                                                                                                                                                                                                                                                                                                     |                                                       | Method of mixtures | Reported value <sup>b</sup> (ref. 6) | Present technique <sup>c</sup> |
| 15.1% CH <sub>4</sub> + 8.2% C <sub>2</sub> H <sub>6</sub> + 24.9% C <sub>3</sub> H <sub>8</sub><br>+ 21.9% C <sub>4</sub> H <sub>10</sub> + 13.4% C <sub>5</sub> H <sub>12</sub><br>+ 2.6% C <sub>6</sub> H <sub>14</sub> + 13.5% N <sub>2</sub> + 0.18% He                                                        | 92.0 ± 0.8                                            | 485.4 ± 3.5        | 490.9                                | 485.1 ± 4.2                    |
| 37.9% CH <sub>4</sub> + 14.6% C <sub>2</sub> H <sub>6</sub> + 23.90% C <sub>3</sub> H <sub>8</sub><br>+ 17.2% C <sub>4</sub> H <sub>10</sub> + 3.87% C <sub>5</sub> H <sub>12</sub> + 1.3% C <sub>6</sub> H <sub>14</sub><br>+ 0.7% N <sub>2</sub> + 0.5% CO <sub>2</sub>                                           | 104.8 ± 1.0                                           | 425.5 ± 3.4        | 426.7                                | 425.7 ± 4.0                    |
| 27.3% CH <sub>4</sub> + 9.5% C <sub>2</sub> H <sub>6</sub> + 22.7% C <sub>3</sub> H <sub>8</sub><br>+ 13.2% C <sub>4</sub> H <sub>10</sub> + 7.8% C <sub>5</sub> H <sub>12</sub> + 2.1% C <sub>6</sub> H <sub>14</sub><br>+ 17.0% N <sub>2</sub> + 0.1% H <sub>2</sub> + 0.2% CO <sub>2</sub> + 0.16% He            | 113.3 ± 1.0                                           | 392.2 ± 3.2        | 394.3                                | 393.6 ± 3.8                    |
| 21.5% CH <sub>4</sub> + 12.7% C <sub>2</sub> H <sub>6</sub> + 25.2% C <sub>3</sub> H <sub>8</sub><br>+ 12.5% C <sub>4</sub> H <sub>10</sub> + 4.6% C <sub>5</sub> H <sub>12</sub> + 1.0% C <sub>6</sub> H <sub>14</sub><br>+ 16.2% N <sub>2</sub> + 0.1% Ar + 6.1% H <sub>2</sub> + 0.15% He                        | 121.6 ± 1.3                                           | 366.3 ± 3.0        | 367.4                                | 366.6 ± 3.9                    |
| 25.8% CH <sub>4</sub> + 12.0% C <sub>2</sub> H <sub>6</sub> + 22.2% C <sub>3</sub> H <sub>8</sub><br>+ 10.2% C <sub>4</sub> H <sub>10</sub> + 3.7% C <sub>5</sub> H <sub>12</sub> + 0.6% C <sub>6</sub> H <sub>14</sub><br>+ 24.8% N <sub>2</sub> + 0.2% Ar + 0.1% H <sub>2</sub> + 0.1% CO <sub>2</sub> + 0.32% He | 136.2 ± 1.3                                           | 325.3 ± 2.8        | 326.0                                | 327.1 ± 3.1                    |
| 79.6% CH <sub>4</sub> + 4.4% C <sub>2</sub> H <sub>6</sub> + 5.0% C <sub>3</sub> H <sub>8</sub><br>+ 7.6% C <sub>4</sub> H <sub>10</sub> + 1.9% C <sub>5</sub> H <sub>12</sub><br>+ 0.7% C <sub>6</sub> H <sub>14</sub> + 0.6% N <sub>2</sub> + 0.1% O <sub>2</sub>                                                 | 154.8 ± 1.6                                           | 287.9 ± 2.8        | 285.5                                | 287.5 ± 3.0                    |
| 13.7% CH <sub>4</sub> + 7.4% C <sub>2</sub> H <sub>6</sub> + 20.0% C <sub>3</sub> H <sub>8</sub> + 11.9% C <sub>4</sub> H <sub>10</sub><br>+ 2.9% C <sub>5</sub> H <sub>12</sub> + 0.2% C <sub>6</sub> H <sub>14</sub> + 34.8% N <sub>2</sub><br>+ 0.1% Ar + 6.7% H <sub>2</sub> + 0.1% CO <sub>2</sub> + 2.03% He  | 160.4 ± 1.7                                           | 276.3 ± 2.8        | 277.6                                | 277.4 ± 2.9                    |
| 73.9% CH <sub>4</sub> + 11.6% C <sub>2</sub> H <sub>6</sub> + 5.5% C <sub>3</sub> H <sub>8</sub> + 3.2% C <sub>4</sub> H <sub>10</sub><br>+ 1.2% C <sub>5</sub> H <sub>12</sub> + 0.5% C <sub>6</sub> H <sub>14</sub> + 0.6% N <sub>2</sub> + 3.4% CO <sub>2</sub>                                                  | 166.5 ± 1.7                                           | 266.9 ± 2.7        | 264.2                                | 267.2 ± 2.7                    |
| 75.7% CH <sub>4</sub> + 13.4% C <sub>2</sub> H <sub>6</sub> + 5.5% C <sub>3</sub> H <sub>8</sub> + 1.9% C <sub>4</sub> H <sub>10</sub><br>+ 0.4% C <sub>5</sub> H <sub>12</sub> + 0.1% C <sub>6</sub> H <sub>14</sub> + 2.9% N <sub>2</sub> + 0.02% He                                                              | 172.5 ± 1.8                                           | 257.7 ± 2.7        | 254.6                                | 257.8 ± 2.6                    |
| 81.8% CH <sub>4</sub> + 10.0% C <sub>2</sub> H <sub>6</sub> + 4.1% C <sub>3</sub> H <sub>8</sub> + 1.8% C <sub>4</sub> H <sub>10</sub><br>+ 0.8% C <sub>5</sub> H <sub>12</sub> + 0.3% C <sub>6</sub> H <sub>14</sub> + 0.9% N <sub>2</sub> + 0.2% H <sub>2</sub><br>+ 0.1% CO <sub>2</sub> + 0.05% He              | 174.2 ± 1.8                                           | 255.4 ± 2.7        | 252.3                                | 255.3 ± 2.7                    |

<sup>a</sup>The errors on the values of  $n$  and  $H$  (method of mixtures) result from an assumed error of  $\pm 1\%$  of the reported concentrations of the various mixture components.

<sup>b</sup>The BOM heats of combustion in Btu/ft<sup>3</sup> (60°F) have been transformed to kcal/mol (77°F) as follows:

$$\begin{aligned} \frac{\text{kcal}}{\text{mol}}(77^\circ\text{F}) &= 0.199 \left( \frac{298.15}{288.70} \right) \left[ \frac{\text{Btu}}{(\text{ft})^3}(60^\circ\text{F}) \right] \\ &= 0.206 \left[ \frac{\text{Btu}}{(\text{ft})^3}(60^\circ\text{F}) \right] \end{aligned}$$

(0.199 is the conversion factor for the gas at 32°F)

<sup>c</sup>The errors on the values of  $H$  (present technique) result from the errors on the values of the test gas flowrate,  $n$ .

Table V. Concluded

(b)  $n > 175$  sccm

| Test mixture                                                                                                                                                                                                                                                                                                                           | Calculated <sup>a</sup> test gas flowrate, $n$ , sccm | $H$ , kcal/mol     |                                      |                                |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------|--------------------|--------------------------------------|--------------------------------|
|                                                                                                                                                                                                                                                                                                                                        |                                                       | Method of mixtures | Reported value <sup>b</sup> (ref. 6) | Present technique <sup>c</sup> |
| 81.9% CH <sub>4</sub> + 11.1% C <sub>2</sub> H <sub>6</sub> + 3.5% C <sub>3</sub> H <sub>8</sub> + 1.3% C <sub>4</sub> H <sub>10</sub><br>+ 0.4% C <sub>5</sub> H <sub>12</sub> + 0.2% C <sub>6</sub> H <sub>14</sub> + 1.0% N <sub>2</sub> + 0.1% H <sub>2</sub><br>+ 0.5% CO <sub>2</sub> + 0.01% He                                 | 178.8 ± 1.8                                           | 248.7 ± 2.7        | 245.1                                | 247.7 ± 2.7                    |
| 86.6% CH <sub>4</sub> + 8.1% C <sub>2</sub> H <sub>6</sub> + 2.6% C <sub>3</sub> H <sub>8</sub> + 1.0% C <sub>4</sub> H <sub>10</sub><br>+ 0.5% C <sub>5</sub> H <sub>12</sub> + 0.2% C <sub>6</sub> H <sub>14</sub><br>+ 0.7% N <sub>2</sub> + 0.1% H <sub>2</sub> + 0.2% CO <sub>2</sub> + 0.06% He                                  | 184.1 ± 1.8                                           | 241.5 ± 2.7        | 237.9                                | 240.5 ± 2.4                    |
| 90.4% CH <sub>4</sub> + 4.8% C <sub>2</sub> H <sub>6</sub> + 1.8% C <sub>3</sub> H <sub>8</sub> + 0.8% C <sub>4</sub> H <sub>10</sub><br>+ 0.7% C <sub>5</sub> H <sub>12</sub> + 0.7% C <sub>6</sub> H <sub>14</sub> + 0.2% N <sub>2</sub><br>+ 0.1% H <sub>2</sub> + 0.4% CO <sub>2</sub> + 0.03% He                                  | 186.4 ± 1.8                                           | 238.3 ± 2.6        | 234.8                                | 237.5 ± 2.2                    |
| 86.9% CH <sub>4</sub> + 7.6% C <sub>2</sub> H <sub>6</sub> + 2.1% C <sub>3</sub> H <sub>8</sub> + 0.8% C <sub>4</sub> H <sub>10</sub><br>+ 0.3% C <sub>5</sub> H <sub>12</sub> + 0.1% C <sub>6</sub> H <sub>14</sub> + 0.4% N <sub>2</sub> + 1.8% CO <sub>2</sub><br>+ 0.01% He                                                        | 190.2 ± 1.8                                           | 233.5 ± 2.6        | 229.9                                | 232.7 ± 2.2                    |
| 75.2% CH <sub>4</sub> + 7.2% C <sub>2</sub> H <sub>6</sub> + 4.1% C <sub>3</sub> H <sub>8</sub> + 1.9% C <sub>4</sub> H <sub>10</sub><br>+ 0.8% C <sub>5</sub> H <sub>12</sub> + 0.2% C <sub>6</sub> H <sub>14</sub> + 9.8% N <sub>2</sub><br>+ 0.2% H <sub>2</sub> + 0.2% CO <sub>2</sub> + 0.33% He                                  | 192.1 ± 1.8                                           | 230.6 ± 2.6        | 227.8                                | 230.4 ± 2.1                    |
| 96.8% CH <sub>4</sub> + 0.8% C <sub>2</sub> H <sub>6</sub> + 0.1% C <sub>3</sub> H <sub>8</sub> + 0.1% N <sub>2</sub> + 0.1% H <sub>2</sub><br>+ 2.0% CO <sub>2</sub>                                                                                                                                                                  | 211.8 ± 1.9                                           | 209.6 ± 2.0        | 205.6                                | 208.5 ± 1.9                    |
| 70.5% CH <sub>4</sub> + 8.3% C <sub>2</sub> H <sub>6</sub> + 2.7% C <sub>3</sub> H <sub>8</sub> + 0.8% C <sub>4</sub> H <sub>10</sub><br>+ 0.1% C <sub>5</sub> H <sub>12</sub> + 0.1% C <sub>6</sub> H <sub>14</sub> + 15.9% N <sub>2</sub> + 0.2% H <sub>2</sub><br>+ 1.4% CO <sub>2</sub> + 0.09% He                                 | 217.5 ± 1.9                                           | 202.8 ± 1.8        | 199.8                                | 202.9 ± 1.8                    |
| 93.7% CH <sub>4</sub> + 0.4% C <sub>2</sub> H <sub>6</sub> + 0.2% N <sub>2</sub> + 0.1% H <sub>2</sub> + 5.6% CO <sub>2</sub>                                                                                                                                                                                                          | 220.3 ± 1.9                                           | 201.0 ± 1.9        | 197.1                                | 200.3 ± 1.9                    |
| 31.6% CH <sub>4</sub> + 4.3% C <sub>2</sub> H <sub>6</sub> + 3.8% C <sub>3</sub> H <sub>8</sub> + 2.1% C <sub>4</sub> H <sub>10</sub><br>+ 1.2% C <sub>5</sub> H <sub>12</sub> + 0.6% C <sub>6</sub> H <sub>14</sub> + 54.6% N <sub>2</sub> + 0.1% O <sub>2</sub><br>+ 0.1% Ar + 0.1% H <sub>2</sub> + 0.3% CO <sub>2</sub> + 1.17% He | 316.9 ± 2.3                                           | 134.7 ± 1.1        | 133.3                                | 135.9 ± 1.1                    |
| 24.7% CH <sub>4</sub> + 1.4% C <sub>2</sub> H <sub>6</sub> + 0.3% C <sub>3</sub> H <sub>8</sub> + 73.3% N <sub>2</sub><br>+ 0.1% O <sub>2</sub> + 0.1% CO <sub>2</sub>                                                                                                                                                                 | 663.8 ± 5.1                                           | 59.4 ± 0.5         | 58.3                                 | 59.3 ± 0.5                     |

<sup>a</sup>The errors on the values of  $n$  and  $H$  (method of mixtures) result from an assumed error of ±1% of the reported concentrations of the various mixture components.

<sup>b</sup>The BOM heats of combustion in Btu/ft<sup>3</sup> (60°F) have been transformed to kcal/mol (77°F) as follows:

$$\begin{aligned} \frac{\text{kcal}}{\text{mol}} (77^\circ\text{F}) &= 0.199 \left( \frac{298.15}{288.70} \right) \left[ \frac{\text{Btu}}{(\text{ft})^3} (60^\circ\text{F}) \right] \\ &= 0.206 \left[ \frac{\text{Btu}}{(\text{ft})^3} (60^\circ\text{F}) \right] \end{aligned}$$

(0.199 is the conversion factor for the gas at 32°F)

<sup>c</sup>The errors on the values of  $H$  (present technique) result from the errors on the values of the test gas flowrate,  $n$ .

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# Report Documentation Page

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| 16. Abstract<br>A simplified technique for determination of the heat of combustion of natural gas has been developed. It is a variation of the previously developed technique wherein the carrier air, in which the test sample was burnt, was oxygen enriched to adjust the mole fraction of oxygen in the combustion product gases up to that in the carrier air. The new technique eliminates the need for oxygen enrichment of the carrier air without affecting the sensitivity of the technique. It has been tested on a number of experimental mixtures and natural gas samples and has been found to predict their heats of combustion to an uncertainty of the order of 1 percent. |                                                     |                                                                                                                      |                                 |
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