Introduction to Combustion Analysis

INTRODUCTION

These notes introduce simple combustion models. Such models can be used to analyze many industrial combustion processes and determine such factors as energy release and combustion efficiency. They can also be used to relate measured pollutant concentrations to other measures of emissions such as mole fractions, mass fractions, mass of pollutant per unit mass of fuel, mass of pollutant per unit fuel heat input, etc. These notes provide the derivation of all the equations that are used for these relations.

BASIS OF THE ANALYSIS

The simple combustion model assumes complete combustion in which all fuel carbon forms CO_2, all fuel hydrogen forms H_2O, all fuel sulfur forms SO_2, and all fuel nitrogen forms N_2. This provides results that are accurate to about 0.1% to 0.2% for well operating combustion processes in stationary combustion devices. It is not valid when the combustion process is fuel rich.

Complete combustion of model fuel formula with oxygen – The typical fuel can be represented by the fuel formula $C_xH_yS_zO_wN_v$. With this fuel formula we can analyze a variety of fuels including pure chemical compounds, mixtures of compounds, and complex fuels such as petroleum and coals where the elemental composition of the fuel is measured. This type of measurement is said to provide an ultimate analysis.

Regardless of the source of data for x, y, z, w and v, the mass of fuel represented by this formula[1] can be found from the atomic weights of the various elements:

$$M_{fuel} = x M_C + y M_H + z M_S + w M_O + v M_N \qquad [1]$$

The oxygen required for an assumed complete combustion of this fuel formula can is determined from the oxygen requirements for complete combustion of the individual elements. The C_x part of the fuel would require x moles of O_2 for

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[1] We will later consider the inert mineral matter that is present in some petroleum fuels and coal. In this case the value of M_{fuel} will represent the mass of the combustible part of the fuel.

complete combustion of all fuel carbon to CO_2. Similarly, y/4 moles would be required to convert the hydrogen to H_2O and z moles for conversion of sulfur to SO_2. The oxygen in the fuel will supply a portion of the oxygen required for combustion; w/2 moles of O_2 need not be provided by the combustion air. Using these values we can find the minimum moles of O_2 required for complete combustion of one fuel mole. This amount of oxygen is called the stoichiometric O_2 requirement. It is given the symbol A and is found from the equation:

$$A = x + \frac{y}{4} + z - \frac{w}{2} \qquad [2]$$

In the real combustion process, the actual oxygen used will be greater than this stoichiometric amount. The actual amount is defined in terms of the stoichiometric amount by the oxidizer-fuel equivalence ratio, λ, i.e.

$$Actual\ Moles\ O_2 = \lambda\ A \qquad [3]$$

With this definition, we can immediately write an expression for the moles of O_2 that will appear in the exhaust if the combustion is complete. This will simply be the initial moles, λA, minus the moles required for complete combustion, i.e.,

$$Moles\ O_2\ in\ Exhaust = \lambda A - A = (\lambda - 1)A \qquad [4]$$

With these expressions for the moles of oxygen in the combustion air and in the exhaust the equation for the combustion of the fuel, (ignoring the other components of the combustion air, which are discussed below) can be written as follows:[2]

$$C_x H_y S_z O_w N_v + \lambda A\ O_2 \rightarrow x\ CO_2 + \frac{y}{2} H_2 O + z\ SO_2 + (\lambda - 1)A\ O_2 + \frac{v}{2} N_2 \qquad [5]$$
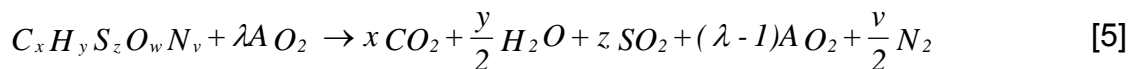
Combustion in air – In industrial combustion processes and engine combustion, air is the oxidizer. Here, the other components of air must be considered in the process. For the simple analysis presented here, these other components are considered inert. For combustion in air, the oxidizer-fuel equivalence ratio is called the air-fuel equivalence ratio; this is also called the percent theoretical air; the quantity (λ - 1), expressed as a percentage, is the percent excess air.

The following analysis for dry air can be used to determine the additional components that enter the combustion equation through the combustion air.

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[2] The correctness of this equation can be checked by substituting the definition for A and showing that each chemical element is balanced.

Species:	N_2	O_2	Ar	CO_2	Trace
Mole Fraction:	0.78084	0.20946	0.00934	0.00033	0.00003

The trace gases and the argon may be lumped together giving a modified argon mole fraction of 0.00937. The main components of the trace gases are Neon and Helium; so the molecular weight of air will be a bit low by lumping the trace gases with Argon, but the error will be less than that caused by the assumption of complete combustion.

In addition, the humidity of normal air means that some H_2O will be present in the combustion air. If the absolute humidity (mass of water per unit mass of dry air) of the air is denoted as ω the moles of water in the air will be given by $M_{da} \omega / M_w$ where M_{da} is the molecular weight of dry air (which is 28.965 for the composition shown above) and M_w is the molecular weight of water.[3]

Providing λA moles of combustion air then provides a certain number of moles of CO_2, H_2O, N_2, and Argon; the moles of each of these species can be expressed as $r_k \lambda A$, where r_k is the ratio of the moles of species k in combustion air to the moles of O_2 in the air. For the standard analysis of air these ratios are found as

$$r_{N_2} = \frac{0.78084}{0.20946} = 3.72787$$

$$r_{Ar} = \frac{0.00937}{0.20946} = 0.044734$$

[6]

$$r_{CO_2} = \frac{0.00033}{0.20946} = .0015755$$

$$r_{H_2O} = \frac{\omega \dfrac{M_{da}}{M_w}}{0.20946} = \omega \frac{\dfrac{28.965}{18.0152}}{.20946} = 7.67597\,\omega$$

Various other assumptions for the composition of atmospheric air can be used in this analysis by selecting the appropriate values of r. For example, most

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[3] The humidity is sometimes expressed in alternative units (*e.g.*, grains of water per pound of dry air or grams of water per kilogram of dry air.) In these cases, it is necessary to use a unit conversion so that the mass of both the water and the dry air are in the same units. If the relative humidity, φ, and barometric pressure, P_{baro}, are given, it is necessary to determine the vapor pressure of water, P_w, at the air inlet temperature. Then the humidity is given by the equation
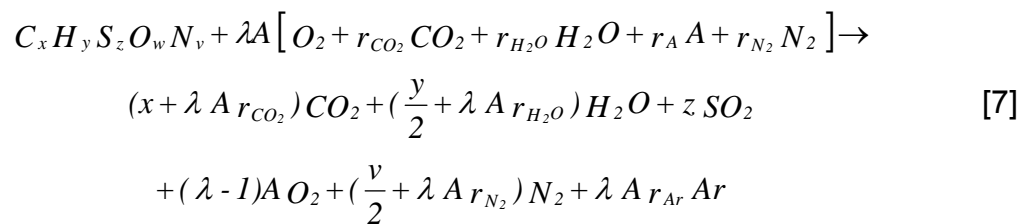
$$\omega = \frac{M_w}{M_{da}} \frac{\phi\, P_w}{P_{baro} - \phi\, P_w}$$

introductory analyses assume that the only other constituent of combustion air is nitrogen. This is equivalent to setting $r_{Ar} = r_{CO2} = r_{H2O} = 0$ and $r_{N2} = 3.77$.

ANALYSIS OF COMPLETE COMBUSTION

This section of the notes considers the case of complete combustion. Here the exhaust composition is uniquely specified by the fuel formula and the *relative amounts* of fuel and oxygen. The analyses done in this section are independent of the amount of fuel in an actual process. We will do all the analyses here for one mole of fuel. Results for processes which use other amounts of fuel can be simply found by scaling by the ratio of the actual fuel used to one mole of fuel. This concept is known as the basis of the calculation. Here we say that we are using one mole of fuel as the basis of the calculation. In subsequent analyses of incomplete combustion we will choose an alternative basis for the calculation.

Relating exhaust composition to initial air/fuel composition – If the full set of species in the combustion air is included in the reactants for the combustion reaction the following equation is obtained:[4]

$$C_x H_y S_z O_w N_v + \lambda A \left[O_2 + r_{CO_2} CO_2 + r_{H_2O} H_2 O + r_A A + r_{N_2} N_2 \right] \rightarrow$$

$$(x + \lambda A r_{CO_2}) CO_2 + (\frac{y}{2} + \lambda A r_{H_2O}) H_2 O + z SO_2 \qquad [7]$$

$$+ (\lambda - 1) A O_2 + (\frac{v}{2} + \lambda A r_{N_2}) N_2 + \lambda A r_{Ar} Ar$$

This equation can be used to find various relations among the fuel, air, and combustion products. For this equation, the mass of fuel is simply the molecular weight of the fuel. The mass of air is λA times the molecular weight of the various species in air weighted by their ratio to oxygen. Thus, the air/fuel ratio, on a mass basis, is given by the following equation:

$$\frac{Air}{Fuel} = \frac{\lambda A \sum_{air} r_k M_k}{M_{Fuel}} = \frac{\lambda A \left[M_{O_2} + r_{CO_2} M_{CO_2} + r_{H_2O} M_{H_2O} + r_{Ar} M_{Ar} + r_{N_2} M_{N_2} \right]}{x M_C + y M_H + z M_S + w M_O + z M_N} \qquad [8]$$

If we consider the humidity in the air separately, we can compute a numerical value for the other components as shown below.

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[4] Although this equation is stated without proof, the reader can show that the equation is balanced for each chemical element. For example, the moles of carbon on the left side of the equation are $n + \lambda A r_{CO2}$. The moles of carbon atom on the right side are seen to be the same. Similar calculations can be done for all atoms appearing in the equation. The analysis for O atoms is more complex, requiring the use of the definition of A in the analysis.

$$M_{O_2} + r_{CO_2} M_{CO_2} + r_{Ar} M_{Ar} + r_{N_2} M_{N_2} = 31.9988 + 0.0015755(44.0095)$$
$$+ 0.044734(39.948) + 3.72787(28.0134) = 138.27$$

Thus, we can write the air/fuel ratio on a mass basis as follows:

$$\frac{Air}{Fuel} = = \frac{(138.27 + 0.767597\omega M_{H_2O})\lambda A}{M_{Fuel}} = \frac{(138.27 + 13.828\omega)\lambda A}{xM_C + yM_H + zM_S + wM_O + vM_N} \quad [8a]$$

This represents only the combustible portion of the fuel. For fuels with noncombustible mineral matter known as ash, the actual fuel mass, m_{fuel}, will be given as

$$Actual \ Fuel \ Mass = \frac{Fuel}{1 - Ash \ Fraction} \quad \Leftrightarrow \quad m_{Fuel} = \frac{M_{Fuel}}{1 - Ash \ Fraction} \quad [9]$$

The exhaust composition can be determined from the product components in equation [7]. To get mole fractions, we have to determine the total moles. If we add the coefficients for all components in the products in equation [7], we get the total number of product moles, including water. This is called the total wet moles, W.

$$W = x + \lambda A \, r_{CO_2} + \frac{y}{2} + \lambda A \, r_{H_2O} + z + (\lambda - 1)A + \frac{v}{2} + \lambda A \, r_{N_2} + \lambda A \, r_{Ar} \quad [10]$$

This may be simplified as follows

$$W = x + \frac{y}{2} + z + \frac{v}{2} + \lambda A \, B_w - A \quad [11]$$

where B_w is defined as

$$B_w = r_{CO_2} + r_{H_2O} + 1 + r_{N_2} + r_{Ar} \quad [12]$$

For many combustion product analyses, the water is removed before the analysis and the total moles are the dry moles, D. This is the total wet moles minus the moles of water, which is given by the equation

$$D = x + z + \frac{v}{2} + \lambda A \, B_d - A \quad [13]$$

where B_d is defined as

$$B_d = r_{CO_2} + 1 + r_{N_2} + r_{Ar} \quad [14]$$

From the values of the r_i given in equation [6] the value of B_d is seen to be a constant and the value of B_w depends on the humidity, ω.

$$B_d = 4.7742 \qquad and \qquad B_w = 4.7742 + 7.67597\,\omega \qquad [15]$$

The value of B_d is simply the reciprocal of the mole fraction of oxygen in air. It represents the sum of the moles of all components in air divided by the moles of oxygen.

The values of the total product moles in the equations used here refer to the combustion equation for one mole of the typical fuel. The actual number of product moles in any real process can be found by multiplying the total moles computed here by the number of fuel moles in a particular combustion process.

The mass of combustion products is the same as the mass of air plus the combustible mass of fuel into the process. Thus, the mean molecular weight of the wet combustion products may be found as

$$M_{ex,wet} = \frac{Fuel + Air}{W} \qquad [16]$$

A consistency check on the computations is obtained by using the combustion product composition may be used to compute the mean molecular weight of the wet exhaust

$$M_{ex,w} = \frac{\left[\begin{array}{c} (x + \lambda\,A\,r_{CO_2})\,M_{CO_2} + (\frac{y}{2} + \lambda\,A\,r_{H_2O})\,M_{H_2O} + z\,M_{SO_2} \\[2em] + (\lambda - 1)A\,M_{O_2} + (\frac{v}{2} + \lambda\,A\,r_{N_2})\,M_{N_2} + \lambda\,A\,r_{Ar}\,M_{Ar} \end{array} \right]}{W} \qquad [17]$$

In a similar manner the molecular weight of the dry combustion products may be found from an overall mass balance,

$$M_{ex,d} = \frac{Fuel + Air - (\frac{x}{2} + \lambda\,A\,r_{H_2O})\,M_{H_2O}}{D} \qquad [18]$$

and verified by a direct calculation from the composition of the dry exhaust products,

$$M_{ex,d} = \frac{\left[\begin{array}{c} (x + \lambda\,A\,r_{CO_2})\,M_{CO_2} + z\,M_{SO_2} \\[2em] + (\lambda - 1)A\,M_{O_2} + (\frac{v}{2} + \lambda\,A\,r_{N_2})\,M_{N_2} + \lambda\,A\,r_{Ar}\,M_{Ar} \end{array} \right]}{D} \qquad [19]$$

RELATION BETWEEN λ, EXHAUST OXYGEN AND OTHER EXHAUST CALCULATIONS

The amounts of each product species allow the development of a relation between the air-fuel equivalence ratio, λ, and the exhaust oxygen concentration, $\%O_2$. For dry exhaust the oxygen mole fraction is the moles of oxygen divided by the number of dry moles. From equations [7] and [13] we can write this mole fraction as

$$\%O_2 = \frac{100(\lambda - 1)A}{D} = \frac{100(\lambda - 1)A}{x + \lambda A B_d - A + z + \dfrac{v}{2}} \qquad [20]$$

If the air-fuel equivalence ratio is given, this equation may be used to solve for the resulting exhaust O_2 concentration. The equation can be rearranged to solve for the air-fuel equivalence ratio when the exhaust O_2 concentration is given:

$$\lambda = \frac{A + \dfrac{\%O_2}{100}\left[x - A + z + \dfrac{v}{2} \right]}{A - A B_d \dfrac{\%O_2}{100}} \qquad [21]$$

Equations [20] and [21] provide the essential relation between a measured exhaust oxygen concentration and a specified air/fuel ratio. Either of these variables can be used to characterize a combustion process and it is important to be able to relate one to the other.

Correction to standard concentrations – Many regulatory standards for combustion gases require that the measured exhaust concentrations, C_{meas}, at the actual exhaust O_2 concentration, $(\%O_2)_{meas}$, be converted to the equivalent concentration, C_{std}, at a standard oxygen concentration, $(\%O_2)_{std}$. The basis for this conversion is the assumption that the mole number of pollutant species is small compared to the total moles and will not change the total number of moles. In this case the measured and standard concentrations are given in terms of the total number of moles under measured and standard conditions (N_{meas} and N_{std}). For the pollutant moles of N_{pol}, the concentration (really mole fraction) equations are

$$C_{std} = \frac{N_{pol}}{N_{std}} \qquad and \qquad C_{meas} = \frac{N_{pol}}{N_{meas}} \qquad [22]$$

Eliminating N_{pol} from these equations gives

$$C_{std} = C_{meas} \frac{N_{meas}}{N_{std}} \qquad [23]$$

Because the standards are usually based on dry moles, the equation for total dry moles can be used to replace N_{meas} and N_{std}. Before doing this equation [21] for λ can be substituted into equation [13] for the total dry moles, D, giving

$$D = x + z + \frac{v}{2} \; A + AB_d \; \frac{A + \dfrac{\% O_2}{100} \left[x - A + z + \dfrac{v}{2} \right]}{A - A \; B_d \; \dfrac{\% O_2}{100}} \qquad [24]$$

Rearranging this equation gives

$$D = \frac{\left[x + z + \dfrac{v}{2} - A \right] \left[\dfrac{1}{B_d} - \dfrac{\% O_2}{100} \right] + A + \dfrac{\% O_2}{100} \left[x - A + z + \dfrac{v}{2} \right]}{\dfrac{1}{B_d} - \dfrac{\% O_2}{100}} \qquad [25]$$

The oxygen concentration terms in the numerator cancel leaving

$$D = \frac{A + \dfrac{x + z + \dfrac{v}{2} - A}{B_d}}{\dfrac{1}{B_d} - \dfrac{\% O_2}{100}} \qquad [26]$$

When this equation is used for N_{meas} and N_{std} in equation [23] the oxygen concentration is subscripted to denote the different measured oxygen concentrations in the measured and standard case. This gives

$$C_{std} = C_{meas} \; \frac{\dfrac{A + \dfrac{x + z + \dfrac{v}{2} - A}{B_d}}{\dfrac{1}{B_d} - \dfrac{[\% O_2]_{meas}}{100}}}{\dfrac{A + \dfrac{x + z + \dfrac{v}{2} - A}{B_d}}{\dfrac{1}{B_d} - \dfrac{[\% O_2]_{std}}{100}}} \qquad [27]$$

The constant term, $A + (x + z + v/2 - A)/B_d$ can be cancelled giving the final form for the correction equation (after multiplying top and bottom by 100),

$$C_{std} = C_{meas} \frac{\dfrac{100}{B_d} - [\%O_2]_{std}}{\dfrac{100}{B_d} - [\%O_2]_{meas}}$$ [28]

Using the value of B_d = 4.7742 from equation [15] the value of $100/B_d$ is 20.946,[5] which is usually rounded to 21, 20.9 or 20.95 in regulatory conversion equations. (If the oxygen is represented as a mole fraction rather than a mole percent, the correct value of the constant is 0.20946.)

Alternative approach using CO_2 – An alternative dilution correction is based on the measured dry CO_2 concentration. From the balanced chemical equation [7], the number of CO_2 moles is $x+\lambda Ar_{CO2}$. Using equation [13] for the number of dry moles, D, gives the mole percentage of CO_2 in the dry exhaust, $\%CO_2$, by the following equation.

$$\frac{\%CO_2}{100} = \frac{x + \lambda Ar_{CO_2}}{D} = \frac{x + \lambda Ar_{CO_2}}{x + z + \dfrac{v}{2} + \lambda AB_d - A}$$ [29]

Solving this equation for λ gives

$$\lambda = \frac{x - \left[x + z + \dfrac{v}{2} - A\right]\dfrac{\%CO_2}{100}}{AB_d\dfrac{\%CO_2}{100} - Ar_{CO_2}}$$ [30]

Substituting this equation into equation [13] for D gives the total dry moles in terms of the CO_2 concentration

$$D = x + z + \frac{v}{2} - A + AB_d \frac{x - \left[x + z + \dfrac{v}{2}\ A\right]\dfrac{\%CO_2}{100}}{AB_d\dfrac{\%CO_2}{100} - Ar_{CO_2}}$$ [31]

Rearranging this equation gives

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[5] As noted above $1/B_d$ is simply the mole fraction of oxygen in air so $100/B_d$ is the mole percentage of oxygen in air.

$$D = \frac{\left[x + z + \dfrac{v}{2} - A\right]\left[\dfrac{\%CO_2}{100} - \dfrac{r_{CO_2}}{B_d}\right] + x - \left[x + z + \dfrac{v}{2} - A\right]\dfrac{\%CO_2}{100}}{\dfrac{\%CO_2}{100} - \dfrac{r_{CO_2}}{B_d}} \qquad [32]$$

Canceling the CO_2 terms in the numerator gives the following result, which may be simplified by ignoring the small terms from CO_2 in the inlet air.

$$D = \frac{x - \left[x + z + \dfrac{v}{2} - A\right]\dfrac{r_{CO_2}}{B_d}}{\dfrac{\%CO_2}{100} - \dfrac{r_{CO_2}}{B_d}} \approx \frac{x}{\dfrac{\%CO_2}{100}} \qquad [33]$$

Substituting the simplified equation for N_{meas} and N_{std} in equation [23] (with appropriate subscripts to denote the measured and standard CO_2 concentrations) gives the result that

$$C_{std} = C_{meas}\frac{[\%CO_2]_{std}}{[\%CO_2]_{meas}} \qquad [34]$$

COMPUTING EMISSIONS PER UNIT OF FUEL ENERGY

Pollutant ratio equations – The various relationships outlined above can be used to compute the pollutant flow rate from the measured concentration and the measured fuel flow rate. This is based on the knowledge of the ratio of total exhaust moles to the fuel mass. Since most pollutant concentrations are reported on the basis of dry exhaust gases the relevant ratio is D/m_{fuel}. From equations [9] and [26] this ratio is given by the following equation

$$\frac{D}{m_{fuel}} = \frac{A + \dfrac{x + z + \dfrac{v}{2} - A}{B_d}}{\dfrac{1}{B_d} - \dfrac{\%O_2}{100}}\frac{1 - Ash\ Fraction}{M_{fuel}} \qquad [35]$$

A slight rearrangement of this equation gives an explicit representation of fuel properties and the air/fuel ratio (as measured by the exhaust oxygen concentration).

$$\frac{D}{m_{fuel}} = \frac{\left[A(B_d - 1) + x + z + \dfrac{v}{2}\right][1 - Ash\ Fraction]}{M_{fuel}}\frac{\dfrac{100}{B_d}}{\dfrac{100}{B_d} - \%O_2} \qquad [36]$$

The molecular weight of the fuel is found from equation [1]. Using the molecular weight of the exhaust from equation [19] gives the mass flow rate of dry exhaust, $\dot{m}_{ex,d}$, in terms of the fuel flow rate, $\dot{m}_{fuel}$, as follows.

$$\dot{m}_{ex,d} = \dot{m}_{fuel} \frac{D}{m_{fuel}} M_{ex,d} \qquad [37]$$

The relation between mass flow rate and volume flow rate can be found using the standard density of the exhaust gases. This is usually given for a standard pressure and temperature, P_{std} and T_{std}, and can be found from the ideal gas law for either a wet or a dry basis. These densities are

$$\rho_{wet} = \frac{M_{ex,w} P_{std}}{R T_{std}} \qquad or \qquad \rho_{dry} = \frac{M_{ex,d} P_{std}}{R T_{std}} \qquad [38]$$

where R is the universal gas constant (R = 0.7302 ft^3-atm/lbmole-R). The volume flow rate of dry exhaust gases, $\dot{V}_{ex,d}$, can be found as

$$\dot{V}_{ex,d} = \frac{\dot{m}_{ex,d}}{\rho_{dry}} = \dot{m}_{fuel} \frac{D}{m_{fuel}} M_{ex,d} \frac{R T_{std}}{M_{ex,d} P_{std}} = \dot{m}_{fuel} \frac{D}{m_{fuel}} \frac{R T_{std}}{P_{std}} \qquad [39]$$

The U. S. Environmental Protection Agency (EPA) Method 19 uses the ratio of dry exhaust gas volume flow rate divided by the heat input rate. The input heat rate of the fuel, $\dot{Q}_{fuel}$, is simply the product of the fuel flow rate and the heat of combustion of the fuel, Q_c. Dividing equation the left side of equation [39] by $\dot{Q}_{fuel}$, and the right side of the equation by the equivalent product, $\dot{m}_{fuel} Q_c$, gives the desired Method 19 ratio.

$$\frac{\dot{V}_{ex,d}}{\dot{Q}_{fuel}} = \frac{1}{Q_c} \frac{D}{m_{fuel}} \frac{R T_{std}}{P_{std}} \qquad [40]$$

Using equation [36] to eliminate the D/m$_{fuel}$ ratio gives

$$\frac{\dot{V}_{ex,d}}{\dot{Q}_{fuel}} = \frac{R T_{std}}{P_{std}} \frac{\left[A(B_d - 1) + x + z + \dfrac{v}{2} \right] [1 - Ash\ Fraction]}{Q_c M_{fuel}} \frac{\dfrac{100}{B_d}}{\dfrac{100}{B_d} - \%O_2} \qquad [41]$$

The F factor – The right hand side of the equation has three distinct components. The first is the variables used to compute the density (R, P_{std}, and T_{std}); the middle term depends on the fuel properties. The final term, using the measured exhaust oxygen concentration, is a measure of the excess air. The first two terms are defined as the dry F-factor, F_d, in EPA method 19, i.e.

$$F_d = \frac{RT_{std}}{P_{std}} \frac{\left[A(B_d - 1) + x + z + \frac{v}{2} \right] \left[1 - Ash\ Fraction \right]}{Q_c M_{fuel}} \qquad [42]$$

A typical standard for boiler and furnace operation is 3% exhaust oxygen concentration. For methane combustion, $x = 1$, $y = 4$, and $v = w = z = $ Ash Fraction $= 0$. From equation [2], $A = 2$. The heat of combustion and molecular weight of methane are 23,861 Btu/lb and 16.04 lb/lb-mol, respectively. The standard temperature and pressure are typically 527.69°R (= 68°F = 20°C) and atmospheric pressure,[6] and the gas constant with consistent units is 0.7302 ft³-atm/lbmole-R. With these substitutions the value of F_d for pure methane, computed from equation [42] is 8604.8 ft³/MMBtu.

The equation for F_d can be rearranged to express the coefficients in terms of the ultimate analysis of the fuel. The term containing $A(B_d - 1)$ can be rearranged, using the definition of A from equation [2].

$$A(B_d - 1) + x + z + \frac{v}{2} = \left[x + \frac{y}{4} + z - \frac{w}{2} \right](B_d - 1) + x + z + \frac{v}{2}$$

$$A(B_d - 1) + x + z + \frac{v}{2} = B_d(x + z) + (B_d - 1) \left[\frac{y}{4} - \frac{w}{2} \right] + \frac{v}{2} \qquad [43]$$

The total fuel mass, m_{fuel}, is related to the molecular weight of the combustible portion of the fuel and the ash fraction by equation [9]

$$m_{fuel} = \frac{M_{fuel}}{1 - Ash\ Fraction} \qquad [44]$$

The individual stoichiometric coefficients in the fuel formula, $C_xH_yO_wN_vS_z$, are related to their ultimate analysis (in elemental weight percents) by the following formulae

$$x = \frac{wt\%C}{100} \frac{m_{fuel}}{M_C} \qquad y = \frac{wt\%H}{100} \frac{m_{fuel}}{M_H} \qquad z = \frac{wt\%S}{100} \frac{m_{fuel}}{M_S}$$

$$[45]$$

$$v = \frac{wt\%N}{100} \frac{m_{fuel}}{M_N} \qquad w = \frac{wt\%O}{100} \frac{m_{fuel}}{M_O}$$

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[6] Sometimes a temperature of 15°C = 59°F or 60°F = 15.56°C is used. A standard pressure of 14.73 psia = 30 in Hg is sometimes used as the standard pressure instead of the standard atmosphere = 14.696 psia = 29.92 in Hg.

In equations [45], M_C, M_H, M_S, M_N, and M_O represent the atomic weights of elemental carbon, hydrogen, sulfur, nitrogen and oxygen, respectively. Substituting equations [45] into equation [43] gives

$$A(B_d - 1) + x + z + \frac{v}{2} = \frac{m_{fuel}}{100} \left\{ B_d \left[\frac{wt\%C}{M_C} + \frac{wt\%S}{M_S} \right] + \frac{1}{2} \frac{wt\%N}{M_N} + \frac{B_d - 1}{4} \left[\frac{wt\%H}{M_H} - 2 \frac{wt\%O}{M_O} \right] \right\}$$ [46]

Substituting this result and equation [44] into equation [42] gives the basic equation for F_d in terms of the ultimate analysis of the fuel,

$$F_d = \frac{RT_{std}}{100\, P_{std}\, Q_c} \left\{ B_d \left[\frac{wt\%C}{M_C} + \frac{wt\%S}{M_S} \right] + \frac{1}{2} \frac{wt\%N}{M_N} + \frac{B_d - 1}{4} \left[\frac{wt\%H}{M_H} - 2 \frac{wt\%O}{M_O} \right] \right\}$$ [47]

This can be expressed in the following form

$$F_d = \frac{1}{Q_c} \sum_{species = C,H,O,N,S} K_{species} \left[wt\% \right]_{species}$$ [48]

where

$$K_C = \frac{RT_{std}\, B_d}{100\, P_{std}\, M_C} \qquad K_S = \frac{RT_{std}\, B_d}{100\, P_{std}\, M_S} \qquad K_N = \frac{RT_{std}}{200\, P_{std}\, M_N}$$

[49]

$$K_H = \frac{RT_{std}(B_d - 1)}{400\, P_{std}\, M_H} \qquad K_O = \frac{RT_{std}(1 - B_d)}{200\, P_{std}\, M_O}$$

Substituting the appropriate values for these coefficients gives the results in Table 1. This table also contains, for comparison, the values for these coefficients given in Method 19. The coefficients computed here agree with those in Method 19 to the two significant figures reported in Method 19 except for the oxygen and hydrogen coefficients. The reason for this difference is not known.

Alternative F factors based on CO_2 – Equation [33] which gives the total dry moles as a function of the CO_2 concentration can be used to obtain an alternative expression for the ratio of dry moles per unit mass of fuel.

$$\frac{D}{m_{fuel}} = \frac{x}{\frac{\%CO_2}{100}} \frac{1 - Ash\ Fraction}{M_{fuel}} \qquad [50]$$

If this expression for D/m_{fuel} is substituted into equation [40], the following result is obtained.

$$\frac{\dot{V}_{ex,d}}{\dot{Q}_{fuel}} = \frac{R\,T_{std}}{P_{std}} \frac{x[1 - Ash\ Fraction]}{Q_c\,M_{fuel}} \frac{100}{\%CO_2} \qquad [51]$$

Table 1					
Computed Coefficients for Ultimate Analysis Factors in EPA Method 19 and Comparison with Published Factors					
Coefficient	K_C	K_H	K_S	K_N	K_O
This calculation	1.5316	3.6072	0.5738	0.1375	-0.4545
Method 19	1.53	3.64	0.57	0.14	-0.46

The group of terms on the left-hand side of equation [51] is used to define the F factor for CO_2, F_c.

$$F_c = \frac{RT_{std}}{P_{std}} \frac{x[1 - Ash\ Fraction]}{Q_c\,M_{fuel}} \qquad [52]$$

Substituting the expression for x in terms of the weight percent of fuel carbon from equations [45] into [52] gives the following expression for F_c.

$$F_c = \frac{RT_{std}}{P_{std}} \frac{wt\%C}{100\,Q_c\,M_C} = \frac{K_{cc}}{Q_c} wt\%C \qquad [53]$$

where the constant, K_{cc}, is defined as follows.

$$K_{cc} = \frac{RT_{std}}{100\,P_{std}\,M_C} \qquad [54]$$

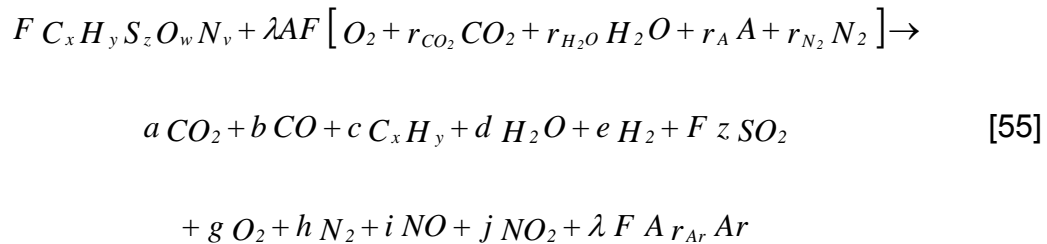The value of K_{cc} found here is 0.32081 ft^3/lb-% which matches the value of 0.321 given in Method 19.

ANALYSES OF INCOMPLETE COMBUSTION

When exhaust measurements are available, an alternative approach to the determination of the various flow rate ratios can be done. This alternative

method uses measured values for the various exhaust species in place of the computed ones. The specific approach depends on the actual measurements. The analysis below assumes that measurements are available for CO, CO_2, HC (representing unburned fuel), O_2, NO and NO_2. Alternative approaches are then used if fewer measurements are available.

In the case where exhaust measurements are available, the usual approach is to determine the amount of fuel required to produce 100 dry moles. This is the basis used for the calculation here. Results for any process that produces a different amount of exhaust products can be simply scaled from the results obtained here. For the basis of 100 dry moles, the combustion equation is written as follows:

$$F \, C_x H_y S_z O_w N_v + \lambda AF \left[O_2 + r_{CO_2} CO_2 + r_{H_2O} H_2O + r_A A + r_{N_2} N_2 \right] \rightarrow$$

$$a \, CO_2 + b \, CO + c \, C_x H_y + d \, H_2O + e \, H_2 + F \, z \, SO_2 \qquad [55]$$

$$+ g \, O_2 + h \, N_2 + i \, NO + j \, NO_2 + \lambda \, F \, A \, r_{Ar} \, Ar$$

The terms for the product moles of sulfur and argon in this equation provides the correct balances for these elements. Additional element balance equations are available for carbon, hydrogen, oxygen and nitrogen. These are, respectively,

$$F(x + \lambda \, A \, r_{CO_2}) = a + b + c \, x \qquad [56]$$

$$F(y + 2 \, \lambda \, A \, r_{H_2O}) = c \, y + 2 \, d + 2 \, e \qquad [57]$$

$$F[w + \lambda \, A \, (2 + 2 \, r_{CO_2} + r_{H_2O})] = 2 \, a + b + d + 2 \, F \, z + 2 \, g + i + 2 \, j \qquad [58]$$

$$F(v + 2 \, \lambda \, A \, r_{N_2}) = 2 \, h + i + j \qquad [59]$$

The use of 100 dry moles as the basis for the calculation gives the following equation

$$a + b + c + d + e + F \, z + g + h + i + j + \lambda \, F \, A \, r_{Ar} = 100 \qquad [60]$$

For convenience the actual moles of oxygen in the fuel-air mixture, λAF, is written as Λ. Making this substitution and rearranging equations [56] to [58] gives the following set of equations. In constructing these equations we assume that measurements will be available for CO, CO_2, HC, NO, NO_2, and O_2. Thus, the values of a, b, c, g, i, and j will be known quantities in this calculation. We can rewrite equations [56] to [60] denoting the sums of known quantities as constants K_1 to K_5.

$$x \, F + r_{CO_2} \Lambda = a + b + c \, x = K_1 \qquad [61]$$

$$-2\,d - 2\,e + y\,F + 2\,r_{H_2O}\,\Lambda = c\,y = K_2 \qquad [62]$$

$$
\begin{aligned}
-d + (w - 2\,z)F + (2 + 2\,r_{CO_2} + r_{H_2O})\,\Lambda \\
= 2\,a + b + 2\,g + i + 2\,j = K_3
\end{aligned}
\qquad [63]
$$

$$2\,h + v\,F + 2\,\Lambda\,r_{N_2} = i + j = K_4 \qquad [64]$$

$$e + h + z\,F + r_{Ar}\,\Lambda = 100 - a - b - c - g - i - j = K_5 \qquad [65]$$

Because of the assumption of 100 dry moles, the values of a, b, c, g, i, and j are simply the measured values for CO_2, CO, HC, O_2, NO, and NO_2 in mole percent (dry). E.g., if the measured dry exhaust CO concentration is 100 ppm (a mole fraction of 10^{-4} or 0.01%) the value of b is 0.01. Thus, the right hand sides of the five equations listed above are known. This system of five equations in five unknowns (d, e, F, h, and Λ) can be solved by algebraic manipulation to obtain the following results. These results use the defined constants K_6, K_7, and K_8, which are given by the following equations.

$$K_6 = \frac{y}{2} - w + 3\,z + \frac{v}{2} \qquad [66]$$

$$K_7 = r_{N_2} + r_{Ar}\ 2\ 2\ r_{CO_2} \qquad [67]$$

$$K_8 = K_5 - K_3 + \frac{K_2 + K_4}{2} \qquad [68]$$

The moles of oxygen in the fuel-air mixture are found from the following equation:

$$\Lambda = \frac{K_8 - \dfrac{K_1\,K_6}{x}}{K_7 - \dfrac{K_6\,r_{CO_2}}{x}} \qquad [69]$$

The value of (combustible) fuel moles is found next by rearranging equation [61].

$$F = \frac{K_1 - \Lambda\,r_{CO_2}}{x} \qquad [70]$$

The relative air/fuel ratio, λ, can be found from the definition of Λ.

$$\lambda = \frac{\Lambda}{F\,A} \qquad [71]$$

The exhaust moles of the remaining constituents, nitrogen, water and hydrogen, can be found as follows

$$h = \frac{v\,F + 2\,\Lambda\,r_{N_2} - K_4}{2} \qquad [72]$$

$$d = (w - 2\,z)\,F + (2 + 2\,r_{CO_2} + r_{H_2O})\,\Lambda - K_3 \qquad [73]$$

$$e = \frac{y\,F}{2} + r_{H_2O}\,\Lambda - \frac{K_2}{2} - d \qquad [74]$$

The amount of hydrogen is usually small. If there are analysis errors the value for hydrogen can become negative or unusually large. As a check the typical values for hydrogen are governed by the water-gas shift reaction,

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad Equilibrium\ Constant : K_{wg} \qquad [75]$$
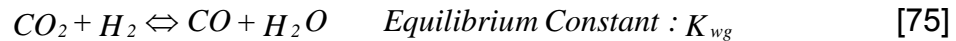
The equilibrium constant provides a relationship among the concentrations of the species in the reaction. The symbols used above, which represent the number of moles of the species, can be used directly in the equilibrium equation for this reaction because the numbers of reactant and product moles are the same. This gives

$$K_{wg} = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{b\,d}{a\,e} \qquad [76]$$

This equation can be solved for the hydrogen moles in terms of the other species moles and the value of K_{wg}. The equilibrium constant depends on temperature. In most combustion analyses, a value of 3.5 is assumed for this constant.[7]

$$e = \frac{b\,d}{a\,K_{wg}} \qquad [77]$$

The value of e found from the element balance equations above should not be significantly greater than the value found from the water-gas equilibrium equation.

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[7] Although this equation has the same form as the equilibrium equation for the water-gas shift reaction, the value of 3.5 used for the equilibrium constant is not the true value of the constant at the measurement temperature. Instead it is an empirical value which has been found to provide a reasonable correlation of actual data for combustion analyses. Fortunately, the H_2 concentration is usually low and the inaccuracies in this equation will not have a significant effect on the overall result.

Correction of F-factor Approach for Incomplete Combustion – An approximate analysis is available using only measurements of CO, CO_2, and exhaust HC. (If exhaust HC measurements are not available, the HC concentration, c, can be assumed zero in the analysis below.) This analysis starts with carbon balance in equation [56], which is repeated below.

$$F(x + \lambda\, A\, r_{CO_2}) = a + b + c\, x \qquad [56]$$

If the small concentration of CO_2 in the combustion air is ignored, the moles of fuel, F, is simply found as (a + b + cx)/x. The fuel mass is simply this number of moles divided by the molecular weight of the fuel (with a correction for any fuel ash content):

$$m_{fuel} = \frac{M_{fuel}}{1 - Ash\ Fraction} \frac{a + b + c\,x}{x} \qquad [78]$$

This equation can be used to find the ratio of the mass of any pollutant species to the mass of fuel. The species mass is simply the species mole fraction measured in the analysis times its molecular weight. The $m_{species}/m_{fuel}$ ratio can be divided by the heat of combustion to get the emission factor in units of pollutant mass per unit heat input, e.g., lb/MMBtu. In the above equation the moles of NOx is the sum of the NO plus NO_2 moles, i+j. The mass of NOx per unit heat input of fuel is then given by

$$\frac{\dot{m}_{NOx}}{\dot{Q}_{fuel}} = M_{NOx}(\ i + j\ )\frac{1 - Ash\ Fraction}{Q_c\, M_{fuel}} \frac{x}{a + b + c\,x} \qquad [79]$$

In general, the emission factor for any species with molecular weight, M_i, and mole fraction, y_i, is given in terms of the atoms of carbon in one mole of fuel, x, and the exhaust mole fractions of CO_2, CO, and HC (denoted as y_{CO2}, y_{CO}, and y_{HC}, respectively) as follows.

$$\frac{\dot{m}_i}{\dot{Q}_{fuel}} = M_i\, y_i \frac{1 - Ash\ Fraction}{Q_c\, M_{fuel}} \frac{x}{y_{CO_2} + y_{CO} + x\ y_{HC}} \qquad [80]$$

This can be compared to the usual equation using the F factor based on CO_2. The first step is using that equation is the conversion of the species mole fraction (or ppm) into a mass concentration. The values typically used are a mole fraction in ppm (ppm_i) and a (standard) mass concentration (m_i/V_{std}), typically in lb/ft^3. The conversion between the two is found as follows. The species mass is simply the species moles, n_i, multiplied by the species molecular weight, M_i. The parts per million, multiplied by 10^{-6} gives the mole fraction, n_i/n. The ideal gas equation is used to define the standard volume. These steps are all combined in the following equation.

$$\frac{m_i}{V_{std}} = \frac{M_i\, n_i}{V_{std}} = M_i\, \frac{n_i}{n}\, \frac{n}{V_{std}} = M_i\, 10^{-6}\, ppm_i\, \frac{P_{std}}{RT_{std}} \qquad [81]$$

The mass rate of a pollutant species per unit heat input rate is then found by multiplying this species mass concentration times the ratio of exhaust volume flow rate to input heat rate.

$$\frac{\dot{m}_i}{\dot{Q}_{fuel}} = \frac{m_i}{V}\, \frac{\dot{V}_{ex,dry}}{\dot{Q}_{fuel}} = M_i\, 10^{-6}\, ppm_i\, \frac{P_{std}}{R\, T_{std}}\, \frac{\dot{V}_{ex,dry}}{\dot{Q}_{fuel}} \qquad [82]$$

Using equation [51] for $\underline{V}_{ex,d} / \underline{Q}_{fuel}$ gives the following result for the mass of the pollutant species per unit heat input:

$$\frac{\dot{m}_i}{\dot{Q}_{fuel}} = M_i\, 10^{-6}\, ppm_i\, \frac{x\left[1 - Ash\ Fraction\right]}{Q_c\, M_{fuel}}\, \frac{100}{\%CO_2} \qquad [83]$$

Replacing $10^{-6}\, ppm_i$ by the equivalent mole fraction y_i and $100/\%CO_2$ by its equivalent mole fraction, y_{CO2}, allows equation [83] to be rewritten as

$$\frac{\dot{m}_i}{\dot{Q}_{fuel}} = M_i\, y_i\, \frac{x\left[1 - Ash\ Fraction\right]}{Q_c\, M_{fuel}}\, \frac{1}{y_{CO_2}} \qquad [84]$$

This is the value that would be computed from the conventional (CO_2 based) F-factor approach. By comparison with equation with equation [80], which accounts for partial combustion, we can get a corrected emission factor in terms of the emission factor computed by the F-factor approach. This is given by

$$\left[\frac{\dot{m}_i}{\dot{Q}_{fuel}}\right]_{corrected} = \left[\frac{\dot{m}_i}{\dot{Q}_{fuel}}\right]_{F\ factor}\, \frac{y_{CO_2}}{y_{CO_2} + y_{CO} + x\ y_{HC}} \qquad [85]$$

The correction factor involves the ratio of carbon in incomplete combustion products to the carbon in CO_2. If this ratio is small, then the use of the F-factor approach should give reasonable results.

$$\left[\frac{\dot{m}_i}{\dot{Q}_{fuel}}\right]_{corrected} = \left[\frac{\dot{m}_i}{\dot{Q}_{fuel}}\right]_{F\ factor}\, \frac{1}{1 + \dfrac{y_{CO} + x\ y_{HC}}{y_{CO_2}}} \qquad [86]$$

For example, if the mole fraction of CO_2 is 0.05 and the $y_{CO} + x\ y_{HC}$ term is 1000 ppm = 0.001, then the correction factor is 1/[1+.001/.05] = 1/1.02 = 0.98. In a very rich combustion example the ratio of CO + xHC to CO_2 might be 1:1; in this case the correction factor would be 0.5. Note that the correction factor

always gives a smaller emission factor than the one computed by the standard F-factor approach.

CHEMICAL ENERGY TERMS

The usual calculation of thermodynamic property changes uses an arbitrary reference point at a given temperature and pressure. For example, we can start with the usual differential equation for the enthalpy as a function of temperature and pressure.

$$dh = c_p dT + v(1 - T\alpha_p)dP \qquad where \qquad \alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \qquad [87]$$

In this equation, h, c_p, and v represent the *per-unit-mole* values of enthalpy, isobaric heat capacity, and specific volume, respectively. If we integrate the dh equation between an arbitrary reference temperature and pressure, T_{ref} and P_{ref}, to some other temperature, T, and pressure, P, we can write the result formally as follows.

$$h - h_{ref} = h(T,P) - h(T_{ref}, P_{ref}) = \int_{h_{ref}}^{h} dh' = \int_{T_{ref}}^{T} c_p dT' + \int_{P_{ref}}^{P} v(1 - T\alpha_p)dP' \qquad [88]$$

In the absence of chemical reactions, the reference enthalpy is arbitrary. However, in order to account for the energy of chemical reactions we have to have to include this energy in the reference term. This is done by the following process.

- The enthalpy of formation of chemical elements in their natural state is set to zero.

- The enthalpy of formation of a compound from its elements, in a process in which the products are at the same temperature and pressure as the elements, which form it, is taken as the reference enthalpy for a compound.

The enthalpy of formation is typically measured at a reference temperature of 25 C = 298.15 K = 77 F and a reference pressure of one atmosphere. For combustion analyses the effect of pressure on enthalpy is negligible and equation [88] may be written for one chemical species as follows:

$$h_i(T) = h_i(T_{ref}) + \int_{T_{ref}}^{T} c_{p_i} dT' \qquad [89]$$

Values of $h_i(T_{ref})$ may be found in various thermodynamic tables.[8]

We have previously discussed the heat of combustion or heat content of fuels. The heat of combustion is defined in terms of the enthalpy change for complete stoichiometric combustion. The reaction of our typical fuel formula with oxygen in shown in equation [5]; we can use the coefficients from that equation, setting λ equal to one, and recognizing that the heat of formation of oxygen and nitrogen are zero, to write the following enthalpy change equation.

$$\Delta H_R(T_{ref}) = x h_{CO_s}(T_{ref}) + \frac{y}{2} h_{H_2O}(T_{ref}) + z h_{SO_2}(T_{ref}) - h_{Fuel}(T_{ref}) \qquad [90]$$

This will be a negative enthalpy change (indicating that heat is liberated by the reaction).[9] The heat of combustion of the fuel is defined as the negative of this enthalpy change divided by the molecular weight of the fuel to get units on a mass basis.

$$Q_c = -\frac{\Delta H_R(T_{ref})}{m_{fuel}} = -\frac{x h_{CO_s}(T_{ref}) + \frac{y}{2} h_{H_2O}(T_{ref}) + z h_{SO_2}(T_{ref}) - h_{Fuel}(T_{ref})}{m_{fuel}} \qquad [91]$$

For example, the enthalpy change for formation of methane, liquid water, and CO_2 are –74.87 kJ/mol, -285.83 kJ/mol, and –393.52 kJ/mol, respectively. We can compute the enthalpy change for the reaction $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ from equation [90] as 1(-393.52) + 2(-285.83) – (-74.87) = -830.31 kJ/mol. Using the molecular weight of methane, we can compute the heat of combustion as follows: Q_c = -(-830.31 kJ/mol) / (16.04262 g/mol) = 55.497 kJ/g = 55,497 kJ/kg = 23,859 Btu/lb_m.[10]

The analysis of a real combustion process, using typical applications of the first law of thermodynamics, must use these chemical enthalpies as the reference enthalpy. The usual first law for open systems uses specific enthalpies based on

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[8] Chase, M. W., Jr., *NIST-JANAF Thermochemical Tables, Fourth Edition*, **J. Phys. Chem. Ref. Data, Monograph 9**, 1998, 1-1951. Note that the usual symbol for this reference enthalpy, called the enthalpy of formation, is ΔH_f^o. This is based on the convention that the reference enthalpy for the elements in their natural state is zero and the reference enthalpy for compounds is the enthalpy difference between, measured as the energy input, when a compound is formed from its elements. The superscript "o" denotes that the enthalpy of formation is determined at atmospheric pressure.

[9] Reactions in which heat is liberated are called exothermic reactions; reactions which have a positive enthalpy change, indicated that heat input is required, are called endothermic.

[10] The density of methane at 68°F (= 20°C) and atmospheric pressure is 0.41634 lb_m/ft³. Multiplying this by the heat of combustion of 23,859 Btu/lb_m gives a heat of combustion per unit volume of 993.4 Btu/ft³, close to the rule-of-thumb value of 1,000 ft³/lb_m for natural gas.

mass units, not molar units. However, it is possible to use molar units, so long as there is dimensional consistency with the heat and work terms.

For an open system, in steady-state, with one inlet and one outlet, the first law reduces to the following form, when changes in kinetic and potential energy terms are negligible.

$$\dot{Q} = \dot{W} + \dot{H}_{out} - \dot{H}_{in} \qquad [92]$$

The terms $\dot{H}_{out}$ and $\dot{H}_{in}$ represent the enthalpy changes from mass flows in the inlet and outlet streams.

Energy balance for complete combustion – If we regard the molar quantities in equation [7] for complete combustion of a hydrocarbon fuel in air as moles per unit time, we can write terms like $\dot{H}_{out}$ and $\dot{H}_{in}$ as the product of a molar flow rate times a molar enthalpy, such as the one in equation [89]. If the inlet is a fuel-air mixture at a temperature T_{in}, and the outlet contains exhaust products (as given by the molar quantities in equation [7]) at a temperature T_{out}, we can write the first law balance of equation [92] as follows.

$$\dot{Q} = \dot{W} + (x + \lambda\, A\, r_{CO_2})\, h_{CO_2}(T_{out}) + (\frac{y}{2} + \lambda\, Ar_{H_2O})\, h_{H_2O}(T_{out}) + z\, h_{SO_2}(T_{out})$$

$$+ (\lambda - 1)Ah_{O_2}(T_{out}) + (\frac{v}{2} + \lambda\, A\, r_{N_2})h_{N_2}(T_{out}) + \lambda\, A\, r_{Ar}\, h_{Ar}(T_{out}) \qquad [93]$$

$$- h_{Fuel}(T_{in}) - \lambda\, A\Big[h_{O_2}(T_{in}) + r_{CO_2}\, h_{CO_2}(T_{in}) + r_{H_2O}\, h_{H_2O}(T_{in}) + r_{Ar}\, h_{Ar}(T_{in}) + r_{N_2}h_{N_2}(T_{out})\Big]_x$$

In this case we are taking the combustion process as the control volume with reactants at the inlet and products at the outlet. The heat transfer term is then the heat transfer to the combustion gases and the work term is the work output from any device that has reactants as an inlet and products as an outlet. Substituting equation [89] for the chemical enthalpy term into this equation gives the following result.

$$\dot{Q} = \dot{W} + (x + \lambda\, A\, r_{CO_2})\left[h_{CO_2}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{CO_2}}\, dT' \right] + (\frac{y}{2} + \lambda\, Ar_{H_2O})\left[h_{H_2O}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{H_2O}}\, dT' \right]$$

$$+ z\left[h_{SO_2}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{SO_2}}\, dT' \right] + (\lambda - 1)A\left[h_{O_2}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{O_2}}\, dT' \right]$$

$$+ (\frac{v}{2} + \lambda\, A\, r_{N_2})\left[h_{N_2}(T_{out}) + \int_{T_{ref}}^{T_{out}} c_{p_{N_2}}\, dT' \right] + \lambda\, A\, r_{Ar}\left[h_{Ar}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{Ar}}\, dT' \right]$$

$$- \left[h_{Fuel}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{Fuel}}\, dT' \right] - \lambda\, A\left[h_{O_2}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{O_2}}\, dT' \right] - \lambda\, A r_{CO_2}\left[h_{CO_2}(T_{in}) + \int_{T_{ref}}^{T_{in}} c_{p_{CO_2}}\, dT' \right]$$

$$- \lambda\, A r_{H_2O}\left[h_{H_2O}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{H_2O}}\, dT' \right] - \lambda\, A\, r_{Ar}\left[h_{Ar}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{Ar}}\, dT' \right]$$

$$- \lambda\, A\, r_{N_2}\left[h_{N_2}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{N_2}}\, dT' \right] \tag{94}$$

We can simplify this equation by defining reactant and product heat capacities by the equations below.[11]

$$C_{p_{React}} = c_{p_{Fuel}} + \lambda\, A\left[c_{p_{O_2}} + r_{CO_2} c_{p_{CO_2}} + r_{H_2O} c_{p_{H_2O}} + r_{Ar} c_{p_{Ar}} + r_{N_2} c_{p_{N_2}} \right] \tag{95}$$

$$C_{p_{Prod}} = (x + \lambda\, A\, r_{CO_2}) c_{p_{CO_2}} + (\frac{y}{2} + \lambda\, Ar_{H_2O}) c_{p_{H_2O}} + z c_{p_{SO_2}} + (\lambda - 1)A c_{p_{O_2}}$$
$$+ (\frac{v}{2} + \lambda\, A\, r_{N_2}) c_{p_{N_2}} + \lambda\, A\, r_{Ar} c_{p_{Ar}} \tag{96}$$

The reference enthalpies of the elements nitrogen, oxygen, and argon are zero, so we can drop these terms from equation [94]. In addition, we see that the terms involving CO_2 and H_2O in the inlet air have the same coefficient multiplying the reference enthalpies for these terms on both sides of equation [94]. Hence these terms can be cancelled. If we then collect the remaining reference enthalpy terms in equation [94] and introduce the heat capacity definitions in equations [95] and [96], we can rewrite equation [94] as follows.

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[11] Here we use a capital C for the heat capacity because there are no longer the specific heat capacities. Instead, these heat capacities are extensive properties that depend on the amount of mass in the system. They will have units of energy/temperature.

$$\dot{Q} = \dot{W} + \int_{T_{ref}}^{T_{out}} C_{p_{Prod}} dT' - \int_{T_{ref}}^{T_{in}} C_{p_{React}} dT'$$

$$+ x h_{CO_s}(T_{ref}) + \frac{y}{2} h_{H_2O}(T_{ref}) + z h_{SO_2}(T_{ref}) - h_{Fuel}(T_{ref}) \qquad [97]$$

However, we see that the reference enthalpy terms in equation [97] are just the negative of the heat of combustion defined in equation [89] times the molecular weight of the fuel. We thus have the following result.

$$\dot{Q} = \dot{W} + \int_{T_{ref}}^{T_{out}} C_{p_{Prod}} dT' - \int_{T_{ref}}^{T_{in}} C_{p_{React}} dT' - Q_c m_{Fuel} \qquad [98]$$

We wrote the process using the combustion of one mole of fuel as the basis. The total mass of reactants (which is also the total mass of products) in this basis is the fuel mass plus the air mass. This can be written in terms of the air/fuel mass ratio as follows.

$$m = m_{Prod} = m_{React} = m_{Fuel} + m_{Air} = m_{Fuel}\left[1 + \frac{Air}{Fuel}\right] \qquad [99]$$

If we divide by the total mass and use the definition that q and w are the heat transfer and work per unit mass, we can write equation [98] as follows.

$$q = w + \frac{1}{m}\int_{T_{ref}}^{T_{out}} C_{p_{Prod}} dT' - \frac{1}{m}\int_{T_{ref}}^{T_{in}} C_{p_{React}} dT' - \frac{Q_c}{\left[1 + \dfrac{Air}{Fuel}\right]} \qquad [100]$$

Up to this point, we have not made any assumptions about the properties (other than the assumption of complete combustion). If we now assume that the per unit mass heat capacity of the reactants is the same as that of the products, and further assume that this heat capacity is about the same as that of air we have the following simplification.

$$q = w + \int_{T_{in}}^{T_{out}} c_{p_{Air}} dT' - \frac{Q_c}{\left[1 + \dfrac{Air}{Fuel}\right]} \qquad [101]$$

Recall that the control volume definition made the combustor the control volume. In a heat transfer process, then, we expect the heat transfer to be negative indicating that heat is transferred from the combustion gases. We want this to be as large as possible and equation [101] tells us that we obtain this maximum heat transfer when the inlet and outlet temperatures are the same. Increases in the
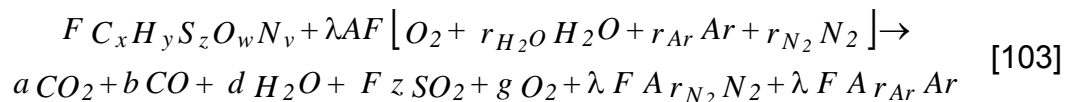
outlet temperature above the inlet temperature indicate a less efficient heat transfer. The combustion efficiency may be defined as follows as the ratio of the actual heat delivered by the combustion process (the absolute value of the right side of equation [101] with w = 0) to the maximum heat transfer (the absolute value of the right side of equation [101] with w = 0 and T_{in} = T_{out}).

$$\eta_{comb} = \frac{|q|}{|q|_{max}} = \frac{\dfrac{Q_c}{\left[1 + \dfrac{Air}{Fuel}\right]} - \displaystyle\int_{T_{in}}^{T_{out}} c_{p_{Air}} \, dT'}{\dfrac{Q_c}{\left[1 + \dfrac{Air}{Fuel}\right]}} = 1 - \frac{\left[1 + \dfrac{Air}{Fuel}\right]}{Q_c} \int_{T_{in}}^{T_{out}} c_{p_{Air}} \, dT' \qquad [102]$$

If we had not made the assumption that the reactant and product heat capacities were the same, we could still obtain the same qualitative result. The combustion efficiency is greatest when the inlet (reactant) and outlet (product) temperatures are the same. Combustion efficiencies in practical systems attempt to reach this goal by using the energy in the exhaust to preheat the incoming air.

COMBUSTION EFFICIENCY FOR INCOMPLETE COMBUSTION

Incomplete combustion products will reduce the combustion efficiency defined above. The simplest (and most important) case to consider is the reduction in efficiency due to the production of CO instead of complete combustion to CO_2. To analyze this case we use the simplification of the reaction equation [55] (for a basis of 100 dry product moles) shown in equation [103], below, where all incomplete combustion products except CO have been removed. For simplicity, the presence of CO_2 in the incoming air is ignored.

$$F \, C_x H_y S_z O_w N_v + \lambda AF \left[O_2 + r_{H_2O} \, H_2O + r_{Ar} \, Ar + r_{N_2} \, N_2 \right] \rightarrow$$
$$a \, CO_2 + b \, CO + d \, H_2O + F \, z \, SO_2 + g \, O_2 + \lambda \, F \, A \, r_{N_2} \, N_2 + \lambda \, F \, A \, r_{Ar} \, Ar \qquad [103]$$

The element balances for sulfur, nitrogen and argon are already present in equation [103]. The remaining element balances can be used to obtain the following equations. The carbon balance gives.

$$x F = a + b \quad \Rightarrow \quad F = \frac{a + b}{x} \qquad [104]$$

The hydrogen balance gives

$$F\left(y + 2\lambda Ar_{H_2O}\right) = 2d \quad \Rightarrow \quad yF = 2d - 2\lambda FAr_{H_2O} \qquad [105]$$

The oxygen balance gives

$$(w - 2\,z)F + (2 + r_{H_2O})\lambda AF = 2\,a + b + d + 2\,g \qquad [106]$$

Because the basis was selected to be 100 dry moles, the following sum holds for the product moles.

$$a + b + g + F\left[z + \lambda A(r_{N_2} + r_{Ar})\right] = 100 \qquad [107]$$

Using the symbols for the moles of different species in this equation, we can replace the first law energy balance in equation [94] by the following equation.

$$\dot{Q} = \dot{W} + a\left[h_{CO_2}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{CO_2}} dT'\right] + b\left[h_{CO}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{CO}} dT'\right] + d\left[h_{H_2O}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{H_2O}} dT'\right]$$

$$+ Fz\left[h_{SO_2}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{SO_2}} dT'\right] + g\left[h_{O_2}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{O_2}} dT'\right]$$

$$+ h\left[h_{N_2}(T_{out}) + \int_{T_{ref}}^{T_{out}} c_{p_{N_2}} dT'\right] + \lambda F\,A\,r_{Ar}\left[h_{Ar}(T_{ref}) + \int_{T_{ref}}^{T_{out}} c_{p_{Ar}} dT'\right]$$

$$- F\left[h_{Fuel}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{Fuel}} dT'\right] - \lambda\,AF\left[h_{O_2}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{O_2}} dT'\right]$$

$$- \lambda\,FAr_{H_2O}\left[h_{H_2O}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{H_2O}} dT'\right] - \lambda\,FA\,r_{Ar}\left[h_{Ar}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{Ar}} dT'\right]$$

$$- \lambda\,FA\,r_{N_2}\left[h_{N_2}(T_{ref}) + \int_{T_{ref}}^{T_{in}} c_{p_{N_2}} dT'\right] \qquad [108]$$

We can simplify this equation by defining reactant and product heat capacities by the equations below, which are similar to equations [95] and [96].

$$C_{p_{Re\,act}} = Fc_{p_{Fuel}} + \lambda\,AF\left[c_{p_{O_2}} + +r_{H_2O}c_{p_{H_2O}} + r_{Ar}c_{p_{Ar}} + r_{N_2}c_{p_{N_2}}\right] \qquad [109]$$

$$C_{p_{Prod}} = ac_{p_{CO_2}} + bc_{p_{CO}} + dc_{p_{H_2O}} + zFc_{p_{SO_2}} + gc_{p_{O_2}} + (\frac{v}{2} + \lambda\,A\,r_{N_2})c_{p_{N_2}} + \lambda\,A\,r_{Ar}c_{p_{Ar}} \qquad [110]$$

Substituting these heat capacity definitions into equation [108] gives the following result.

$$\dot{Q} = \dot{W} + \int_{T_{ref}}^{T_{out}} C_{p\,Prod}\, dT' - \int_{T_{ref}}^{T_{in}} C_{p\,React}\, dT'$$

$$+ ah_{CO_2}(T_{ref}) + bh_{CO}(T_{ref}) + \left(d - \lambda AFr_{H_2O}\right)h_{H_2O}(T_{ref}) + zFh_{SO_2}(T_{ref}) - Fh_{Fuel}(T_{ref})$$

[111]

Assuming a fuel with no ash content the mass of the fuel is equal to the moles of the fuel, F, times the fuel molecular weight. Using the result from equation [104] that F = (a + b)/x gives.

$$m_{fuel} = FM_{fuel} = \frac{a+b}{x} M_{fuel}$$

[112]

The total mass, $m_{air} + m_{fuel}$, is given by the following equation.

$$m = m_{fuel} + m_{air} = m_{fuel}\left(1 + \frac{Air}{Fuel}\right) = FM_{fuel}\left(1 + \frac{Air}{Fuel}\right)$$

[113]

Dividing equation [111] by this total mass gives the specific heat capacities $c_{p,react}$, and $c_{p,prod}$, in the integrals, providing the following result.

$$q = w + \int_{T_{ref}}^{T_{out}} c_{p\,Prod}\, dT' - \int_{T_{ref}}^{T_{in}} c_{p\,React}\, dT' + \frac{ah_{CO_2}(T_{ref}) + bh_{CO}(T_{ref})}{\left(1 + \dfrac{Air}{Fuel}\right)FM_{fuel}}$$

$$+ \frac{\left(d - \lambda AFr_{H_2O}\right)h_{H_2O}(T_{ref}) + zFh_{SO_2}(T_{ref}) - Fh_{Fuel}(T_{ref})}{\left(1 + \dfrac{Air}{Fuel}\right)FM_{fuel}}$$

[114]

From equation [105] we see that the term multiplying h_{H2O} in the second row of equation [114] is simply equal to yF/2. Making this substitution and canceling the F terms in the numerator and denominator in second row of [114] gives.

$$q = w + \int_{T_{ref}}^{T_{out}} c_{p\,Prod}\, dT' - \int_{T_{ref}}^{T_{in}} c_{p\,React}\, dT' + \frac{ah_{CO_2}(T_{ref}) + bh_{CO}(T_{ref})}{\left(1 + \dfrac{Air}{Fuel}\right)FM_{fuel}}$$

$$+ \frac{\dfrac{y}{2} h_{H_2O}(T_{ref}) + zh_{SO_2}(T_{ref}) - h_{Fuel}(T_{ref})}{\left(1 + \dfrac{Air}{Fuel}\right)M_{fuel}}$$

[115]

The terms with the CO and CO_2 enthalpies can be manipulated as follows, using equation [104] that F = (a + b)/x.

$$\frac{ah_{CO_2}(T_{ref})+bh_{CO}(T_{ref})}{\left(1+\dfrac{Air}{Fuel}\right)FM_{fuel}}=\frac{(Fx-b)h_{CO_2}(T_{ref})+bh_{CO}(T_{ref})}{\left(1+\dfrac{Air}{Fuel}\right)FM_{fuel}}$$

$$=\frac{xh_{CO_2}(T_{ref})}{\left(1+\dfrac{Air}{Fuel}\right)M_{fuel}}+\frac{b\left[h_{CO}(T_{ref})-h_{CO_2}(T_{ref})\right]}{\left(1+\dfrac{Air}{Fuel}\right)\left(\dfrac{a+b}{x}\right)M_{fuel}}$$

[116]

Substituting this result into equation [115] gives the enthalpy terms that define the heat of combustion in equation [91].

$$q=w+\int_{T_{ref}}^{T_{out}}c_{P_{Prod}}dT'-\int_{T_{ref}}^{T_{in}}c_{P_{React}}dT'+\frac{b\left[h_{CO}(T_{ref})-h_{CO_2}(T_{ref})\right]}{\left(1+\dfrac{Air}{Fuel}\right)\left(\dfrac{a+b}{x}\right)M_{fuel}}$$

$$+\frac{xh_{CO_2}(T_{ref})+\dfrac{y}{2}h_{H_2O}(T_{ref})+zFh_{SO_2}(T_{ref})-Fh_{Fuel}(T_{ref})}{\left(1+\dfrac{Air}{Fuel}\right)M_{fuel}}$$

[117]

$$=w+\int_{T_{ref}}^{T_{out}}c_{P_{Prod}}dT'-\int_{T_{ref}}^{T_{in}}c_{P_{React}}dT'-\frac{Q_c}{\left(1+\dfrac{Air}{Fuel}\right)}+\frac{b\left[h_{CO}(T_{ref})-h_{CO_2}(T_{ref})\right]}{\left(1+\dfrac{Air}{Fuel}\right)\left(\dfrac{a+b}{x}\right)M_{fuel}}$$

In this case, the combustion efficiency equation [102] is replaced by equation [118], to account for the presence of CO in the reaction products. As before, we assume that the heat capacity of the reactants and the products can be approximated as the heat capacity of air. The maximum heat transfer occurs when the inlet and outlet temperatures are the same (so the integrals in equation [117] vanish) and there is no CO produced (b = 0). We find this maximum heat transfer from equation [117] and divide the result into equation [117] to obtain the equation below. In that equation, the term with CO enthalpy is summarized as D' and D for convenience

$$\eta_{comb}=\frac{|q|}{|q|_{max}}=\frac{\dfrac{Q_c}{\left[1+\dfrac{Air}{Fuel}\right]}-\displaystyle\int_{T_{in}}^{T_{out}}c_{P_{Air}}dT'-D'}{\dfrac{Q_c}{\left[1+\dfrac{Air}{Fuel}\right]}}=1-\frac{\left[1+\dfrac{Air}{Fuel}\right]}{Q_c}\left[\int_{T_{in}}^{T_{out}}c_{P_{Air}}dT'\right]-D$$

[118]

Comparing equations [116] and [118] shows that we can write the D term as follows.

$$D = \frac{\left(1 + \dfrac{Air}{Fuel}\right) b\left[h_{CO}(T_{ref}) - h_{CO_2}(T_{ref})\right]}{Q_c \left(1 + \dfrac{Air}{Fuel}\right)\left(\dfrac{a+b}{x}\right) M_{fuel}} = \frac{b}{a+b} \frac{1}{Q_c} \frac{x}{M_{fuel}}\left[h_{CO}(T_{ref}) - h_{CO_2}(T_{ref})\right] \quad [119]$$

In equation [119] the ratio b/(a+b) is the ratio of the CO concentration to the sum of the CO and CO_2 concentrations in the exhaust and x/M_{fuel} is the number of carbon atoms in the fuel formula divided by the molecular weight of the fuel. The value of the enthalpy difference $h_{CO} - h_{CO2}$ is 282,990 kJ/kgmol = 121,665 Btu/lbmol at a reference temperature of 25°C. Defining this enthalpy difference as ΔH_{CO} allows us to write the D in the following simplified manner.

$$D = \frac{b}{a+b} \frac{x \Delta H_{CO}}{Q_c M_{fuel}} \quad [120]$$

ADIABATIC FLAME TEMPERATURE

The maximum temperature achieved in a combustion process is called the adiabatic flame temperature, T_{AFT}. This temperature may be estimated from equation [101] by setting q = w = 0, and assuming that the heat capacity is constant at some mean value, $\overline{c_{p_{Air}}}$. This gives the following result.

$$\int_{T_{in}}^{T_{AFTt}} c_{p_{Air}} dT' = \overline{c_{p_{Air}}}(T_{AFT} - T_{in}) = \frac{Q_c}{\left[1 + \dfrac{Air}{Fuel}\right]} \quad [121]$$

For a typical liquid hydrocarbon fuel for which the lower heating value, Q_C = 18,000 Btu/lb$_m$ and the practical air-fuel ratio is about 18:1 we can compute the adiabatic flame temperature from equation [103]. If we assume that the mean heat capacity for air is about 0.27 Btu/lbm-F and the inlet temperature is 60 F, we find the following result.

$$T_{AFT} = T_{in} + \frac{Q_c}{c_{p_{Air}}\left[1 + \dfrac{Air}{Fuel}\right]} = 60\ F + \frac{\dfrac{18,000\,Btu}{lb_m}}{\dfrac{0.27\,Btu}{lb_m - F}[1+18]} = 3569\,F \quad [122]$$

This calculation can be repeated, in a trial-and-error fashion, to ensure that a correct value for the mean heat capacity is used. However, there is another effect that takes place at high temperatures that tends to depress the adiabatic flame temperature. CO_2 dissociates into CO and oxygen. In addition, H_2O dissociates into H_2, O_2, and the hydroxyl radical. (There is also some dissociation of diatomic gases H_2, O_2, and N_2 into monatomic species H, O, and N. All of these dissociation reactions produce species that have a large

reference enthalpy. The production of these species reduces the adiabatic flame temperature. The computation of complex chemical equilibrium, with multiple species is readily handled by codes such as the NASA chemical equilibrium code. Some results from that code are provided below.

The adiabatic flame temperatures for stoichiometric combustion of a series of fuels in air are shown in the table below. In all cases the fuel is a gas and the fuel and air are both at an initial temperature of 25 C.

Fuel	H_2	NH_3	N_2H_4	CH_4	C_3H_8	C_8H_{18}
T_{AFT} (K)	2,384	2,074	2,435	2,227	2,268	2,277
T_{AFT} (F)	3,832	3,274	3,923	3,549	3,623	3,639

If the combustion is fuel rich, it will not be possible to obtain the full energy release from complete combustion. If the combustion is fuel lean, there will be excess air that will absorb some of the chemical energy release from the fuel. Maximum adiabatic flame temperatures tend to occur when the mixture is stoichiometric. The table below shows the adiabatic flame temperature for a variety of relative air/fuel ratios, λ, where $\lambda < 1$ indicates fuel-rich (air lean) and $\lambda > 1$ indicates fuel-lean (air-rich) combustion.

λ	0.667	1	1.25	1.667	2.5	5
T_{AFT} (K)	1,982	2,302	2,046	1,697	1,298	840
T_{AFT} (F)	3,108	3,684	3,223	2,595	1,877	1,052

These results assume that chemical equilibrium has been obtained in the combustion reaction. This is often a good assumption for predicting the energy release and adiabatic flame temperatures. However, the prediction of pollutant formation requires an examination of the rate of the chemical reactions that are involved in the combustion process.