FABER
Burner Company

Stoichiometric Equations for Hydrocarbon Combustion

J. Colannino, Ph.D.

Hydrocarbon Combustion

Most fuels are hydrocarbons. This includes natural gas, fuel oils, and coal. As such, things like the amount of air they consume, the products they produce, etc. may be characterized in large part by the ratio of hydrogen to carbon in the fuel ($\psi = H/C$). Table 1 gives some approximate values of ψ for various fuels.

Table 1, H/C Ratio for Some Fuels

Fuel	ψ
Methane	4.00
Natural Gas	3.90
Ethane	3.00
Propane	2.67
Butane	2.50
Gasoline	2.25
Fuel Oils #2 – #6	2.13
Olefins, Cyclic Saturates	2.00
Propyne, C_3H_4	1.33
Acetylene, Coal, Benzene	1.00

The minimum amount of air required to complete combustion the fuel is known as the *theoretical air*. However, because mixing in a combustion system is never perfect, the typical practice is to provide some *excess air*, ϵ to assure complete combustion. Oxygen is diatomic and is written as O_2, meaning that the oxygen molecule comprises two atoms; likewise for nitrogen, N_2. When hydrocarbons combust, they produce carbon dioxide (CO_2) and water (H_2O). One volume of air comprises roughly 21% oxygen and 79% nitrogen. Since combustion reactions can neither create nor destroy matter, one can write an equation that shows this principle of conservation and known as the *stoichiometric equation*. As an example, consider the combustion of methane (CH_4) – the major constituent of natural gas – with oxygen.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Here we see that one molecule of methane reacts with two molecules of oxygen to produce one molecule of carbon dioxide and two molecules of water. Since this reaction occurs in the gas phase, one may also say that one volume of methane plus two volumes of oxygen react to produce one volume of carbon dioxide and two volumes of water vapor. However, it is unlikely that we will burn methane with pure oxygen. Air comprises a ratio of nitrogen to oxygen of approximately 79/21. Rewriting the stoichiometric equation with air gives the following equation.

$$CH_4 + 2\left[O_2 + \frac{79}{21}N_2\right] \rightarrow CO_2 + 2H_2O + 2\left(\frac{79}{21}\right)N_2$$

On the left side of the equation, we have the fuel and air. On the right side we have the combustion products, also known as flue gas. As before, the oxygen is completely consumed but the unreacted nitrogen from the air is left to join the carbon dioxide and water vapor as part of the flue gas. Practical systems provide excess air (ϵ) to assure more than enough air for complete combustion. The next equation accounts for that.

$$CH_4 + 2(1+\epsilon)\left[O_2 + \frac{79}{21}N_2\right] \rightarrow CO_2 + 2H_2O + 2(1+\epsilon)\left(\frac{79}{21}\right)N_2 + \epsilon O_2$$

Note that when the excess air is zero ($\epsilon = 0$), the equation reduces to the previous one. However, if we add some excess air, say 15%, then $1 + \epsilon = 1.15$ and the flue gas contains 1 volume of CO_2, for every 2 volumes of H_2O, $\left[2(1.15)\left(\frac{79}{21}\right) = \right]$ 8.652 volumes of N_2, and 0.15 volumes of O_2. The presence of oxygen in the flue gas indicates air in excess. Good combustion practice requires excess air to avoid generation of products of incomplete combustion. Gas fired boilers often operate with sufficient excess air to leave 3% oxygen in the flue gas. Fuel-oil-fired boilers often operate at 5% oxygen. Equation (1) makes use of ψ to provide a generic expression for any hydrocarbon fuel.

$$\begin{aligned} &\mathrm{CH}_\psi + \left(1+\frac{\psi}{4}\right)(1+\epsilon)\left[\mathrm{O}_2 + \frac{79}{21}\mathrm{N}_2\right] \rightarrow \\ &\qquad \mathrm{CO}_2 + \frac{\psi}{2}\mathrm{H}_2\mathrm{O} + \frac{79}{21}\left(1+\frac{\psi}{4}\right)(1+\epsilon)\mathrm{N}_2 + \epsilon\left(1+\frac{\psi}{4}\right)\mathrm{O}_2 \end{aligned} \tag{1}$$

Flue Gas Relationships

The amount of oxygen we measure in the flue gas will depend on whether the analyzer is *in-situ* or as an *extractive*. An in-situ analyzer measures the oxygen in the furnace itself while the water is still vapor also known as a *wet* measurement. An extractive system withdraws its sample of flue gas and condenses the water before sending it on to the analyzer, also known as a *dry* measurement. The two measurements will differ because the wet measurement is diluted by water vapor while the dry measurement is not. Therefore, dry measurements of O_2 and CO_2 will always be higher. We may define the molar or (equivalently) volumetric air/fuel ratio (α) as

$$\alpha = \frac{79}{21}\left(1+\frac{\psi}{4}\right)(1+\epsilon) + \left(1+\frac{\psi}{4}\right)\epsilon = \frac{100}{21}\left(1+\frac{\psi}{4}\right)(1+\epsilon)$$

Add the volumes of the wet species in Equation (1) gives the wet flue-gas/fuel ratio, ϕ_{wet}.

$$1 + \frac{\psi}{2} + \frac{79}{21}\left(1+\frac{\psi}{4}\right)(1+\epsilon) + \left(1+\frac{\psi}{4}\right)\epsilon = \alpha + \frac{\psi}{4} = \phi_{wet}$$

We may do the same for the dry flue-gas/fuel ratio, ϕ_{dry}.

$$1 + \frac{79}{21}\left(1+\frac{\psi}{4}\right)(1+\epsilon) + \epsilon\left(1+\frac{\psi}{4}\right) = \alpha - \frac{\psi}{4} = \phi_{dry}$$

In fact, the ratio among wet and dry species will always differ by the ratio $\frac{y_{x,wet}}{y_{x,dry}} = 1 - y_{H2O}$. Being that this is the case, one may theoretically determine the water concentration of the flue gas if oxygen is known on both a wet and dry basis: $y_{H2O} = 1 - \frac{y_{O2,wet}}{y_{O2,dry}}$. However, in practice the moisture calculation may meet with considerable error as wet and dry measurements report from different spaces and times. That is, the in-situ analyzer takes the wet measurement directly in the furnace with very little delay, while the extractive analyzer takes the dry measurement near the flue gas exit in the stack. The stack may allow infiltration of outside air and there is no way to correct for such an error unless some other species is also measured on both a wet and dry basis. Moreover, the extractive analyzer draws its sample through a long distance which delays the measurement and one must correct for this delay in the comparison whenever the oxygen concentration is changing.

Flue Gas Species Equations

From Equation (1), one may derive the following formulas for the various flue gas species where *y* indicates the molar or volume fraction of the subscripted species.

$\phi_{dry} = \alpha - \frac{\psi}{4}$	$\phi_{wet} = \alpha + \frac{\psi}{4}$	(2a, b)
$y_{O2,dry} = \left(\frac{\epsilon}{\phi_{dry}}\right)\left(1 + \frac{\psi}{4}\right)$	$y_{O2,wet} = \left(\frac{\epsilon}{\phi_{wet}}\right)\left(1 + \frac{\psi}{4}\right)$	(3a, b)
$y_{N2,dry} = \left(\frac{\epsilon}{\phi_{dry}}\right)\left(\frac{79}{21}\right)\left(1 + \frac{\psi}{4}\right)$	$y_{O2,wet} = \left(\frac{\epsilon}{\phi_{wet}}\right)\left(\frac{79}{21}\right)\left(1 + \frac{\psi}{4}\right)$	(4a, b)
$y_{CO2,dry} = \left(\frac{1}{\phi_{dry}}\right)$	$y_{CO2,wet} = \left(\frac{1}{\phi_{wet}}\right)$	(5a, b)
$\alpha = \frac{100}{21}\left(1 + \frac{\psi}{4}\right)(1 + \epsilon)$	$y_{H2O} = \left(\frac{1}{\phi_{wet}}\right)\left(\frac{\psi}{2}\right)$	(6a, b)

Another but sometimes more convenient way of calculating flue gas species is to use a fuel's *K-factor*, defined as follows.

$K_{dry} = \left(\frac{4 + 0.79\psi}{4 + \psi}\right)$	$K_{wet} = \left(\frac{4 + 1.21\psi}{4 + \psi}\right)$	(7a, b)
$y_{O2,dry} = \left(\frac{0.21\epsilon}{K_{dry} + \epsilon}\right)$	$y_{O2,wet} = \left(\frac{0.21\epsilon}{K_{wet} + \epsilon}\right)$	(8a, b)
$y_{N2,dry} = \frac{0.79(1 + \epsilon)}{K_{dry} + \epsilon}$	$y_{O2,wet} = \frac{0.79(1 + \epsilon)}{K_{wet} + \epsilon}$	(9a, b)
$y_{CO2,dry} = \frac{0.84}{(4 + \psi)(K_{dry} + \epsilon)}$	$y_{CO2,wet} = \frac{0.84}{(4 + \psi)(K_{wet} + \epsilon)}$	(10a, b)

The following figures contain graphical depictions of the species equations for various fuels.

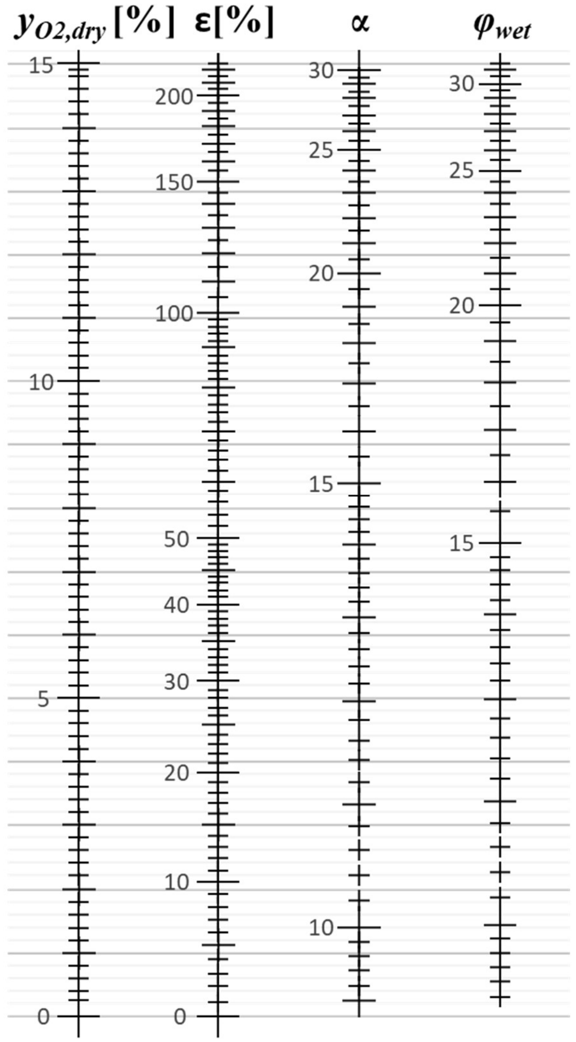

Figure 1. Parallel Scales for Natural Gas. Scale shows the respective readings for $y_{O2,dry}$, ϵ , α and ϕ_{wet} for natural gas as fuel ($\psi = 3.9$). E.g, 3% dry O_2 ≈ 15% excess air ≈ 10.8 air/fuel ≈ 14.7 wet flue gas/fuel.

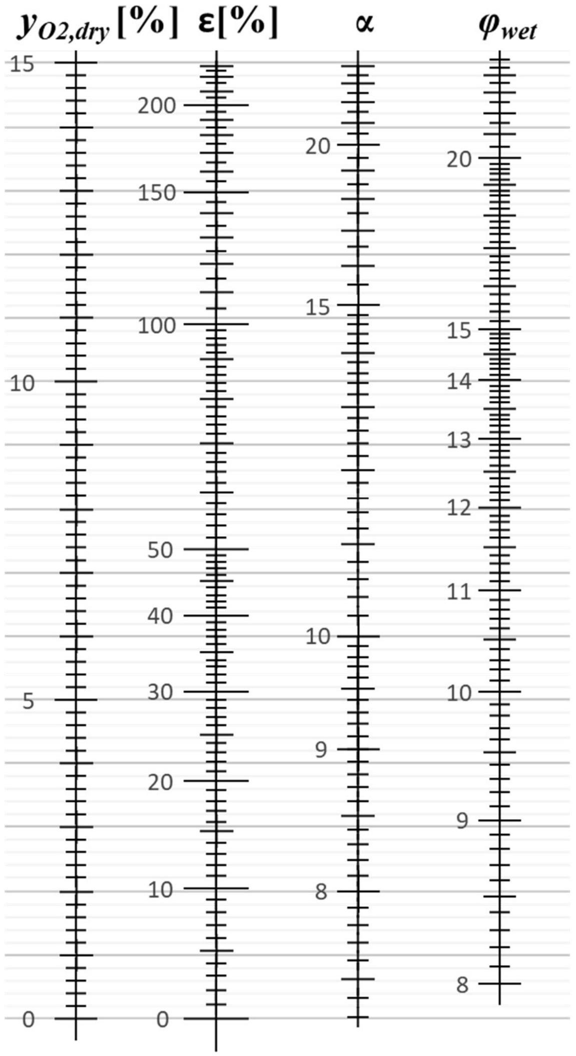

Figure 2. Parallel Scales for Fuel Oils. Scale shows the respective readings for $y_{O2,dry}$, ϵ , α and ϕ_{wet} for fuel oils #2 – #6 ($\psi = 2.13$). E.g, 3% dry O_2 ≈ 15.5% excess air ≈ 8.42 air/fuel ≈ 8.95 wet flue gas/fuel.

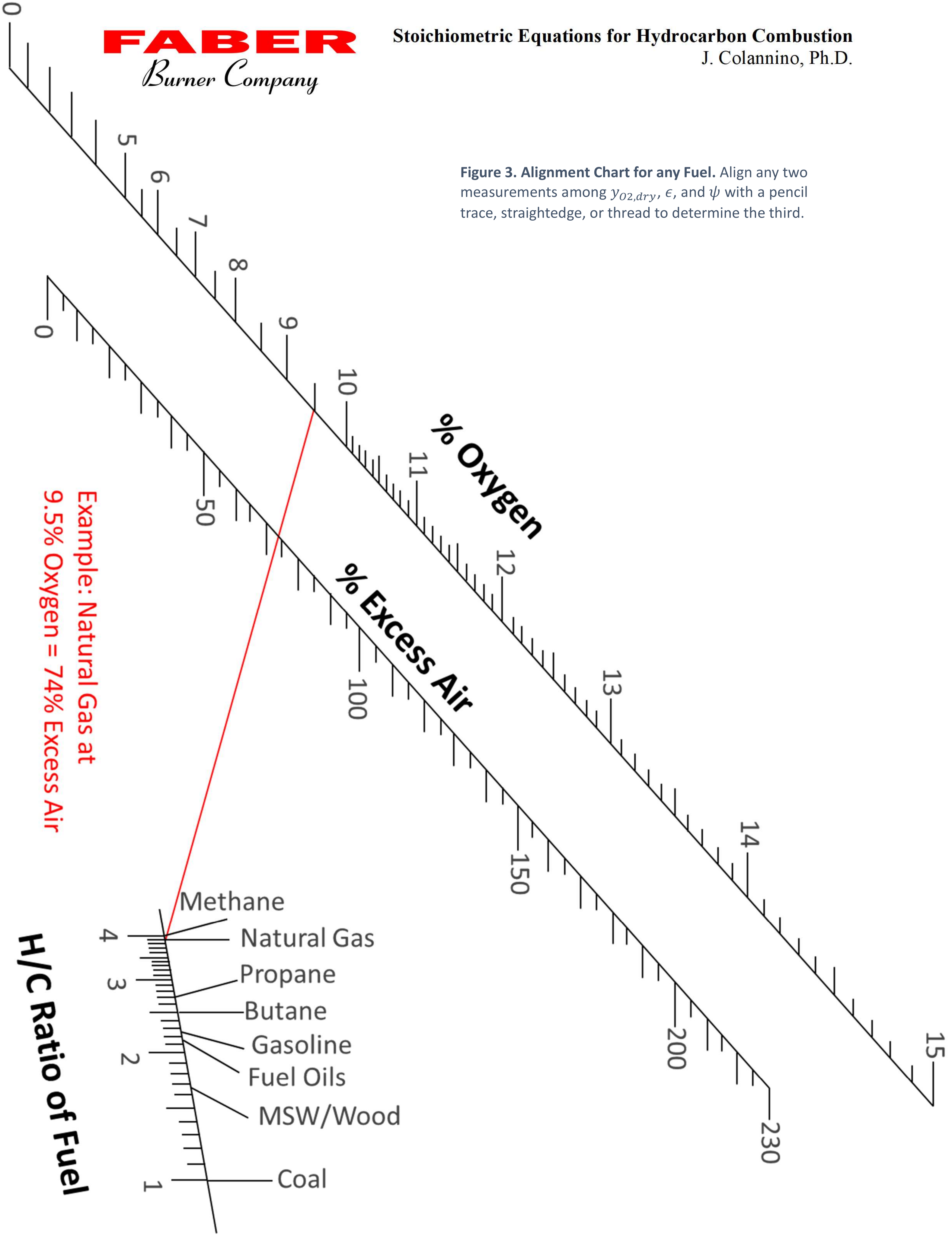

Figure 3. Alignment Chart for any Fuel. Align any two measurements among $y_{O2,dry}$, ϵ, and ψ with a pencil trace, straightedge, or thread to determine the third.