

THEORETICAL INTRODUCTION TO THE USE OF A RESIDUAL OXYGEN MEASUREMENT METHOD FOR THE ANALYSIS OF COMBUSTION AIR REQUIREMENT INDEX (CARI) AND WOBBE INDEX OF FUEL GASES.

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ABSTRACT

A Residual Oxygen Measurement Method can be used to directly measure the Combustion Air Requirement Index (CARI) of a natural gas and other fuel gases. When the amount of energy supplied to the burners is required, CARI can be directly correlated to the Wobbe Index of the fuel gas. This paper will review how to calculate a fuel's Stoichiometric Air to Fuel Ratio requirement, CARI and discuss CARI's relationship to the Wobbe Index.

INTRODUCTION

In the Residual Oxygen Measurement method, a continuous gas sample is mixed with dry air at a precisely maintained constant ratio. This fuel air mixture is then oxidized in a combustion furnace in the presence of a catalyst at 800C. A zirconia oxide cell is used to determine the residual oxygen concentration in the combusted sample.

The residual oxygen is a direct measurement of the Combustion Air Requirement Index (CARI), a dimensionless parameter indicating how much air is required for the stoichiometric combustion of a fuel

gas. CARI can be mathematically correlated to the Wobbe Index of the fuel gas for an indication of the amount of energy supplied to the burner.

However, to understand the residual oxygen measurement method, one must be familiar the stoichiometric air requirement, the definition of CARI and its relationship to the Wobbe Index. Lastly, the effect of alkenes, hydrogen, and carbon monoxide on the relationship between CARI and the Wobbe Index will be discussed.

STOICHIOMETRIC AIR/FUEL RATIO¹

The Stoichiometric Air Requirement of a gas is the amount of dry air required to completely combust one mole of fuel gas. A simplified combustion equation using Methane as the fuel is typically written as:



Equation (1) can be re-written to represent any hydrocarbon fuel whereby the hydrocarbon is represented by C_xH_y . Balancing the equation you now have:



In looking at this combustion equation (2), the stoichiometric requirement for oxygen, α_s , can be defined as

$$\alpha_s = (x + y/4), \quad (3)$$

However, this equation represents using pure oxygen for combustion. But normally, combustion takes place using air not pure oxygen. Taking into account the use of air as your source of oxygen, equation (2) now becomes



Although there are other components such as Argon and Carbon Dioxide in air, for the equation (4), we assumed that air is made up of 20.9% oxygen and the rest (79.1%) is made up of Nitrogen. Based upon these percentages, for every O₂ moles in air you will have 3.785 N₂ moles. (79.1/20.9 = 3.785). Note that Nitrogen does not add to the combustion, but it is included to insure the equation is balanced. Since, Air is only 20.9% Oxygen, for complete combustion to occur, for every mole of a hydrocarbon fuel you will require:

$$4.785\alpha s \text{ moles of air} \quad \frac{[\text{moles air}]}{[\text{moles fuel}]} \quad (5)$$

Using equation (5) the air requirement for complete combustion can be calculated for any hydrocarbon. Table 1 shows a table of selected hydrocarbons and their corresponding air requirements.^{2,3}

TABLE 1 – AIR TO FUEL RATIO REQUIREMENT FOR THE COMBUSTION OF SELECTED ALKANES

COMPONENT	FORMULA	# C's (x)	# H's (y)	αs	Air/Fuel Ratio
METHANE	CH ₄	1	4	2.0	9.570
ETHANE	C ₂ H ₆	2	6	3.5	16.748
PROPANE	C ₃ H ₈	3	8	5.0	23.925
n-BUTANE	C ₄ H ₁₀	4	10	6.5	31.103
i-BUTANE	C ₄ H ₁₀	4	10	6.5	31.103
PENTANE	C ₅ H ₁₂	5	12	8.0	38.280
i-PENTANE	C ₅ H ₁₂	5	12	8.0	38.280
HEXANE	C ₆ H ₁₄	6	14	9.5	45.458
HEPTANE	C ₇ H ₁₆	7	16	11.0	52.635
OCTANE	C ₈ H ₁₈	8	18	12.5	59.813

COMBUSTION AIR REQUIREMENT INDEX (CARI)

The volumetric flow of a fuel gas through a burner orifice (restriction) is dependent upon the specific gravity of that fuel. Therefore, the amount of air required for complete combustion of a fuel will vary with the density of the fuel gas. The Combustion Air Requirement Index (CARI) is a dimensionless parameter indicating how much air is required for the stoichiometric combustion of a fuel gas.

$$\text{CARI} = \frac{\text{Air/Fuel Ratio}}{(\text{specific gravity})^{1/2}} \quad (6)$$

For a mixture of gases, the CARI can be calculated by

$$\text{CARI} = \frac{\sum (\text{AFR}_i * X_i)}{(\sum (\text{SG}_i * X_i))^{1/2}} \quad (7)$$

Where
X = Component Mol %
AFR = Air to fuel Ratio for each component
SG = specific gravity for each component
i = component

Table 2 displays the air/fuel ratios and associated CARI value for selected alkanes.

TABLE 2 – AIR TO FUEL RATIO AND CARI FOR SELECTED ALKANES

COMPONENT	Relative Density	Air/Fuel Ratio	CARI
METHANE	0.55392	9.57	12.86
ETHANE	1.03820	16.75	16.44
PROPANE	1.52260	23.93	19.39
n-BUTANE	2.00680	31.10	21.96
i-BUTANE	2.00680	31.10	21.96
PENTANE	2.49120	38.28	24.25
i-PENTANE	2.49120	38.28	24.25
HEXANE	2.97550	45.46	26.35
HEPTANE	3.45980	52.64	28.30
OCTANE	3.94410	59.81	30.12

As you can see from the scatter plot in Figure 1, the relationship between the Air/Fuel ratio and CARI is linear with a correlation of $R^2 = 0.9846$.

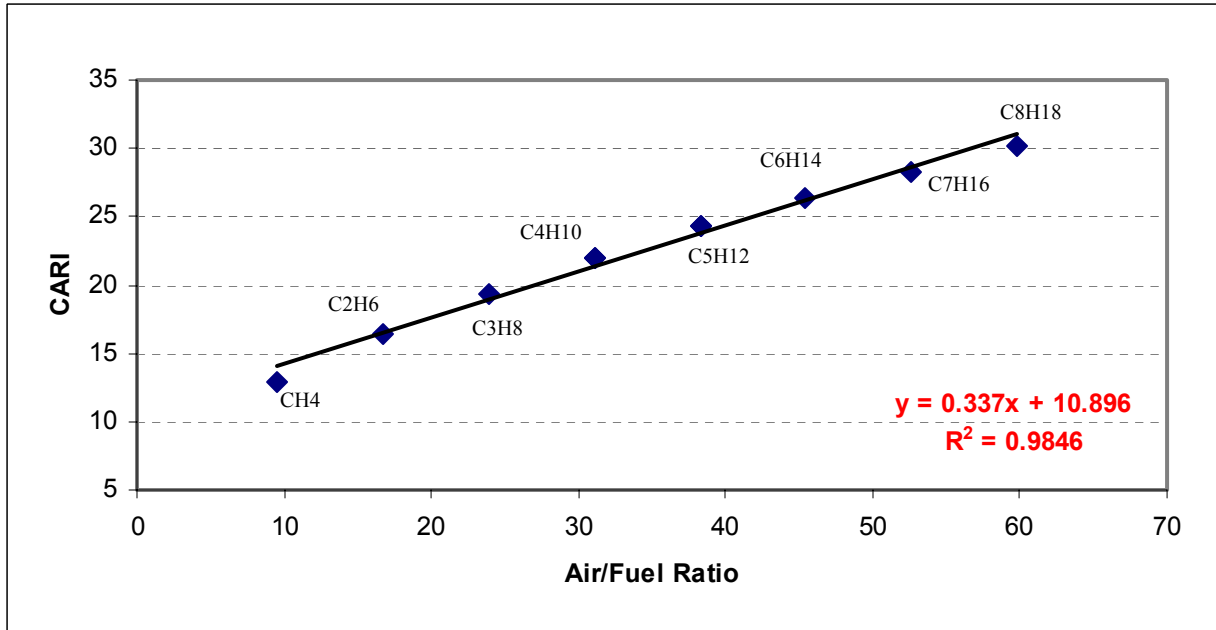


FIG. 1 – RELATIONSHIP BETWEEN AIR/FUEL RATIO AND CARI FOR ALKANES

WOBBE INDEX

If the flow of the fuel across a burner orifice varies then it follows that the energy produced during combustion will also change. The Wobbe Index is defined as the amount of energy introduced to the burners.

$$\text{Wobbe Index} = \frac{\text{Calorific Value}}{(\text{specific gravity})^{1/2}} \quad (8)$$

Table 3 displays the calculated parameters for each of the selected alkanes.

TABLE 3 – DATA AND CALCULATED VALUES FOR SELECTED ALKANES

COMPONENT	Relative Density	CARI	Net Heating Value (BTU/SCF)	Net Wobbe Index (BTU/SCF)	Ratio Between CARI and Wobbe
METHANE	0.55392	12.86	909	1221.35	94.98
ETHANE	1.03820	16.44	1619	1588.94	96.67
PROPANE	1.52260	19.39	2315	1876.11	96.76
n-BUTANE	2.00680	21.96	3011	2125.49	96.81
i-BUTANE	2.00680	21.96	3000	2117.72	96.46
PENTANE	2.49120	24.25	3707	2348.65	96.84
i-PENTANE	2.49120	24.25	3699	2343.58	96.63
HEXANE	2.97550	26.35	4404	2553.10	96.88
HEPTANE	3.45980	28.30	5100	2741.86	96.89
OCTANE	3.94410	30.12	5796	2918.46	96.90

The CARI – Wobbe relationship is linear, for hydrocarbon fuels with a mix of alkanes (C_x H_{x+2}). As the scatter plot in Figure 2 illustrates, the Wobbe Index can be mathematically calculated with a correlation of R² = 0.9999.

As both Table 3 and the Figure 2's trend-line indicate, the ratio between CARI and the Wobbe Index is fairly constant. With the line intercept set at 0 the linear relationship between CARI and Wobbe for alkanes becomes:

$$Y = 96.732 X \quad (9)$$

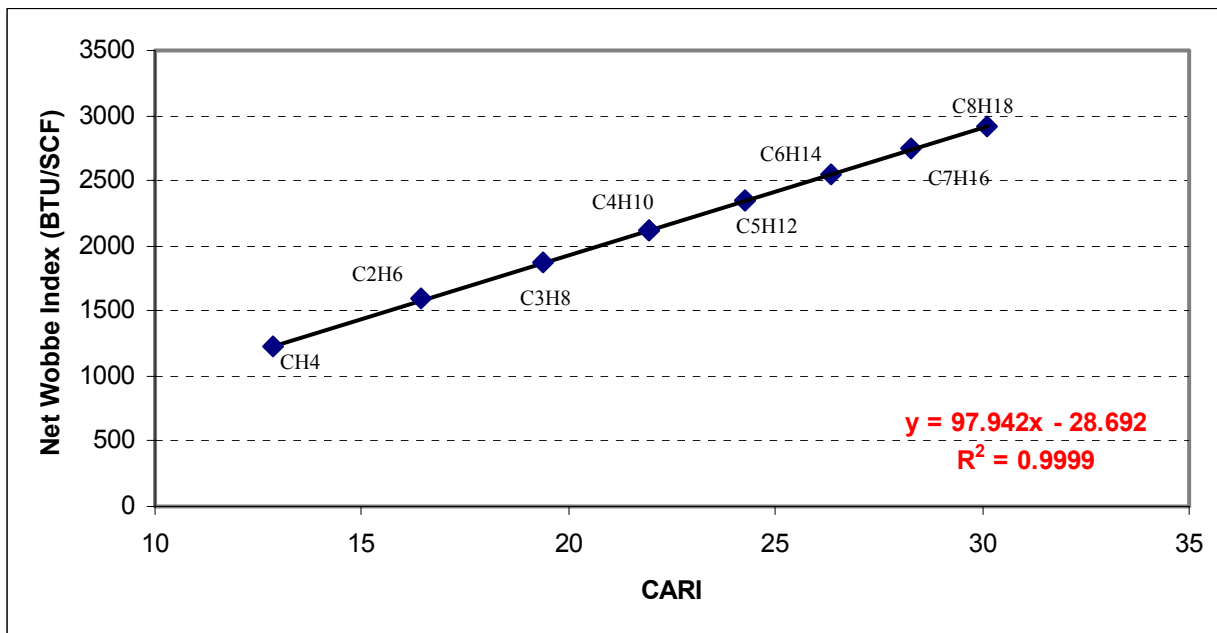


FIG. 2 - RELATIONSHIP BETWEEN CARI AND WOBBE INDEX FOR ALKANES

RESIDUAL OXYGEN MEASUREMENT METHOD

In the Residual Oxygen Measurement method, a continuous gas sample is mixed with dry air at a precisely maintained constant ratio. This fuel air mixture is then oxidized in a combustion furnace in the presence of a catalyst at 800C. A zirconia oxide cell is used to determine the residual oxygen concentration in the combusted sample.

The Residual Oxygen Measurement Method mimics what takes place in your burner and provides a direct measurement of the Combustion Air Requirement Index (CARI). As the above equations indicate CARI can be mathematically correlated to the Wobbe Index of the fuel gas for an indication of the amount of energy supplied to the burner.

GAS MIXING CHAMBER

Figure 3 is an illustration of a basic flow diagram of the typical gas inlets and mixing chamber configuration of an analyzer designed for Residual Oxygen Measurement Method. The purpose of the mixing chamber is to combine the air and fuel gas streams into an air/fuel gas mixture for combustion.

- The air and fuel gas streams must first be equalized for temperature and pressure
 - Pre-regulators and dome loaded pressure regulators (booster relays) are used to equalize the pressure of the fuel gas and air streams
 - A heat exchanger is used to equalize the temperature of the fuel gas stream and air

- The two streams then pass through a set of precision orifices operating at supercritical stage into the gas mixing chamber where a air/fuel gas mixture is created
 - Orifices are sized according to the fuel gas composition and BTU range; the ratio of the diameter of the orifices controls the
 - The amount of air/oxygen introduced is a constant controlled by the orifice size. This amount will be in excess of what is required for complete combustion of the fuel gas
 - Changes in ambient conditions affect the air stream and fuel gas stream equally and have no effect on the fuel to air ratio

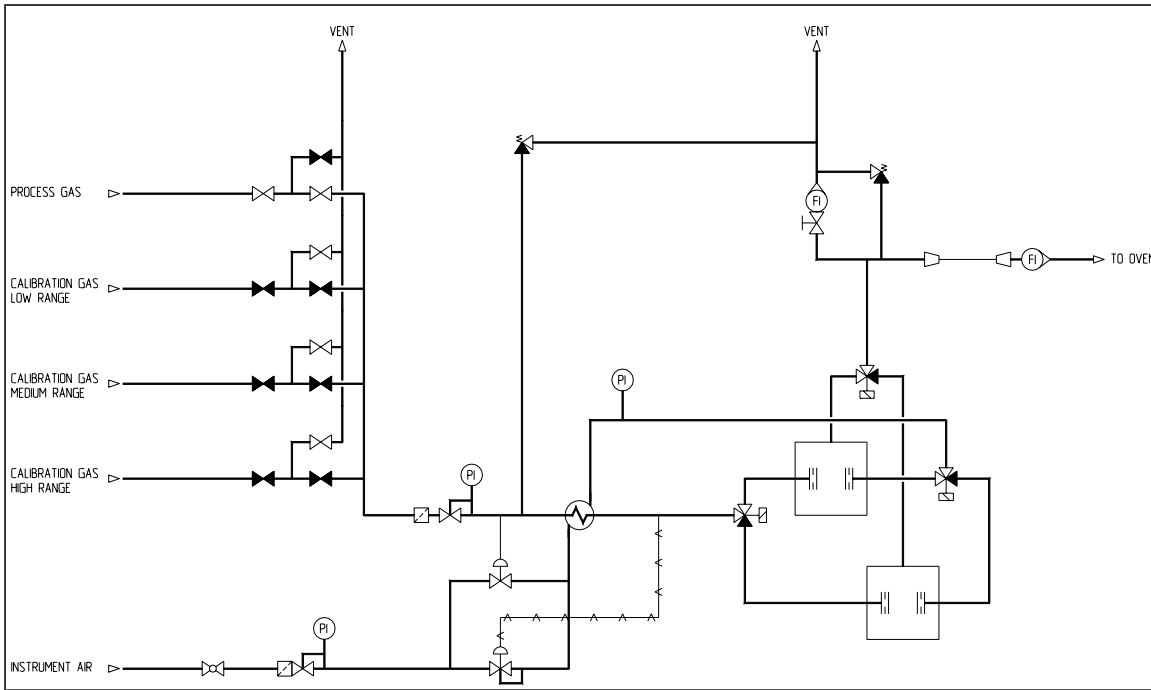


FIG. 3 – SYSTEM FLOW DIAGRAM ⁴

RESIDUAL OXYGEN MEASUREMENT

The air/fuel gas mixture flows out of the mixing chamber into an oven containing a zirconia oxide cell. The zirconia oxide cell, similar to that shown in Figure 4, is held at a temperature of 800C and provides the source of combustion. The amount of oxygen in the air/fuel mixture that is not used during the combustion process, the residual oxygen, is measured by the zirconia oxide cell. The amount of oxygen used during the combustion process is representative of CARI.

In theory, knowing the initial amount of oxygen and the residual oxygen in the combusted stream, the amount of oxygen used during the combustion process can be calculate by simple subtraction.

$$\text{CARI} = \text{O}_2 \text{ Used for Combustion} = \text{Initial O}_2 - \text{Residual O}_2 \quad (10)$$

The Wobbe Index can then be calculated from the CARI value, given the linear relationship between the two parameters.

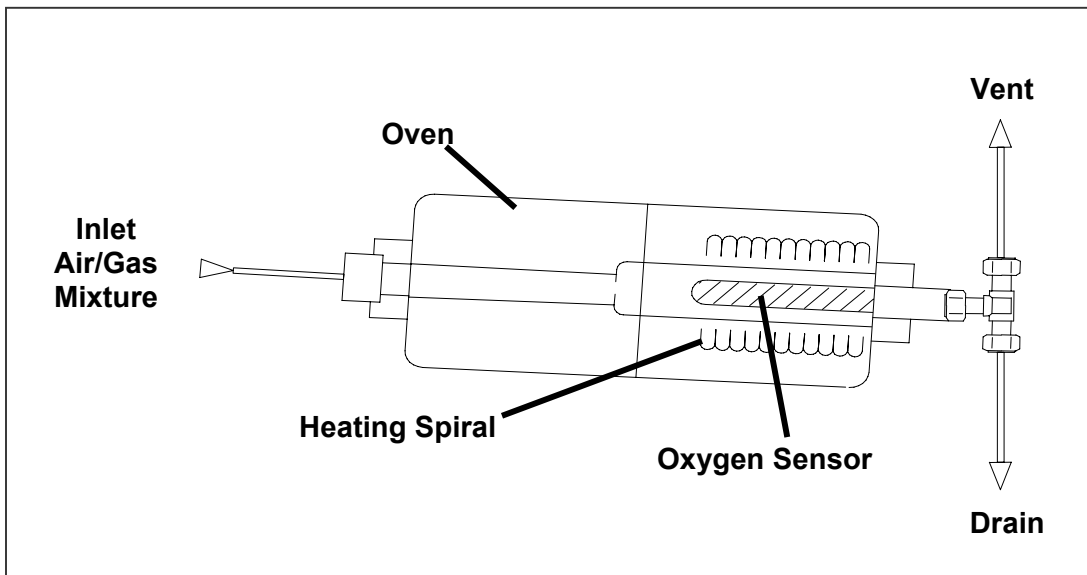


FIG. 4 – ZIRCONIA OXIDE CELL⁴

USING CALIBRATION GASES TO CALCULATE WOBBE INDEX⁴

Two calibration standards, a High and Low calibration gas mixture representing the range of the Wobbe Index of the process stream, can be used to establish the linear relationship between CARI and the Wobbe Index. By measuring the concentration of Oxygen in the flue gas after calibrating the instrument, the Wobbe index can be calculated by solving the linear equation:

$$\text{Wobbe Index} = aO + b \quad (11)$$

Where;

a,b = calibration constants

O = concentration of residual oxygen in the flue gas

Equation (11) can be re-written as:

$$\text{Wobbe Index} = \frac{W_H - W_L}{O_H - O_L} * (O - O_L) + W_H \quad (12)$$

Where;

W_H = Wobbe Index, High Calibration gas

W_L = Wobbe Index, Low Calibration gas

O_H = concentration of residual oxygen after combusting High Calibration Gas

O_L = concentration of residual oxygen after combusting Low Calibration Gas

O = concentration of residual oxygen in the sample gas

EFFECT OF ALKENES, HYDROGEN AND CARBON MONOXIDE ON THE RELATIONSHIP OF CARI AND WOBBE INDEX

TABLE 4 – DATA AND CALCULATED VALUES FOR SELECTED ALKANES, ALKENES, HYDROGEN AND CARBON MONOXIDE

COMPONENT	Relative Density	CARI	Net Heating Value (BTU/SCF)	Net Wobbe Index (BTU/SCF)	Ratio Between CARI and Wobbe
HYDROGEN	0.06960	9.07	274	1038.59	114.52
CARBON MONOXIDE	0.96707	4.87	321	326.42	67.08
METHANE	0.55392	12.86	909	1221.35	94.98
ETHANE	1.03820	16.44	1619	1588.94	96.67
ETHYLENE	0.96858	14.59	1502	1526.17	104.63
PROPANE	1.52260	19.39	2315	1876.11	96.76
PROPYLENE	1.45286	17.86	2188	1815.24	101.61
n-BUTANE	2.00680	21.96	3011	2125.49	96.81
i-BUTANE	2.00680	21.96	3000	2117.72	96.46
BUTENE	1.93715	20.63	2877	2067.09	100.21
PENTANE	2.49120	24.25	3707	2348.65	96.84
i-PENTANE	2.49120	24.25	3699	2343.58	96.63
PENTENE	2.42144	23.06	3574	2296.77	99.59

As you can see by Table 4, the ratio between CARI and Wobbe Index is not the same across alkanes, alkenes, carbon monoxide and hydrogen. However, for fuel gases containing a mix of these components, a suitable choice of calibration gases can compensate for this error.

CONCLUSION

The Residual Oxygen Measurement Technique provides a direct measurement of the Combustion Air Requirement Index (CARI). CARI is a dimensionless parameter indicating how much air is required for the stoichiometric combustion of a fuel gas.

The Wobbe Index, a measure of energy supplied to the burner, can be then readily calculated from the CARI value. The ratio between CARI and the Wobbe Index is a constant for gas mixtures containing alkanes. For fuel gas mixtures containing large amounts of alkenes, hydrogen or carbon monoxide calibration gases can be used to compensate for the non-linearity of the CARI/Wobbe relationship across these components.

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