

## METHODOLOGY FOR RESIDUAL OXYGEN CALORIMETRY

J. David Hailey Ph.D.  
Vice President, Sales  
COSA Xentaur Corp.  
7125 North Loop East  
Houston, TX 77028

### KEYWORDS

Combustion Air Requirement Index (CARI) Air/Fuel Ratio, CARI Index, Wobbe Index, Fuel Gas, Stoichiometric Air to Fuel Ratio, Choked Flow, Mass Flow Rate, Sonic Flow, Ideal Gas Law, Specific Heat, Exothermic Oxidation

### ABSTRACT

This paper describes the methodology of flameless calorimetry for determination of Calorific Value (Heating Value) utilizing CARI Index, Wobbe Index and specific gravity in a real-time reporting basis. The fuel gases are exothermically oxidized in a catalytic converter and the residual oxygen from the reaction is correlated to the CARI and Wobbe Index. This measurement methodology offers an extremely fast speed of response and reliable measurements over large range of gas compositions and calorific values without the concern of flameouts or the need for assist gases.

### INTRODUCTION

The basic components of a residual oxygen combustion calorimeter are the Fuels Conditioning Section, where the gas to be measured is blended with air using critical sized orifices for both gas and air to obtain a resulting excess oxygen reading that varies with combustible constituent content and Choked Flow thus a stable Sonic Flow Rate is achieved with only the Mass Flow Rate varying with the mixed gas composition, the Combustion Section, where the mixed gas and air are reduced down to their elemental states by Exothermic Oxidation in a catalytic over at over 800°C, and the Measurement Section, where the device measures the residual oxygen remaining from the mixed gas after Exothermic Oxidation and correlates this residual oxygen reading by a Zirconium Oxide Oxygen Sensor reading that is correlated to CARI Index, Wobbe Index and Calorific Value (BTU's/SCF, or Joules/meter) with a densitometer for the calculation of Wobbe to Calorific Value by means of the Specific Gravity value of the gas being measured.

## COMBUSTION BASICS

Stoichiometric reactions are ones in which a mixture of reactants are exactly proportioned on a molal basis so that no excess of any reactant is present after the reaction. A Stoichiometric combustion is one in which all the oxygen atoms and fuel molecules are chemically reacted (oxidized). More plainly put, it is the point where just enough or excess oxygen is present to burn all of the combustible reactants in the stream. Carbon (C) to carbon dioxide (CO<sub>2</sub>), hydrogen (H) to water vapor (H<sub>2</sub>O) and all sulfur (S) to sulfur dioxide (SO<sub>2</sub>). The basic chemical equation for combustion of a fossil fuel is as follows (1):

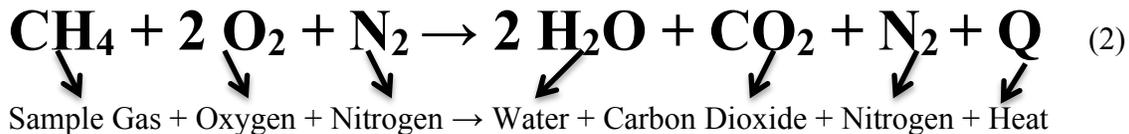


Where C<sub>n</sub>H<sub>m</sub> is a fossil fuel, with “n” the number of Carbon atoms in the reaction, and “m” the number of Hydrogen atoms.

O<sub>2</sub> + 3.76N<sub>2</sub> is air, which is used as the source of oxygen.

Q is the heat released from the combustion process.

The combustion process of the combustible gases such as Hydrocarbons in Instrument Air (N<sub>2</sub> + O<sub>2</sub>) is best described as; Sample Gas + Oxygen + Nitrogen → Water + Carbon Dioxide + Nitrogen + Heat. Wherein the combusted Sample Gas in the presences of excess Oxygen will produce Heat, Water, Carbon Dioxide & Nitrogen which are considered to be the products of combustion and can be expressed as follows (2):



To assure complete combustion of a gas, the combustion process is ran at higher oxygen levels than needed to theoretically burn all of the gas given the range and variability of the gas constituent(s) molar percentage content matrix being introduced. This extra amount is called excess oxygen, or because air is used, excess air. In most combustion processes, excess O<sub>2</sub> is generally measured to assure all fuel is burned. Standard practice is to use a Zirconium Oxide analyzer to perform this measurement.

The Calorimeter’s Instrument Air to Gas ratio is typically 14:1 and fixed by different Air & Gas orifice sizes and pressure to assure Choked Flow to achieve Sonic Flow stability so that there is excess Oxygen present regardless of the combustible gas composition, and this is stated as Residual Oxygen, also referred to as Combustion Air Requirement Index, which is the unit of measurement used to determine the Wobbe Index, CARI, and with the use of an intergraded density cell the Calorific Values such as Lower Heating Value (LHV) or Higher Heating Value (HHV) is also reported in BTU, MJ, Kcal, etc...

## FUELS CONDITIONING SECTION

The Fuels Conditioning portion of a Gas Calorimeter is comprised of a continuous gas sample that is mixed with dry air and maintained at a constant temperature and ratio determined by Air/Gas orifices in the Mixing Chamber (Figure 1). The gas and air stream pressures are first equalized by a dome loaded pressure regulator.

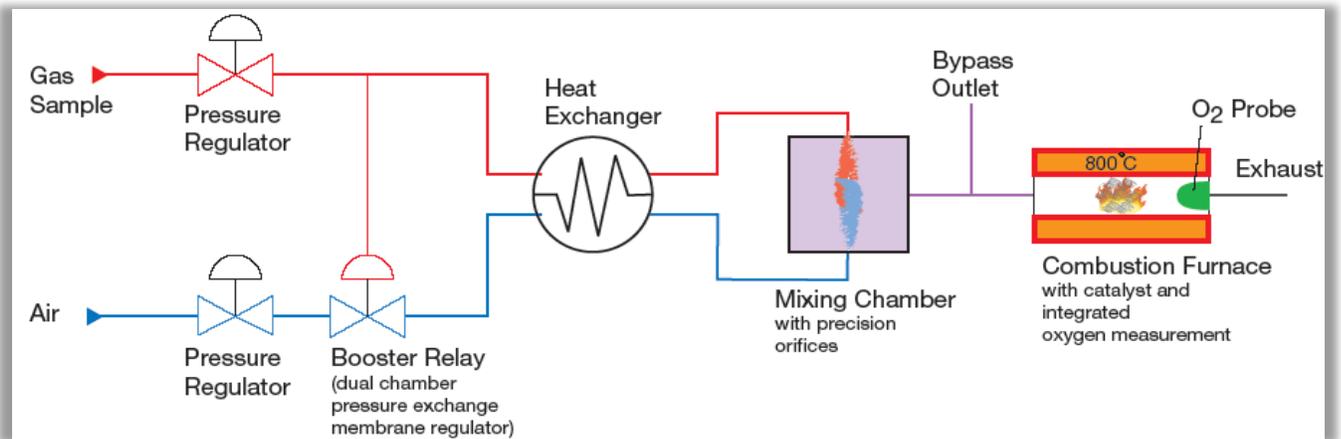


Figure 1.

These streams are then temperature regulated by means of a heater in the sample system compartment and use of a heat exchange to equilibrate the Instrument Air and Sample Gas upstream of the Mixing Chamber. The flow to their respective orifice plates are regulated at critical flow rates, and then fed to a mixing chamber creating a homogeneous mixture of the gas and air as shown in figure 2.

### Mixing Chamber for turbulent blending of Instrument Air with Sample Gas

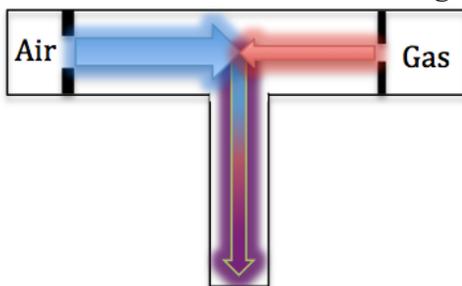


Figure 2.

Specific gravity of the process gas is measured when Calorific Value (CV) needs be reported in BTU/SCF, or MJ/Nm<sup>3</sup> and a densitometer (S.G.) is placed in the sample gas line upstream of the Mixing Chamber utilizing the Equation of State (3) wherein CV equals the Wobbe Index (WI) multiplied by the square root of the Specific Gravity (S.G.) of the gas being measured and the Wobbe

Index Equation of State (4) is Wobbe Index (WI) divided by the square root of the Specific Gravity (S.G.) of the sample gas.

$$CV = WI \times \sqrt{S.G.} \quad (3)$$

$$WI = CV \div \sqrt{S.G.} \quad (4)$$

where;

CV = calorific value (heating value)

WI = wobbe index

S.G. = specific gravity (relative density)

Utilizing Choked Flow with the assumption of ideal gas behavior, the steady state Choked Flow occurs when the ratio of the absolute upstream pressure to the absolute downstream pressure is equal to or

greater than  $[(k+1) / 2]^{k/(k-1)}$ , where  $k$  is the specific heat ratio of the gas (Isentropic Expansion Factor  $\gamma$ )

For most gases,  $k$  ranges from 1.32 for Methane to 1.67 Argon, therefore  $[(k+1) / 2]^{k/(k-1)}$  ranges from 1.11 to approximately 2.1 which means that choked flow usually occurs when the absolute source Pressure Upstream (Pu) is at least 1.7 to 2.1 times as high as the absolute Pressure Downstream (Pd) as shown in table 1 below for a range of these aforementioned gas ranges. Therefore, the minimum Pu/Pd pressure ratio is to be understood as the ratio between the upstream pressure (Pu) and the pressure at the orifice plate (nozzle throat) when the gas is traveling at Sonic Flow Speed as defined as Mach 1 and inversely should the upstream pressure (Pu) become too low as compared to the downstream pressure (Pd) minimum choked ratio, then sonic flow cannot occur at the orifice plate throat.

Gas	Formula	$k = C_p/C_v$ ( $\gamma$ )	Pu/Pd (Choked Minimum)
Acetylene	C2H2	1.300	1.832
Air	-	1.399	1.893
Ammonia	Nh4	1.320	1.845
Argon	Ar	1.669	2.056
n-Butane	C4H10	1.110	1.717
Carbon Dioxide	CO2	1.300	1.832
Carbon Monoxide	CO	1.401	1.893
Chlorine	Cl2	1.329	1.850
Ethane	C2H6	1.220	1.784
Ethylene	C2H4	1.220	1.784
Hydrochloric Acid	HCl	1.411	1.900
Hydrogen	H2	1.410	1.899
Hydrogen Sulfide	H2S	1.301	1.833
Methane	CH4	1.320	1.845
Methyl Chloride	CH2Cl	1.199	1.771
Natural Gas	-	1.270	1.814
Nitrogen	N2	1.411	1.899
Nitrous Oxide	N2O	1.310	1.839
Oxygen	O2	1.401	1.893
Propane	C3H8	1.150	1.742

Table 1

$k = c_p/c_v$  of the gas or gas matrix

$c_p$  = specific heat of the gas at a constant pressure

$c_v$  = specific heat of the gas at a constant volume  
 $P_u$  = pressure upstream at a constant temperature  
 $P_d$  = pressure downstream at a constant temperature

The Conservation of Mass Principle requires that the gas velocity increase as it flows through a smaller cross-sectional region of the restriction while the Venturi Effect causes the static pressure, and therefore, the density to decrease downstream past the restriction, thus the Choked Flow produced and is a limiting condition. This condition occurs when the Mass Flow Rate does not increase with a further decrease in the Pressure Downstream ( $P_d$ ) while the Pressure Upstream ( $P_u$ ) is fixed along with the composition of the gases being measured, thus the gas mixture reaches the physical point at which the Choked Flow occurs for adiabatic conditions and when the orifice exit plane velocity(s) is at a sonic flow condition.

### COMBUSTION SECTION

Now that the fuel is properly mixed with a reducing agent (air) and at this point where the Instrument Air and sample gas have been blended past the critical Air & Gas orifices and are at sonic speed it must be burned or oxidized in order to determine the Calorific Value contained in the gas. The sample gas and air mixture from the Fuels Conditioning System is catalytically combusted in an oven (Figure 3) whose temperature is set to approximately 812°C and by a thermocouple and PID algorithm programmed in the microcontroller

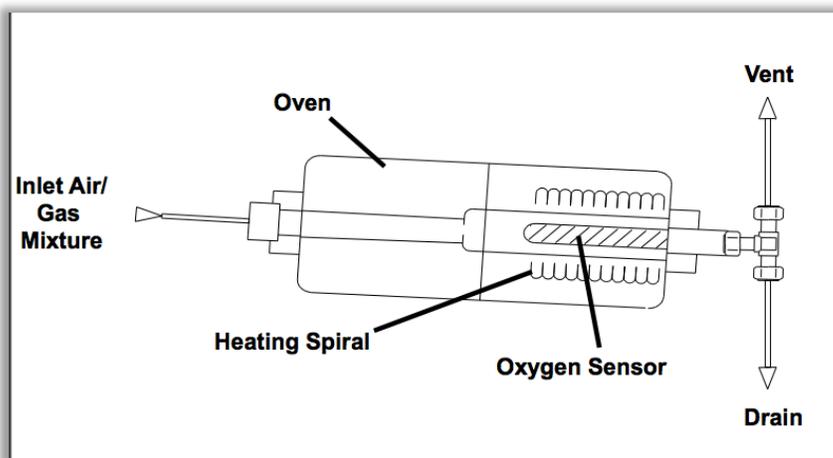


Figure 3

After complete combustion of the sample gas that is mixed with Instrument Air in the Catalytic Oven the measurement of the Residual Oxygen by the Zirconium Oxide Oxygen Sensor is a function of the remaining molar percentage of Oxygen molecules after the combustion process and the demand for Oxygen to combust the gas matrix has been reached the residual Oxygen is then correlated to the CARI and WI values determined by calibration of the system using a lower and higher range of gases

with a CARI and WI value to be representative of the range of the Sample Gas to be measured. Each of the calibration gases that represent the expected range of gases to be measured are combusted and their CARI, WI and CV + S.G. with a density cell are recorded for the low and high range and a midpoint of calibration is added for extended range models, and these values are the calibration factors stored in the calorimeter and used when measuring the unknown Sample Gas matrix to provide a CARI, WI and CV + S.G. Figure 4 below shows the Calibration Manifold where the Process Gas (Sample Gas), and the Low, Medium and the High range if so equipped for an extended CV measurement range.

As the sample gas combined with instrument air flows of a fuel gas through an orifice is dependent upon the specific gravity of this gas matrix. the amount of air required for complete combustion of the sample gas will change with the density of the sample gas. The Combustion Air Requirement Index (CARI) is a dimensionless parameter indicating how much air is required for the stoichiometric combustion of a sample gas (5) .

$$CARI = \frac{Air / Gas}{\sqrt{S.G.}} \quad (5)$$

where;

CARI = Combustion Air Requirement Index

S.G. = specific gravity

Calibration gas mixtures representing the Low, Mid and occasionally the High range of the Wobbe Index of the process gas stream, can be used to establish the linear relationship between CARI and the Wobbe Index by measuring the Residual Oxygen in the Catalytic Combustion Oven after measuring and recording the two or three calibration gases, thus the Wobbe index can be calculated by solving the linear equation (6,7):

$$\text{Wobbe Index} = aO + b \quad (6)$$

where;

a, b = calibration constants

O = concentration of residual oxygen in the flue gas

$$WI = \frac{Wm - Wl}{Om - Ol} \times (O - Ol) + Wl \quad (7)$$

Where;

Wm = Wobbe Index, Mid (High) Calibration gas

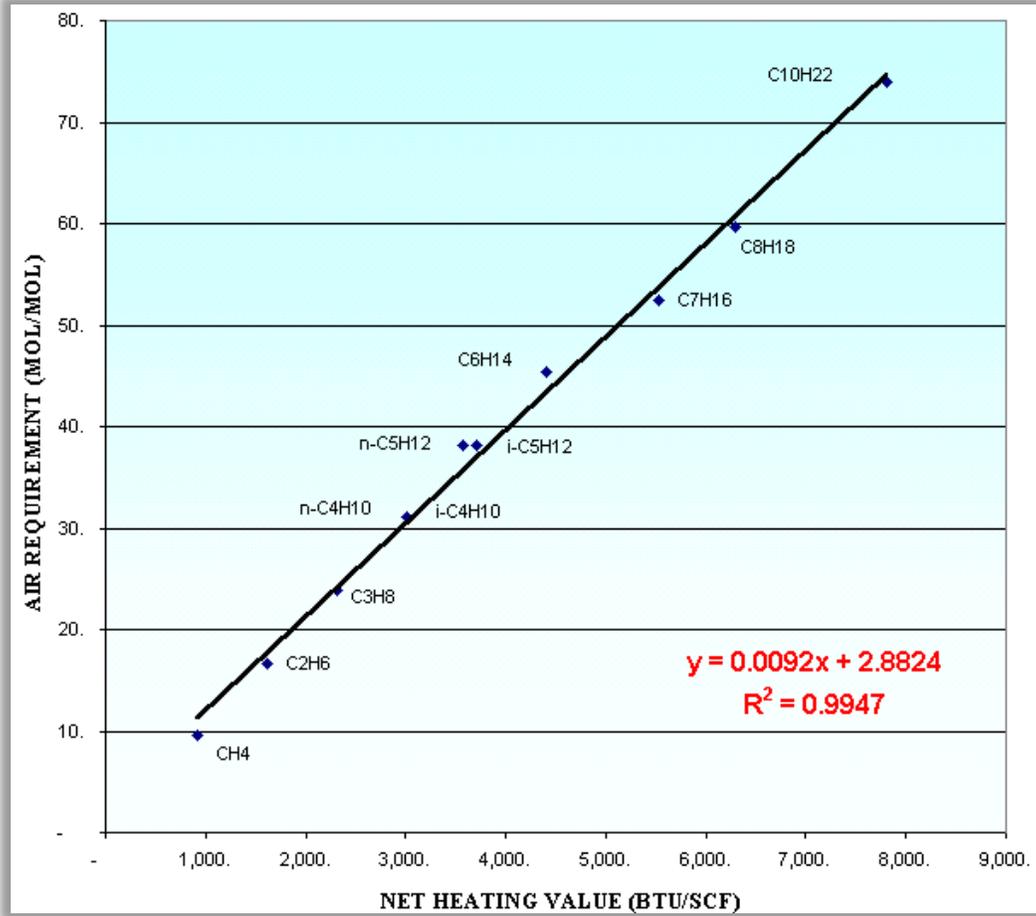
Wl = Wobbe Index, Low Calibration gas

Om = concentration of residual oxygen after combusting mid (high) Calibration Gas

Ol = concentration of residual oxygen after combusting Low Calibration Gas

O = concentration of residual oxygen in the sample gas

In graph 1 you can see that the relationship between the CV (heating value) of the various gases corresponds closely to the CARI, this relationship is even closer when calculation Gross CV.



Graph 1

The Thermal Loading of the Catalytic Combustion Oven is expressed as follows (8, 9, 10, 11):

$$\text{Furnace Thermal Load} = Q_g \times CV \quad (8)$$

$$Q_g = k \times (\sqrt{\quad})P \div \sqrt{S.G.} \quad (9)$$

$$\text{Thermal load} = k \times (\sqrt{\quad})P \times CV / \sqrt{S.G.} \quad (10)$$

$$\text{Thermal load} = k \times (\sqrt{\quad})P \times WI \quad (11)$$

where;

- Q<sub>g</sub> = flow of sample gas thus thermal load
- CV = calorific value (heating value)
- k = cp/cv of the gas or gas matrix (see table 1)
- WI = wobble index

P = pressure for choked flow  $P_u/P_d$  (see table 1)

S.G. = specific gravity (relative density)

Therefore if at a constant sample gas pressure, the Wobbe Index is controlled at constant pressure, then the thermal load to the oven is therefore constant as well. As the compositional matrix of the sample gas changes, so then will the thermal load and will be expressed as residual oxygen level.

The measurement of excess oxygen provides a direct measurement of the Combustion Air Requirement Index (CARI) of the fuel, which can then be mathematically correlated to the Wobbe Index. Differences between the CARI and Wobbe Index values can be cancelled out by the use of calibration gases thus giving this technique the ability to report Wobbe Index values along with CARI. With the addition of a Specific Gravity Cell, CV can be reported as well.

## CONCLUSIONS

This methodology does not suffer from ambient temperature effects as do most other approaches, minimizing or eliminating measurement shelter and associated building and utility costs. There is no flame to go out, so during a low calorific value event the system never shuts down, disrupting plant operation or require a call out service. The constant flow of sample gas allows for a fast speed of response to changing calorific values. This methodology has very low maintenance requirements when compared to the other methodologies with regard to repair, operation, setup, down time and field service.

There is also the added advantage of being able to measure extremely high dew point gases that require the sample gas and analyzer enclosure to be to as much as 95°C to keep the sample gas in a gaseous state. Thus, high BTU gas can be measured without the concern of “heavy” hydrocarbons condensing.

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