AMETEK® PROCESS INSTRUMENTS

THERMOX® Application Note

The Other Side of Zirconium Oxide

Thermox Analyzers for Excess Fuel, Equivalent Combustibles and Premix

Regular Fuel Efficiency Applications

Separate Oxygen and Combustibles Sensors

In standard flue gas applications for Thermox analyzers, the user generally tries to extract the maximum energy from the fuel and transfers as much of that energy as possible to the process. These applications require the process to be operated as efficiently as possible by keeping both oxygen (excess air) and combustibles (incompletely burned fuel) to a minimum. The best way to do this is to measure both oxygen and ppm combustibles simultaneously, using two separate detectors in one analyzer. Thermox WDG-IVC and WDG-HPIIC analyzers have both oxygen and combustibles detectors. Here the term combustibles describes the background amounts of CO and H_2 which occur during normal combustion, typically 50-200 ppm.

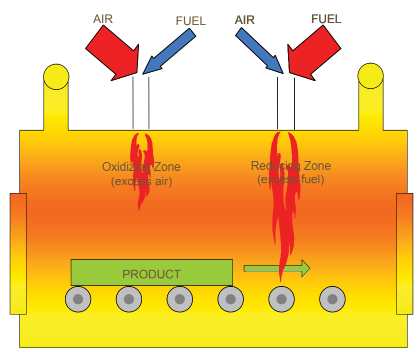

Figure 1. Representation of a furnace showing oxidizing and reducing zones

Excess Fuel or High Millivolt Applications

Oxygen or Combustibles from ZrO_2

Some applications use the flue gas not only to generate heat, but also to alter the properties of the product exposed to it. Here fuel efficiency is not as important as the oxidizing or reducing properties of the flue gas. This is called heat treatment and is used on many metals, ceramics, glasses and other materials. By adjusting the air/fuel ratio to the burner, the flue gas is controlled to be as oxidizing or reducing as needed. The exact air-to-fuel ratio which gives theoretically perfect combustion is called stoichiometric (approximately 9.5 parts air to 1 part fuel for methane). Using more air than the stoichiometric amount creates an oxidizing effect; less air than stoichiometric creates a reducing effect.

This latter condition is known as sub-stoichiometric (other terms include excess fuel, reducing or Lambda <1) and can be used to alter the physical properties of products or to prevent the formation of NOx. For example, reducing conditions are necessary to make colored glass. In some applications, such as bright annealing, a highly reducing atmosphere is required, but the product would be damaged by carbon-containing gases so a flue gas from fossil fuels cannot be used. In such cases a mixture of nitrogen and hydrogen (or cracked ammonia) is commonly used. In many applications, it is easier and less expensive to use a flue gas as the furnace atmosphere. The zirconium oxide cell can also be used to follow sub-stoichiometric as well as oxidizing atmospheres.

What applications maintain excess air conditions?

Most standard heating processes including boilers operate with excess air (excess oxygen)—for example:

- Steam or power boiler
- Process heater
- Sludge incinerator
- Reformer furnace
- Recovery boiler, etc.

What applications run under excess fuel conditions?

In the following applications, it may sometimes be desirable to run sub-stoichiometrically and to have some way of knowing at all times how oxidizing or reducing the process is:

- Heat treatment of metals
- Wire manufacturing
- Heat treatment of ceramics and porcelains
- Primary stage of a thermal oxidizer (incinerator)
- Manufacture of specialty glass, e.g. colored glass
- Primary stage of a low NOx burner

How does it work?

When there is excess oxygen, the output of the cell follows the normal Nernst equation from 0 mV to about 130 mV. In excess fuel (or sub-stoichiometric) conditions, the same cell produces a high output signal from about 550 mV to well over 1000 mV.

From this output reading it is possible, using a single sensor, to determine whether the process is oxidizing or reducing. How can the cell measure anything in reducing atmospheres since there is no longer any oxygen? The zirconium oxide cell is still responding to oxygen—the tiny amount of oxygen produced by dissociation of water vapor and carbon dioxide at the high cell operating temperature.

The cell is actually measuring the water-to-hydrogen ratio and also the carbon dioxide-to-carbon monoxide ratio. Since both are present in flue gas, the cell is really responding to the ratio of total oxides (carbon dioxide and water) to total fuels (hydrogen and carbon monoxide).

$$H_2O \leftrightharpoons H_2 + \tfrac{1}{2}O_2 \quad \text{or} \quad O_2 \propto \frac{H_2O}{H_2}$$

$$CO_2 \leftrightharpoons CO + \tfrac{1}{2}O_2 \quad \text{or} \quad O_2 \propto \frac{CO_2}{CO}$$

$$O2 \propto \frac{H_2O + CO_2}{H_2 + CO}$$ This is the oxides-to-fuels ratio.

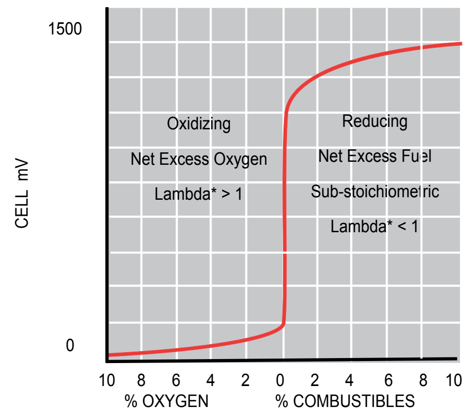

Figure 2. Zirconia cell output for Excess Oxygen and Excess Fuel

** Lambda is the ratio of the air fuel ratio (AFR) to the stoiciometric air fuel ratio (SAFR) so > 1 is air rich, < 1 is fuel rich.*

More fuel in the flue gas reduces the oxides-to-fuels ratio (or increases the fuels-to-oxides ratio) so the cell millivolt output rises. Thus the oxygen cell gives us a way of following how oxidizing or reducing the process is. The oxides-to-fuels ratio depends on the hydrogen-to-carbon ratio of the fuel being burned and so the millivolt signal can be calibrated to read excess fuel, combustibles, oxides/fuels ratio or other units if the fuel is known. In many cases the fuel is natural gas, which has a hydrogen-to-carbon (H/C) ratio of 3.7 (methane is 4.0, coal is 0.68). Common fuel types are listed and selectable using the Thermox Series 2000 control unit. If a fuel is not listed, the customer can enter the actual hydrogen-to-carbon ratio. If the fuel composition varies, such as in a waste incinerator, then the measurement will be less accurate and the worst case limits can be calculated.

The excess fuel option allows any WDG-IV or WDG-HPII to display and output in sub-stoichiometric conditions. This unique combination provides analog outputs and alarms for the following measuring units:

% combustibles	% excess fuel to % excess oxygen
% excess fuel	% combustibles to % excess oxygen
% excess oxygen	% excess oxygen to % excess fuel
oxides/fuels ratio	% excess oxygen to % combustibles
fuels/oxides ratio	cell millivolts

For example, the output can be set so that 4 mA represents 5% Oxygen and 20 mA represents 5% Excess Fuel. The position of the zero point can be adjusted to suit.

Note that here the terms “Excess Fuel” and “Combustibles” both refer to sub-stoichiometric conditions. The difference is that “Excess Fuel” is calculated on the air/fuel mixture coming to the burner, whereas “Combustibles” is calculated in the flue gas and is a higher number than the excess fuel value for the same reducing conditions.

“Combustibles” in this context (which is really excess combustibles) should not be confused with the common use of the word to describe the presence of CO and H_2 together with excess oxygen in normal (oxidizing) combustion.

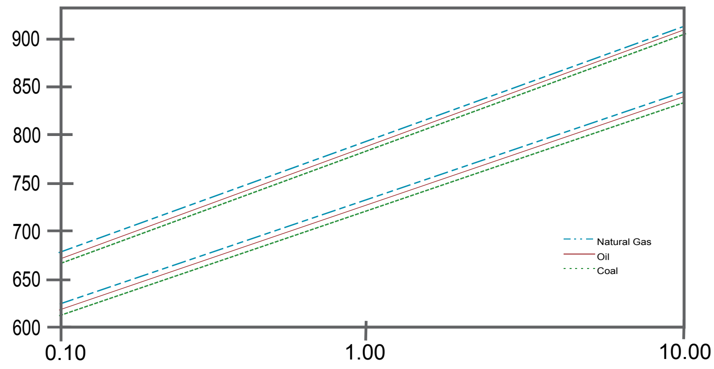

Figure 3. Zirconia cell output (sub-stoichiometric) for various fuels

Equivalent Combustibles

Returning to separate oxygen and combustibles detectors.

On the standard WDG-IVC and WDG-HPIIC, as long as the oxygen reads 0.01% or higher, there is sufficient oxygen to burn any combustibles that may be present and the combustibles detector is reading correctly. Don’t forget that zirconium oxide gives the net oxygen—that is, the oxygen left over after any combustibles are burned. If the process goes sub-stoichiometric, there is no oxygen to burn any combustibles on the detector, and you might expect it to read zero. The detector does not read zero however, because the signal from the zirconia cell is now higher than 130 millivolts and this is used as a trigger to send the combustibles detector to full scale. For example, if the combustibles output range is set at 4-20 mA corresponding to 0 to 10,000 ppm, then the output would jump to 20 mA and the display would read 10,000 ppm.

In normal combustion applications, it is generally undesirable to operate under sub-stoichiometric conditions because it is very costly in fuel, bad for emissions and perhaps dangerous. When you reach zero oxygen, and, therefore, sub-stoichiometric or excess fuel conditions, the very fact that the combustibles detector is at full scale and the oxygen reads zero should be telling you that the process needs more air. Normally you would want to get back to excess air conditions as soon as possible and it is enough to know that your process has gone reducing. Some applications may occasionally need to be sub-stoichiometric. Then you would want to know not only that your process is reducing, but by how much. The equivalent combustibles option for the WDG-IVC and WDG-HPIIC uses the high millivolt signal from the oxygen cell to calculate the amount of excess fuel or equivalent combustibles, as discussed above. It adds this to any signal from the combustibles detector, so that the combustibles reading is provided under all conditions.

What applications would use equivalent combustibles?

The Equivalent Combustibles option is used where there are occasional sub-stoichiometric conditions such as the following examples:

- Decarburizing furnaces
- Cement kilns
- Pulverized coal dryers and injectors
- Ore roasting ovens

IMPORTANT NOTE: *If the process is always reducing, the Excess Fuel option on a WDG-IV or WDG-HPII should be used instead.*

THERMOX®

PreMix 2000

The Thermox PreMix 2000 accurately and continuously measures the proportions of oxygen and fuel in pre-mix gases. The analyzer receives a small sample of the air/fuel mixture, burns it and then measures the results.

The sample gas enters the analyzer and flows through the sample flowmeter and flashback arrestor to the combustion chamber, where the mixture is burned. The resulting products of combustion, either oxygen or combustibles (excess fuel), are measured with a zirconium oxide cell. The PreMix 2000 can operate under either excess oxygen or excess fuel conditions in the same way as described earlier for the zirconium oxide cell.

CMFA-P 2000

The CMFA-P 2000 is a portable combination premix and flue gas analyzer. The operating mode is selected by moving a valve to either the premix or flue gas position. In the premix mode the premix gas is applied via a flowmeter to the premix inlet port. In the flue gas mode, a suitable probe is screwed into the flue gas inlet on the back of the sensor and the sensor can be mounted directly at the measuring point on the furnace.

The CMFA-P 2000 can also operate under either excess oxygen or excess fuel conditions.

What applications can use the Premix 2000 or CMFA-P 2000?

The Premix analyzers measure the air/fuel ratio in open flame applications where flue gas measurements are not practical. The value measured by the analyzer accurately predicts the conditions in the open flame area.

- Flame treating
- Glass forehearth
- Tempering furnaces
- Air/fuel mixtures
- Gas generators
- Glass fiber manufacturing
- Metals and metal forming
- Open flame brazing and soldering

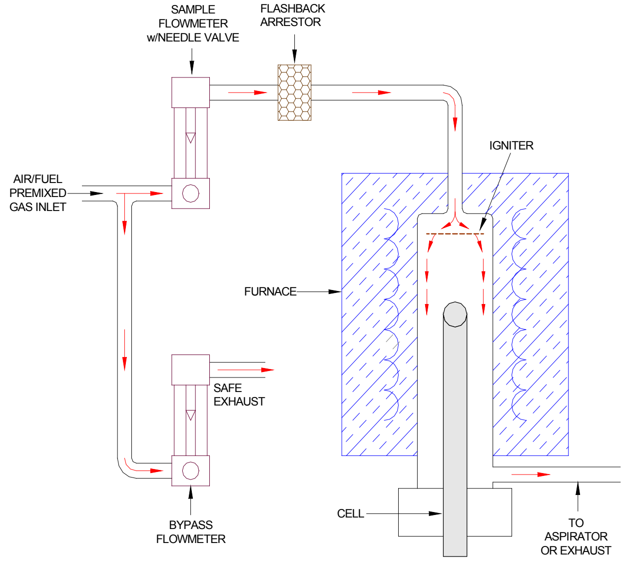

Figure 4. Premix flow diagram

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