White Paper

Fundamental Challenges with Tunable Diode Laser Flue Gas Oxygen Measurement for Combustion Excess Air Control





Introduction

With the introduction of new flue gas oxygen (O_2) measurement technologies, a review of boiler controls philosophy and traditional O_2 measurement technologies is warranted. In this paper, we will discuss how boiler combustion controls have typically been built on direct measurement of excess O_2 using zirconia (ZrO_2) O_2 sensors, and how tunable diode laser (TDL) O_2 sensors – which do not make direct excess O_2 measurements – can introduce risks which may require additional mitigating measures to ensure safe combustion operation.

Boilers, process heaters, and other combustion facilities in industries such as refining, petrochemical, chemical and power, can experience combustion anomalies resulting in unburned fuel in the flue gas. It is widely believed that fuel-rich events are more common than realized⁽¹⁾. Some have reported issues where burner adjustments and burner degradation have caused excessive unburned fuel in the flue gas. Today many process heaters are installing combustion analyzers directly above the furnace exit where there is limited gas residence time to complete fuel-air mixing and combustion. Therefore, when combustion performance deteriorates, unburned fuel may be more likely at this location. While the likelihood of unburned fuel may be low, most of the industry uses conventional excess O₂ controls and direct excess O₂ measurement and is less vulnerable to the risk of fuel-rich events. As TDL O₂ measurement becomes more common, the possibility of unsafe operation may increase unless precautions are implemented.

Combustion control

Combustion control is based on regulating combustion air supply for a given fuel flow rate. The stoichiometric air supply is the theoretical air required to completely burn the fuel with no excess air remaining. The stoichiometric air supply can be calculated for a given fuel composition and flow rate. In most applications, the combustion air supply is greater than the stoichiometric air supply. The amount of air supplied above that required for stoichiometric combustion is called excess combustion air. Typically, excess combustion air is reported as percent excess air and is calculated ⁽²⁾ as follows.

Excess Air (%) = (Air Supply_(actual) - Air Supply_(stoichiometric)) / Air Supply_(stoichiometric) * 100% [Eq. 1]

Different combustion systems typically have different guidelines for setting excess air. For example, coal-fired units typically operate at around 15–20% excess air, gas-fired units around 5–15% excess air, while refuse derived fuel (RDF) and other difficult-to-burn fuels may operate at 30–50% excess air.

The stoichiometric air supply varies with fuel oxygen demand and fuel flow rate. For most boiler controls, fuel flow rate is continuously measured but the fuel's oxygen demand, which can vary with fuel composition, is not typically measured. Instead, to accommodate fuel composition changes and flow measurement and combustion performance variations, the industry typically measures excess air in the combustion flue gas exhaust and uses feedback control to trim combustion air supply.

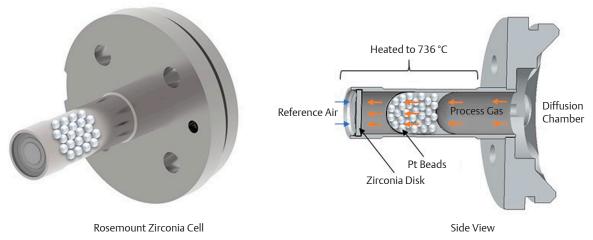
Since excess O_2 can be directly measured, excess O_2 is often used to express the excess air levels. Excess air can be approximated from the combustion flue gas excess O_2 measurement as follows:

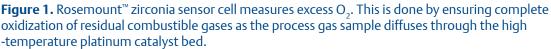
Excess Air (%) =
$$21\% / (21\% - Excess O_{3}(\%))$$
 [Eq. 2]

Because the equation is derived from stoichiometric combustion, the relationship between excess air and flue gas O_2 only applies when combustion is complete. Some have suggested that when carbon monoxide (CO) levels are less than 100 ppm, combustibles can be ignored in the derivation of excess $O_2^{(2)}$, since unburned fuel impact on O_2 readings is not significant until it reaches higher levels. The excess air equation is an approximation that varies slightly with fuel composition and applies to standard combustion with 21% O_2 air. It does not apply to oxygen-enriched combustion systems.

Excess O₂ measurement

Excess O₂ can be directly measured using Emerson's Rosemount^m ZrO₂ O₂ cells. The high temperature cell operating at 736 °C ensures complete combustion and only measures the remaining (or excess) O₂ (Figure 1).





Flue gases from the duct diffuse across the filter media into the chamber based on partial pressure diffusion. The flue gas sample then diffuses through the neck of the O_2 cell which is packed with platinum coated beads. The entire cell is embedded in a heater, maintaining the ZrO_2 and beads at high temperature. The high-surface-area platinum beads catalyze the oxidation of any unburned fuel in the gas sample resulting in the measurement of O_2 with no unburned fuel present, which is the definition of excess O_2 .

TDL analyzers do not directly measure excess O_2 . Unlike ZrO_2 sensors, TDLs are lowtemperature sensors that do not burn off residual fuels. TDLs measure total O_2 which is only equal to excess O_2 when combustion is complete and there is no unburned fuel in the flue gas. When unburned fuel is present, TDL will measure higher O_2 levels than the excess O_2 . Because of this, TDL O_2 measurements could cause combustion controls to reduce combustion air flow and result in unsafe fuel-rich conditions.

The American Petrochemical Industries (API) has recognized the difference between ZrO_2 excess O_2 measurement and TDL total O_2 measurement. API and others also call excess O_2 measurement net O_2 or stoichiometric O_2 . In API 556 second edition, the impact of unburned fuel was characterized as masking the O_2 concentration and a "malfunction low" of the actual oxygen concentration.⁽³⁾ While it is true that the excess O_2 will be lower than total O_2 when unburned fuel is present, the use of the word "malfunction" implies an error but in actuality the ZrO_2 measurement is not malfunctioning but is a direct measurement of excess O_2 , and by extension, of excess combustion air, which is a key combustion control parameter.

Total O₂ measurement

As stated in the previous section, the ZrO_2 technology measures excess O_2 , while TDLs measure total O_2 . To illustrate the difference between excess O_2 and total O_2 , consider the simple and common reaction of methane in air. Air is approximately 20.95% O_2 and 79.05% nitrogen (N_2), so for every mole of O_2 , air includes approximately 3.77 moles of N_2 . The stoichiometric reaction of methane is as follows:

$$CH_4 + 2O_2 + 2(3.77)N_2 \Rightarrow CO_2 + 2H_2O + 2(3.77)N_2$$
 [Eq. 3]

Because the reaction is stoichiometric, there is no oxygen in the product flue gas (right side of the equation).

Now consider the case with 10% excess air, where moles of O₂ and N₂ are increased 10%.

$$CH_4 + 2.2 O_2 + 2.2(3.77) N_2 => CO_2 + 2 H_2O + 2.2(3.77) N_2 + 0.2 O_2$$
 [Eq. 4]

In this case we have 0.2 moles of O₂ in 11.5 moles of total product flue gas, or 1.7% total O₂. The formula for total O₂ is as follows:

Total O_2 % = moles of O_2 /total moles of flue gas x 100% [Eq. 5]

Because combustion is complete and there is no unburned fuel in the product flue gas, the flue gas total O_2 is equivalent to excess O_2 .

Now consider the case where combustion is incomplete and 5% of the methane is unburned.

$$CH_4 + 2.2 O_2 + 2.2(3.77) N_2 => 0.95 CO_2 + 1.9 H_2O + 2.2(3.77) N_2 + 0.05 CH_4 + 0.3 O_2$$
 [Eq. 6]

In this case we have 0.3 moles of O_2 in 11.5 moles of total product flue gas, or 2.6% total O_2 . The excess air supplied (left side of equation 6) has not changed so excess O_2 is still 1.7%, while total O_2 in the flue gas has risen to 2.6% (right side of equation 6). A TDL analyzer would measure 2.6% O_2 , while a well-designed high-temperature ZrO_2 sensor would measure 1.7% O_2 , equivalent to the excess O_2 .

In the previous example, we assumed the unburned methane remained completely unoxidized. There are many reaction pathways and intermediate species for methane. One possibility is to partially oxidize to CO and H_2 . If partially oxidized to CO and H_2 (equation 7), the total O_2 would be 2.4%. Incidentally CO levels would be 0.43% (4,300 ppm).

$$CH_4 + 2.2 O_2 + 2.2(3.77) N_2 \Rightarrow 0.95 CO_2 + 1.9 H_2O + 2.2(3.77) N_2 + 0.05 CO + 0.1 H_2 + 0.275 O_2$$
 [Eq. 7]

On the other hand, if the methane is further oxidized to CO and H_2O (see equation 8), the total O_2 would be 2.0% with CO levels remaining about 4,300 ppm.

$$CH_4 + 2.2 O_2 + 2.2(3.77) N_2 = 0.95 CO_2 + 1.9 H_2O + 2.2(3.77) N_2 + 0.05 CO + 0.1 H_2O + 0.225 O_2$$
 [Eq. 8]

Because it is difficult to measure all the unburned fuel species present in a fuel-rich gas, it would be difficult to calculate excess O_2 from the total O_2 measurement. For partial oxidation of methane resulting in around 4,300 ppm CO, total O_2 could be 2% to 2.4%, which is 0.3% to 0.7% above the 1.7% excess O_2 level. The key is how much oxygen is consumed and how this affects the accuracy of excess O_2 measurements. In very fuel-rich pockets of flue gas, studies suggest methane remains in high concentrations. ⁽⁵⁾⁽⁶⁾⁽⁷⁾

The challenge with using TDL O_2 measurements for boiler control is that if unburned fuel levels increase, total O_2 will increase, even though excess air and excess O_2 levels are constant (Figure 2).

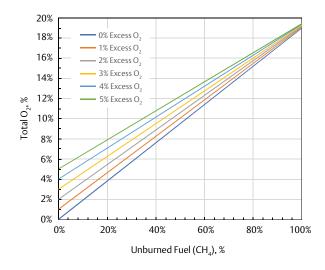


Figure 2. Flue gas total O₂ levels as a function of flue gas unburned fuel at various constant stoichiometric excess O₂ levels. Excess O₂ does not vary with unburned fuel. Total O₂ changes significantly with fuel combustion. When no combustion occurs, such as in a failed burner startup, total O₂ may decrease from 20.9% to about 19% due to fuel gas diluting the combustion air.

Most boilers and furnaces with oxygen trim controls are set to maintain a constant combustion excess O_2 level. If incomplete combustion occurs, TDL O_2 levels will rise and could cause controls or operators to reduce combustion air supply during these critical, poor combustion conditions. This will likely worsen combustion performance, further increasing unburned fuel and total O_2 levels. This could result in potentially unsafe, fuel-rich combustion condition. The degree to which the combustion will go fuel-rich may depend on the control's air and fuel cross limit strategy. One option is to tighten the limits on the combustion air-fuel relationship to prevent O_2 trim control from entering an unsafe zone. It will also be important to ensure the combustion air flow measurements are accurate and reliable.

In cases of incomplete combustion, as unburned fuel increases, TDL will measure higher than the stoichiometric excess O_2 level (Figure 3).

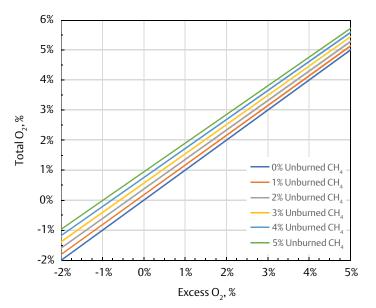
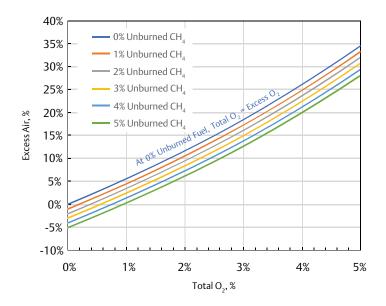
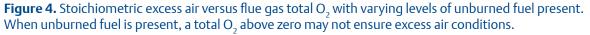


Figure 3. The relationship between flue gas total O₂ and excess O₂ when unburned fuel is present. By the definition of excess O₂, total O₂ equals excess O₂ when reactions are complete (zero unburned fuel).

The impact of using total O_2 measurement to indicate excess combustion air is shown in <u>Figure 4</u>. In situations with the equivalent of 5% unburned fuel, the total O_2 can overestimate excess air by over 5% absolute.





TDL O₂ measurements can drive the boiler controls to sub-stoichiometric combustion conditions as unburned fuel increases. To address the risk when using TDL O₂ measurements, a suitable combustible could be measured to ensure complete combustion. Carbon monoxide measurements would be acceptable for carbon-based fuels but not for 100% hydrogen fuels as is the case in some process heaters ⁽⁸⁾ and a future hydrogen energy economy. Alternatively, combustible measurements made by an instrument such as the Rosemount OCX8800 analyzer, which detects both CO and H₂, are an acceptable option for both hydrogen and fossil fuel-fired facilities.

While O_2 analyzers are not essential to operation in many combustion applications, they are recommended for use as operating guides⁽¹⁾ and more frequently are being integrated into boiler safety functions. However, it is important to use them properly and recognize the differences between ZrO_2 's excess O_2 measurement and TDL's total O_2 measurement.

Likelihood of unsafe events

It is widely known that unburned fuel and flue gas O₂ can coexist when fuel-air mixing is poor. This often occurs when burners are damaged or improperly installed or when fuel and air distribution and tuning is inadequate. NFPA states that "flue gas oxygen and flue gas combustibles can coexist and actually present a more difficult situation than a purely air deficient circumstance".⁽¹⁾

Zirconia O₂ analyzers have been in use for over half a century in hundreds of thousands of applications, but in contrast, TDL has fewer applications and shorter operating

history. In the early 2000s TDL was commercialized for applications in coal-fired utility boilers but only for diagnostics. Zirconia O₂ analyzers continued to be used for the coal boiler excess O₂ trim. More recently TDL technologies are being used for excess O₂ trim control in process heater applications. The industry has far less operating experience with TDL O₂ trim control, but to date, the author is not aware of any cases where unburned fuel led to combustion control or safety issues. However, as TDL becomes more common and the operating history increases, the potential for these events may increase. In addition, TDL is often installed at or near the furnace exit, which means fuel-air mixing is critically important to avoiding unburned fuel and TDL total O₂-related unsafe combustion control conditions.

Mitigating risks of TDL O₂ measurement

When using TDL O₂ measurements, boiler controls should have rigorous combustion air flow cross-limits and may need to be upgraded to something like a CO-constrained excess O₂ trim controller. However, CO-constrained trim controls typically allow fast O₂ response to maintain excess O₂ set point but employ a slower CO control loop to bias the excess O₂ set point. In contrast, with total O₂ measurement, the O₂ trim speed would be limited by the speed of the CO control loop. The logic is illustrated in Figure 5.

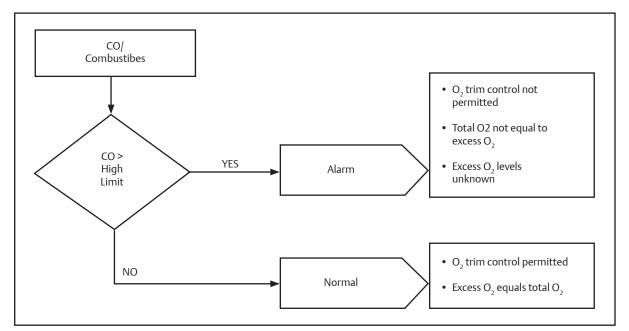


Figure 5. Permissive logic for combustion excess air control using total O₂ and CO/combustibles measurements.

Excess air flow regulation would require total O_2 and the CO/combustibles measurements. The control performance therefore would be limited by the speed, reliability and precision of both these measurements. When unburned fuel increases, CO, H₂ or other combustibles will increase and total O_2 will increase. However, the controls should not be permitted to reduce the total O_2 . With high combustibles and total O_2 measurement, the air-fuel ratio, or excess O_2 , is unknown so it may be safer to shutdown than to attempt to navigate the furnace back to a good combustion condition.

Zirconia O, measurement benefits

Using TDL O₂ for combustion control requires a CO or combustibles measurement and upgrades to the controls. ZrO_2 can directly measure excess O₂, which is directly related to excess combustion air. Most boiler controls are based on excess O₂ and therefore should use ZrO_2O_2 sensors. To convert to TDL O₂ analyzers requires adding a CO or combustibles measurement, modifying the controls and educating operators.

A unique advantage of the Rosemount 6888 In-Situ Oxygen Transmitter is the ability to indicate O_2 demand in fuel-rich conditions. Because ZrO_2 sensors measure the potential difference between flue gas O_2 and a reference gas O_2 (typically air at 20.9% O_2), the sensor will generate greater voltage signals as the O_2 demand increases in fuel-rich gases. Think of the sensor as a sink for O_2 : as the O_2 demand increases on the flue gas side, more O_2 ions transport across the ZrO_2 cell, driving higher voltages. The 6888 Xi Digital Transmitter correlates the cell voltage with O_2 demand up to approximately 2% or about 8% air deficiency (0.92 stoichiometry). Figure 6 illustrates O_2 deficiency measurements in fuel-rich conditions.

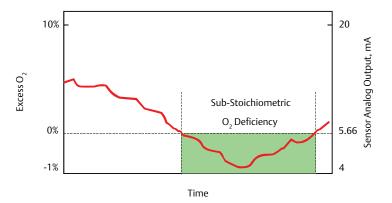


Figure 6. Rosemount[™] 6888 Xi indicates oxygen deficiency during substoichiometric operating excursions.

This feature allows operators to safely navigate out of fuel-rich excursions before having to shut down. Because the reading does not flatline at zero, operators have more confidence in zero readings. Boiler shutdown trips can also be set to occur at safe O_2 levels below zero. Consider that a 2% O_2 demand correlates to approximately 40,000 ppm of CO, which is about 40% of the CO lower explosive limit (LEL). If a boiler shutdown is desired at 25% LEL, roughly 25,000 ppm CO, then the boiler could trip at approximately 1.25% O_2 deficiency.

Summary

In summary, traditional boiler controls are built to regulate combustion air and ensure adequate excess air operation. ZrO_2 sensors measure excess O_2 which is directly related to excess air. Technologies like TDL measure total O_2 , which do not equal of excess air if unburned fuel is present. Total O_2 is only equal to excess O_2 when combustion is complete, and no unburned fuel exists. While a combustion system is never intended to operate with unburned fuel, the risk exists and may be more common than realized. Operators often rely on the flue gas O_2 measurement to indicate they have excess air conditions, but with TDL, this may not be true. If combustion is poor, operators may make incorrect adjustments and drive the combustion to unsafe fuel-rich conditions. To mitigate the risk when using TDL O_2 measurements, a combustibles measurement is needed and operators and/or excess air controls systems need to use the combustibles measurement in their control philosophy.

References

- (1) NFPA 85 Boiler and Combustion Systems Hazards Code, National Fire Protection Association, 2019.
- (2) Richard M. Felder and Ronald W. Rousseau, *Elementary Principles of Chemical Processes*, John Wiley & Sons, NY 2000.
- (3) API RP 556 Instrumentation, Control, and Protective Systems for Gas Fired Heaters, American Petroleum Institute, 2nd Edition, April 2011
- (4) Combustion Source Inspection, Student Reference Manual Office or Air Quality Planning and Standards, EPA-340/1-92-004a, Nov 1991.
- (5) Alfe', M., Barbella, R, Mallardo, M., Tregrossi, A., Ciajolo, A. *The formation of pollutants in fuel-rich methane combustion*, Istituto di Ricerche sulla Combustione, Dipartimento di Ingegneria Chimica Università "Federico II", Naples Italy.
- (6) An experimental and modeling study on the reactivity of extremely fuel-rich methane/dimethylether mixtures, Combustion and Flame, 212 (2020) 107-122.
- (7) K.J. Hughes, T. Turányi, A.R. Clague, M.J. Pilling, *Development and testing of a comprehensive chemical mechanism for the oxidation of methane*, Int. J. Chem. Kinet. 33 (2001) 513–538.
- (8) Cliff Lowea, Nick Brancaccioa, Dan Battenb, Chris Leungb, Dick Waibelc, Technology Assessment of Hydrogen Firing of Process Heaters, Energy Procedia 4 (2011) 1058–1065

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