SAFE COMBUSTION

Stuart Rye, NEO Monitors AS, Norway, considers whether methane can safely exist in a hot-fired process heater during normal operation.

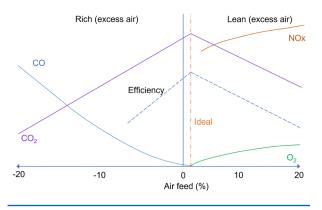
Improve published articles discuss the complexities of combustion measurement and process optimisation of gas-fired process heaters, with a focus on the merits of combustion efficiency and the correlated reduction in operating costs and emissions. Whilst these are obviously crucial factors, there is an overlooked safety consideration, due to the often unexpected presence of unburned methane (CH_4) . This article will highlight the importance of a multi-component measurement approach to mitigate this hazard and provide true insight into the safe operation and control of any gas-fired process heater.

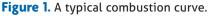
Industrial facilities across the globe, including petrochemical plants, fine chemical plants, and refineries, operate large numbers of process fired heaters, primarily to heat precursor materials, as part of a chemical reaction or for steam generation for use across the plant. Due to the vast quantities of fuel consumed and, increasingly, the cost involved in operating such highly energy-intensive processes, there has long been a necessity to optimise the combustion process to ensure optimal fuel consumption, while reducing plant emissions.

Figure 1 is an illustrated overview of combustion efficiency, demonstrating the ideal control point (crossover point) for

maximum efficiency, thus saving fuel and reducing carbon dioxide (CO_2) emissions – which is of increasing importance due to ongoing decarbonisation programmes – while also maintaining the lowest possible levels of carbon monoxide (CO), nitrogen oxide (NO_x) and sulfur oxide (SO_x) emissions. These requirements have quite rightly led to a focus on the measurement of oxygen and the measurement of CO, or CO equivalent (COe), for optimal trim control.

In order to ensure complete combustion, fired heaters are normally operated with a higher volume of combustion air than the stoichiometric combustion curve would assume. Without this 'excess air', in practice, not all of the fuel would be burnt, as not all of the oxygen would be available for combustion, leading to a fuel-rich condition, incomplete combustion, elevated levels of CO emissions, and increased fuel costs.





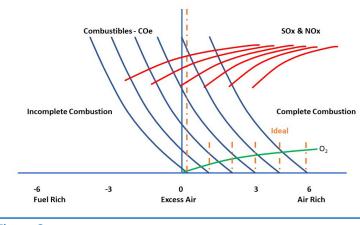




Table 1. Combustion measurement technique comparison	
TDLAS	Zirconia oxide and COe catalytic sensors
Across the burner average reading	Point measurement only
Fast response in seconds	Response time typically 30 – 45 sec.
True oxygen, CO and CH ₄ measurements	Thermal response for CO and CH_4
High temperature operation	Typically 900°C maximum
Safe non-contact optical measurement	Potential for flash back from unburnt fuel
Low maintenance	High maintenance – typically monthly

Regardless of the specific design of the heater, the key to optimal performance is to maintain the balance between the excess air and the detection and control of the emission of combustibles, principally CO or COe, and to operate within the design envelope of the heater, thus preventing instability.

The challenge, however, is that the ideal control point (crossover point) is not fixed, as seen in Figure 2. This point changes, depending on the following factors:

- Load variation.
- Fuel composition, particularly if waste gas fuel feed is used (which has a different heating value).
- Fuel density.
- Atmospheric humidity changes.
- Heater load variations.
- Burner fouling.
- Age and condition of the system.

It is clear that a multi-component measurement approach is needed in order to optimise the process. There are numerous combustion gas analysers that are available for the measurement of oxygen and optional COe to monitor and provide the trim control signal and maintain the desired air-to-fuel ratio. These are typically based on contact-based zirconia oxide and pellistor, or 'thick film' catalytic technologies, for oxygen and COe measurement, respectively.

Although these technologies are widely used, a significant drawback is that they cannot be installed in the radiant zone of the heater due to the high temperatures, and are therefore typically installed in the convection zone where measurement errors can occur

due to air leakage. There is also a significant safety concern to consider, as zirconia cells operate at high temperatures (circa 700°C), so there is potential for flashback to occur, if unburnt fuel comes into contact with the measurement cell.

In recent years, these drawbacks have led to the increasing use of in-situ optical analysers based on tunable diode laser absorption spectroscopy (TDLAS) for combustion measurement, displacing traditional techniques (see Table 1). The drivers for this transition are the demonstrable benefits of using TDLAS analysers for combustion analysis, including measurement across the entire cross section of the radiant zone, ensuring analysis of the total heater profile is performed, the non-contact and

> safe optical measurement technique, and the flexibility of offering a combined multi-component analysis.

An evolution in TDLAS signal processing and hardware design

Large process heaters can have diameters of 25 – 30 m or even greater, equating to a long



optical path length (OPL) for the analysers, i.e., the distance from the laser transmitter to the receiver. Over such long OPLs, substantial signal attenuation occurs. For example, CH_4 is a very strong infrared absorbing gas, and over long path lengths it can affect and distort the adjacent CO absorption peak – and even more so if the fuel composition varies, leading to interference, due to baseline distortion within the scanning range of the laser.

Additionally, there is a requirement for a wide dynamic range for CO measurement, typically from ppm levels during normal operation up to percent levels for safety. Despite all of the obvious advantages of TDLAS analysers that have been highlighted in this article, these specific requirements create a challenge that has to be overcome in order to provide the required performance.

These requirements have led to the development of a new evolution in TDLAS signal processing, combined with innovations in hardware design, to offer a robust, comprehensive and high-performance multi-component combustion analysis.

The first task in doing so was to overcome the problem of baseline distortion, due to strong absorption nearby from the varying background gas compositions within the heater. TDLAS analysers typically work by scanning the laser across a range of wavelengths where the absorption peak of the measured gas resides. It is important that there is no absorption by other gases that are present in the process within this scan range, as a stable baseline is necessary to provide a reference

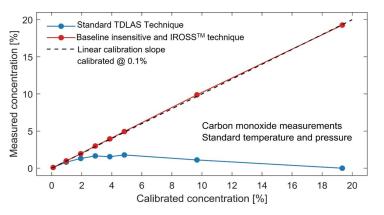


Figure 3. Comparison of dynamic ranges.



Figure 4. T-Flange dual analyser mounting accessory.

(a close wavelength where there is no absorption). If this baseline is not established, this will result in degraded measurement performance.

The solution was the development of a true innovation in signal processing, by combining multi-variate chemometrics and traditional TDLAS methodologies into a robust signal processing algorithm. This solution allowed for the real-time analysis of the gases of interest within complex spectra, even when there are adjacent interfering/overlapping absorption peaks, eliminating interfering species from the measurement in order to derive an accurate and reliable measurement.

This new, advanced in-situ real-time overlapping spectral separation (IROSSTM) signal processing technique is a standard feature of NEO Monitors' LaserGasTM III Ultra analyser, and is utilised for combined CO/CH₄ measurement.

This baseline-free measurement technique also allows for a greatly enhanced dynamic range compared to normal TDLAS techniques. Figure 3 illustrates this further. In traditional TDLAS methods, the dynamic range is limited (blue curve). Using the LaserGas III Ultra algorithm, a near linear response is maintained over a large dynamic range and OPL, which is essential for this application.

One further consideration when planning to utilise TDLAS analysers on a fired heater is the lack of availability of additional flange pairs to mount multiple

> analysers. Usually multiple opposing flange pairs is simply not an option in most cases, as this could potentially impact the integrity of the heater structure. This limitation has been overcome with the development of the T-Flange accessory, which enabled both the LaserGas III oxygen and LaserGas III Ultra CO/CH₄ analysers to be mounted across a single flange pair, as shown in Figure 4, reducing installation costs and offering a robust solution for any process heater, without modification.

Safety considerations

Start-up and shutdown

It is well-documented that some of the most critical periods are during start-up and shutdown of a process heater. One of the greatest concerns at this juncture is the potential for a flame-out situation, where unburned fuel could cause severe damage to the heater if it were to ignite higher up in the structure, potentially damaging the internal tubes or their supports, and even leading to an explosion.

For safe operation of the heater, stability of the combustion is of paramount importance during this critical phase. If the air-to-fuel ratio exceeds the operating tolerances of the burner, instability will occur, which can lead to an unstable flame or a flame-out situation. If this occurs, it is imperative that it is acknowledged, and that action is taken to prevent a potential explosion risk. These scenarios have been increasingly recognised and better understood, and procedures are typically put in place to mitigate such occurrences.

Having a fast-response, in-situ CH_4 analysis tool, capable of detecting such an event, offers a considerable level of increased safety and should be considered as essential in any comprehensive burner management system (BMS). This is particularly important for CH_4 measurements, as the analyser can detect any unburnt fuel pockets across the entirety of the burner, which could otherwise go undetected during start-up and shutdown.

CH₄ present during normal operation

Such a multi-component measurement TDLAS system was recently installed at a customer's site in the US on a three-cell natural gas-fired process heater. Due to the flexibility of the TDLAS technology, a secondary and specific CH_4 measurement was available from the CO analyser. Table 2 details the basic configuration of the two analysers that were installed: a LaserGas III analyser for oxygen and a LaserGas III Ultra analyser for combined CO/CH₄ measurement.

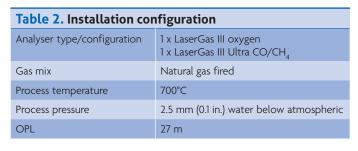
The Ultra version utilised the IROSS advanced signal processing algorithms to remove the background interfering gas influences, and provided the required large dynamic ranges across the very long optical path – ideal for this large process heater installation and beyond what would be typically viable if using traditional TDLAS analysers.

The CH_4 measurement was to be used principally to detect CH_4 during start-up and shutdown of the heater, as previously discussed. However, the operators soon discovered that the analyser was detecting increasing CH_4 levels during periods of normal operation (see Figure 5). From this graph, it can be observed that there is an instant CO breakthrough as the oxygen levels are reduced, as would be expected, followed by an increase in both CO and CH_4 concentration, as increased levels of fuel were introduced, whilst simultaneously maintaining a very low oxygen level.

Under these conditions, combustion was still taking place, but not to completion. However, no flame-out situation was occurring. It is clear from this specific operating profile that under such conditions, CH_4 can indeed be present in the heater, even during what is considered a normal operation cycle. As the autoignition temperature of CH_4 is around 600°C, it is usually assumed that, under normal operating temperatures, there could never be a presence of unburnt fuel, as it would all be combusted. However, this autoignition temperature is defined with oxygen levels close to 50%. Under the reduced oxygen levels present within the process heater, the autoignition temperature increases.

This phenomenon had been unknown to the operator before the TDLAS analysers were installed, which now allow for much greater vigilance of the CH_4 levels during operation, demonstrating why a robust and reliable CH_4

measurement technique should be considered vital for any gas-fired process heater. This realisation has allowed the operator to better understand the operational performance of the heater, and to proactively mitigate any potential explosion hazard.



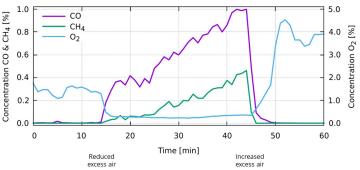


Figure 5. Increasing CH₄ levels detected during normal operation

Conclusion

The real-world measurements in Figure 5, conducted on a large gas-fired process heater, clearly demonstrate that unburnt CH_4 can indeed be present during the normal operation cycle of the heater. The addition of a reliable and interference-free LaserGas III Ultra CH_4 measurement tool, combined into a multi-component measurement oxygen and CO/CH_4 TDLAS measurement solution, provides a true insight into efficient heater performance during all phases of operation, as well as detailed insight into the dynamic and fast-changing conditions within the heater, ensuring safe operation and invaluable protection of personnel and plant assets.

Bibliography

 WESTBERG, J., AVETISOV, V., and GEISER, P., 'Contactless combustion analysis', *Hydrocarbon Engineering*, (October 2021), pp. 33 - 36.

Note

NEO Monitors would like to mention that this article was written in memory of a dear friend and colleague, Larry Sieker, who sadly and unexpectedly passed away in November 2022. Larry was a much respected expert within the gas measurement community and particularly renowned for his expertise in combustion analysis. It was a privilege to work with him, and his knowledge, enthusiasm and friendship are missed.

