INGOLD
Leading Process Analytics

White Paper

Probe-type TDL Oxygen Analyzers
in Critical Applications

Industrial processes involve many steps that need to be measured analytically to ensure safety, efficiency, and reliability of the process. Among the various analytical measurements (pH, CO_2, turbidity, etc.), oxygen measurement and control is essential for process optimization in many industries. Also, accurate and continuous O_2 determination plays a pivotal role in achieving safety and process reliability in a wide range of manufacturing processes. Oxygen analyzers based on Tunable Diode Laser Spectroscopy provide highly reliable performance in many applications where other technologies are faced with application challenges.

Difficult oxygen critical applications in the chemical and petrochemical industries
Harsh process conditions and consequent maintenance requirements present challenges in procuring accurate and reliable measurements. A host of difficult applications are observed across chemical, petrochemical, and other industries.

Oxygen is a part of many chemical reactions and may influence the process significantly. It is important that either O_2 concentra-

METTLER TOLEDO

tion be controlled or the optimal concentration be maintained to ensure process control and safety. The presence of background gases interferes with the accuracy of O_2 measurement and the overall maintenance of the process unit is made difficult.

Propionic acid is a significant preservative in the food industry and also an intermediate in the production of polymers. Its manufacture involves the reaction of propionaldehyd and oxygen in an oxidizer. Since the output contains a mixture of hydrocarbons along with propionic acid and oxygen, swift and accurate measurement of oxygen content is imperative. An optimal oxygen concentration to ensure efficient reaction is required, but must be kept below 11% to avoid explosion. The phenomenon generally referred to as "eating" of oxygen by propionic acid in the sampling line is noted, which causes a decrease in O_2 concentration.

Vinyl chloride monomer (VCM) is the precursor in the production of PVC. VCM production using the ethylene route involves various steps such as direct chlorination, oxy-chlorination (where oxygen is an important reactant), and ethylene dichloride (EDC) cracking. As all the components are not completely consumed, various byproducts are formed. In some cases "oxygen-slip" can be seen at the output of the oxychlorination reactor(s). The oxygen level has to be optimal for the reaction, but at the same time must be maintained below the explosion limit. In direct chlorination, elevation in oxygen concentration may result due to impurities in the chlorine. So from the safety application perspective, this has to be avoided and the oxygen concentration kept at near zero.

Safety monitoring

Flare systems: In refineries, chemical and petrochemical plants, flares are part of a safety system to quickly react in case of critical process instabilities such as abnormal pressure increases. Higher O_2 concentrations due to air leaks presents the risk of explosion in both the continuous and emergent type of flare systems. Therefore, safety monitoring depends upon accurate O_2 measurement. However, the presence of large amount of hydrocarbons in the background interferes with this, which is a pressing problem.

CO boiler: FCC is a refinery process that converts low value heavy oils into high value gasoline and lighter products. Due to coke covering the catalyst and the catalyst regeneration thereof, large quantities of CO are found in the flue gas leaving the regenerator. This is burnt to CO_2 to maintain CO at acceptable levels. Throughout these processes, combustion control has to be optimized by timely O_2 readings. The possible energy loss is a drawback.

Vapor recycling in tanker terminals: The gas produced during the vapor recycling process contains combustibles and oxygen. These, when combined, can prove highly explosive under certain conditions. To execute safety measures in an effective manner, precise measurement of O_2 is essential so that the system is alerted when the critical level is reached. Background interference in the form of hydrocarbons is a hurdle towards effective measurement.

Waste incinerator – combustion and emission control: In optimizing combustion in an incinerator, the amount of excess air is very significant. Too much air causes unnecessary cooling thereby reducing power generation. Maintaining the correct O_2 content helps to ensure efficient combustion. Whereas, oxygen shortage leads to increased CO emissions. Therefore, oxygen measurement in this case aids in optimizing process control.

Extractive oxygen analyzers - problems

Traditional extractive oxygen analyzers such as paramagnetic analyzers, produce measurements under various difficulties that include harsh environment conditions, background interference in the form of various gases, dust load, and moisture. Shortcomings can be attributed to the use of extractive oxygen analyzers, as mentioned below.

Erroneous measurements: In the case of propionic acid, mistakenly low values are measured due to "eating" of oxygen by propionic acid in the sampling line. Paramagnetic analyzers, in particular, produce errors even with the presence of a drop of condensate of propionic acid. This situation is further aggravated by the fact that propionic acid easily condensates.

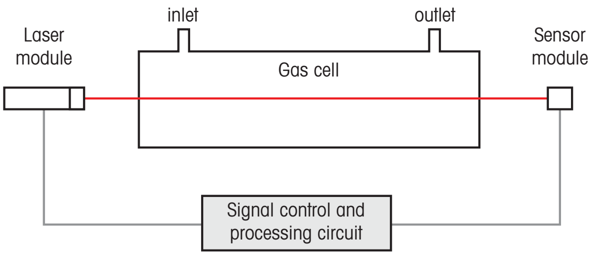
Suboptimal performance: The concerns of suboptimal efficiency and accuracy are raised in extractive analyzers. In the VCM production process, the comparatively slow response of the extractive technique is a clear disadvantage. In incinerators, suboptimal performance of extractive measurement systems in terms of interference from NOx emissions, presence of HCl, and excess air are observed via comparative studies.

Cross interference: O_2 measurement in flare gas systems using paramagnetic analyzers faces the disadvantage of interference of hydrocarbons that are present in large amounts. The various backgrounds of these hydrocarbons make the compensation still more difficult. Similar difficulties of hydrocarbon interference are experienced in vapor recycling processes. The presence of undesirable particles such as dust and moisture in the measurement cell grossly hinders the performance of extractive oxygen analyzers.

Maintenance and high costs: Extractive oxygen analyzers require error-prone sampling and conditioning equipment. Also, they have to face the toughest process conditions. Such systems require extensive maintenance and therefore incur high costs.

TDL analyzers

With all the disadvantages and concerns arising from the use of extractive oxygen analyzers, Tunable Diode Laser analyzers or TDLs have garnered attention and appreciation for their utility in industrial applications. TDL analyzers work on the principle of laser absorption spectroscopy. A focused and tunable laser beam is used to analyze absorption lines that are characteristic of the particular gas species to be measured. TDL oxygen analyzers measure oxygen in situ or directly from the gas stream without any sampling or conditioning.



Basic set up for laser spectroscopy

TDL analyzers for process applications have two basic design types, namely cross-stack and probe-type. In the cross-stack design, the laser source is placed on one side of the pipe or duct and the receiver on the other. The wider the pipe diameter, the more difficult it is to align the laser source and receiver. In the probe type TDL analyzer, the defining feature is the sensor probe that protrudes into the process gas stream. The laser diode and the detector are contained in a single unit, requiring a single flange connection.

Advantages of TDL analyzers

TDL analyzers, with their advanced and attractive traits, help overcome the drawbacks that are associated with the use of traditional extractive analyzers. Due to the benefits and performance attributable to them, TDL oxygen analyzers are increasingly being preferred.

TDL analyzers offer the following advantages over extractive analyzers.

High resolution and accuracy: TDL analyzers are able to achieve high specificity due to the high spectral resolution available. Their ability to scan a very narrow and precise range of the electromagnetic spectrum yields enhanced sensitivity. TDL analyzers deliver accurate measurements even when 80% of the original signal intensity has been lost.

Speed: TDL analyzers are based on laser spectroscopy, which provides a very fast response time.

Resistance against cross interference: Cross interference is not a concern in TDL O_2 measurement as the spectral lines analyzed can only be produced by oxygen, regardless of the background gas mix. Even in the presence of dust, TDLs produce highly reliable measurements.

Resistance against corrosion: Since TDL is a non-contacting method and also because of their robust design, they are able to withstand corrosion and also harsh process environments.

Calibration advantages: Using TDL O_2 measurement, the laser scans across a narrow absorption peak repeatedly and rapidly (one hundred times per second) by ramping the current applied to the laser diode. The continuous measurement of baseline and peak allows ongoing recalculation of the background or zero. So effectively, there is no need for recalibration as is the case with extractive techniques.

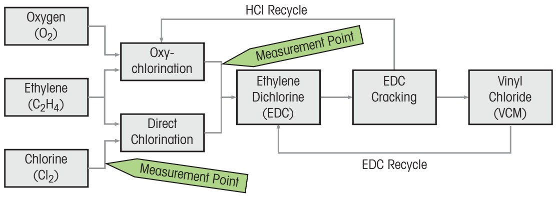
Maintenance: As there is no requirement for sample extraction and conditioning, maintenance is very low compared to extractive techniques. Also, the setup is tolerant of contamination even in the event of a major upset.

Cost: Since maintenance is minimal and sampling and conditioning equipment is not needed, TDL analyzers are much more cost effective than extractive analyzers.

Right measurement point

In order to bring about process optimization and greater yield, the correct locations to measure O_2 concentration must be chosen in the process setup. Listed below are such locations or measurement points in various process steps.

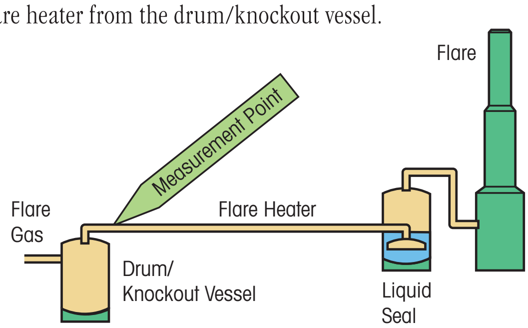
EDC production: In oxy-chlorination, O_2 should be determined at the exit or between the reactors to detect possible O_2 slip. Measurement at the direct chlorination stage, in the feed pipe, ensures that impurities in the chlorine do not contain elevated O_2 levels.



Schematic illustration of the EDC/VCM production process

VCM production process: O_2 must be monitored in the waste gas before the incinerator to check whether the critical level has been reached or not.

Flare gas system: In this setup, control of O_2 is required in the gas stream going to the flare, the measurement point being the flare heater from the drum/knockout vessel.



Measurement point in flare gas system

Incinerators: O_2 measurement points include the hot combustion zone, and at filter optimization.

TDL selection considerations

Along with exact measurement point selection, TDL specifications must be taken into account when choosing a solution. As well as application specific considerations, standard factors include temperature range, path length, and pressure and dust load tolerance.

The GPro 500 series from METTLER TOLEDO

The GPro 500 series TDL oxygen sensor from METTLER TOLEDO combines the benefits of "fit-and-forget" in-line sensors with the performance of a powerful gas analyzer. A number of features are mentioned below.

Innovative probe design: The sensor probe is fitted with a corner cube that directs the laser beam to the detector in the sensor head. This folded optical path design increases measurement accuracy.

In situ measurement: provides more representative measurements.

Single flange connection: makes installation simple.

SpectraID technology: enhances the reliability of the system even after prolonged exposure to zero oxygen containing environments by scanning not one but three adjacent absorption lines that constitute a unique oxygen "signature".

No sampling or conditioning required: Annual verification and periodic optics cleaning are the only maintenance. In addition, the low nitrogen purging consumption reduces operating costs.

Predictive diagnostics: METTLER TOLEDO's Intelligent Sensor Management predictive diagnostics, incorporated in the GPro 500 series, continuously monitor the optical path quality and determine when cleaning will be required.

Conclusion

Tunable Diode Lasers with their various advantages on the technical and lifetime cost fronts are replacing extractive measurement systems. With their superior accuracy and durability, TDLs will hold sway in the field process analytics measurement market in the near future, and additional advances in these regards will only further their acceptability and prevalence.

For more information, visit:
www.mt.com/o2-gas

GPro 500 TDL oxgen sensor

Mettler-Toledo AG
Process Analytics
Im Hackacker 15
CH-8902 Urdorf
Switzerland