Methane Gas Sensing Technologies in Combustion: Comprehensive Review

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Abstract: Major methane (CH_4) gas sensing technologies for the application in a combustion environment are reviewed with many theoretical and practical aspects, as well as basic installation and operation details. A comprehensive CH_4 gas sensing technologies review is supported with the latest development trends. Performance and application options for methane measurements in the process using calorimetric, mixed potential electrochemical CH_4 sensor, semiconductor detector and tunable diode (TD) laser and quantum cascade (QC) laser spectroscopy are discussed for the possible application in power generation, chemical production, heating, process control, safety, and quality. Special attention is given to the technology application limits and analyzer's system requirements.

Keywords: Combustion analysis, Flue gas, Methane gas sensing, Calorimetric catalytic CH_4 sensor, Mixed potential CH_4 sensor, Semiconductor CH_4 detector, TDLS, QCLS.

1. Introduction

In the regular combustion process, hydrocarbon fuel (C_xH_y) would react with oxygen (O_2) producing primarily carbon dioxide (CO_2) and water (H_2O) with traces of other gases, e.g., sulfur dioxide (SO_2), and nitrogen oxides (NO_x) coming from nitrogen and fuel impurities oxidation. The remaining oxygen in the flue gas is measured for reliable and safe combustion control and optimized combustion efficiency. Zirconia oxygen potentiometric technology was applied successfully in the combustion control of power generation boilers, hot stoves for steelmaking, heating and combustion exhaust gas control of coke ovens for steelmaking, lime and cement kilns combustion control, incinerator combustion control, combustion control of heating furnaces for the oil refinery and petrochemical industry, and many other applications [1-4]. Combustion control is mostly accomplished with O_2 measurement alone (Fig. 1) and an improved combustion efficiency and stability can be achieved with the concurrent measurement of carbon monoxide at ~100...200 ppm CO levels and ~1...6 % of oxygen depending on the fuel type (Figs. 1-2). Monitoring of CO in the combustion process offers a new unique opportunity for safe flame operation with CO serving as a marker indicating incomplete or fuel-rich malfunction [5].

Three comprehensive carbon monoxide gas sensing technologies implemented so far in combustion analyzers on the market – calorimetric catalytic, mixed potential electrochemical, and Tunable Diode Laser Spectroscopy (TDLS) or Quantum Cascade Laser Spectroscopy (QCLS) – were recently reviewed [6].

At combustion startup or in the event of a burner malfunction or flame blowout, the combustor can be filled with an explosive mixture faster than the response time of normal flame sensors installed in a combustor. An extra methane (CH_4) measurement in a combustion analyzer [7] would provide an extra safety feature for combustion control and diagnostics (see combustion flue gas diagram, Fig. 1). It will also increase combustion performance efficiency (Fig. 3).
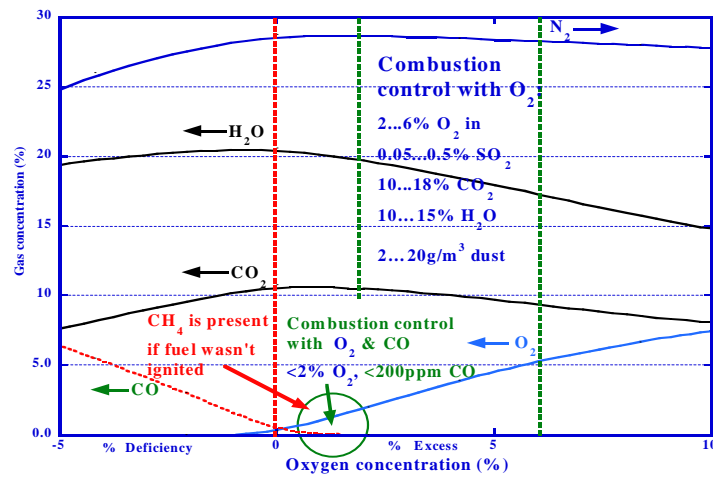

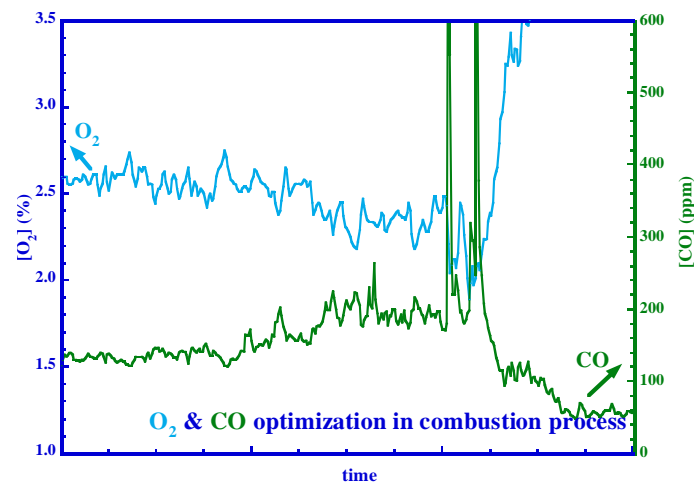**Fig. 1.** Combustion flue gas diagram with methane control needed for safety.

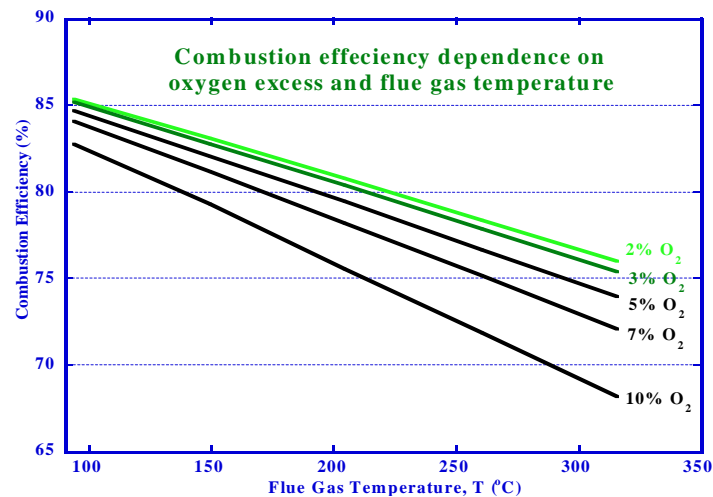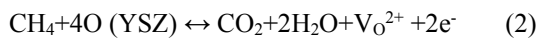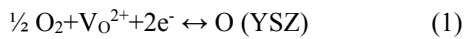**Fig. 2.** Oxygen and carbon monoxide optimization in combustion control at coal fired Power Plant.

Fig. 3. Combustion efficiency dependence on temperature and oxygen excess.

2. Mixed Potential Electrochemical CH₄ Sensor

Mixed-potential gas sensing technology with an oxygen ion conducting zirconia solid electrolyte and two different activity electrodes invented by Sandler [8] was proposed for the detection of combustible gases. The presence of CH_4 or any other combustible species will affect the electrochemical oxygen sensor signal with competing reactions of oxygen reduction (1) and CH_4 or other combustible species oxidation (2) establishing mixed potential highly dependent on the CH_4 concentration (3) (see diagram, Fig. 4):

$$\frac{1}{2} O_2 + V_O^{2+} + 2e^- \leftrightarrow O \; (YSZ) \qquad (1)$$

$$CH_4 + 4O \; (YSZ) \leftrightarrow CO_2 + 2H_2O + V_O^{2+} + 2e^- \qquad (2)$$

$$E_{mix} = E_{eq} - Const * \ln c \; (CH_4) \qquad (3)$$

Mixed potential developed by the CH_4 sensor would depend mostly on kinetic factors and would be a strong function of the process electrode electrochemical and catalytic activities and morphology. The sensor signal will be affected by changes in the gas/electrolyte/electrode triple phase boundary (TPB) area, limited methane or oxygen diffusion in the gas phase, electrodes and TPB, limited adsorption, and other combustion gas interference. The fact that the response is controlled by reaction kinetics places a limit on a maximum operating temperature for the device in order to achieve a usable signal-to-noise in the application. Various metals and metal oxide materials were investigated for sensitive electrodes in the mixed potential sensors in the past [9] and a special signal conditioning pulsed discharge technique was proposed recently to increase sensor sensitivity and selectivity [10-11].

The mixed potential CH_4 sensor is very sensitive and quite reproducible (Fig. 5) with a detection limit of <25 ppm CH_4. Unfortunately, mixed potential sensors reported to date have not been especially selective with strong interference to other hydrocarbons (CxHy), nitrogen oxides (NOx), carbon dioxide (CO_2) and carbon monoxide (CO) (Figs. 6-7) being shown.

Fig. 4. Mixed potential CH₄ sensor electrochemical reactions diagram.
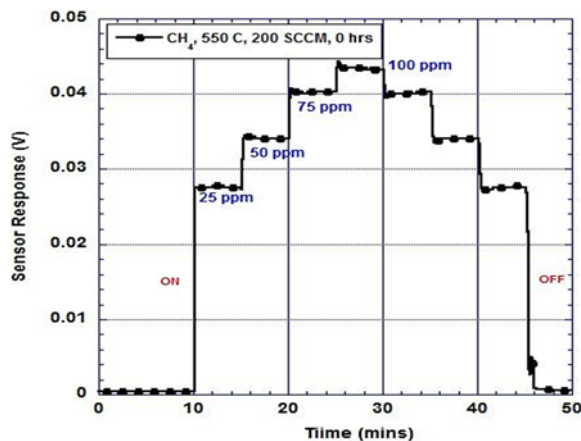

Fig. 5. Sensitivity of mixed potential CH₄ sensor with tin-doped indium oxide sensitive electrode (Adapted from [12], Copyright 2016, with permission from Elsevier).

Fig. 6. Selectivity of mixed potential CH₄ sensor with tin-doped indium oxide sensitive electrode (Adapted from [12], Copyright 2016, with permission from Elsevier).
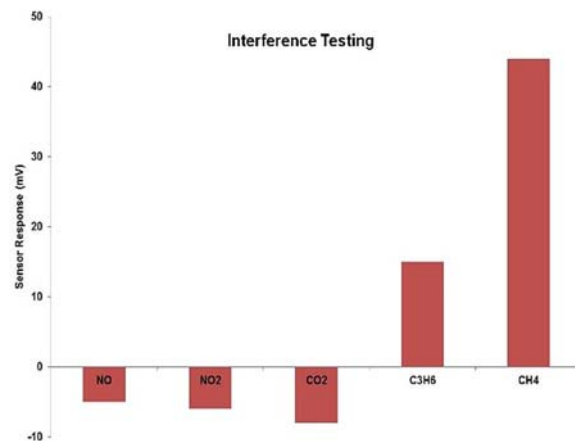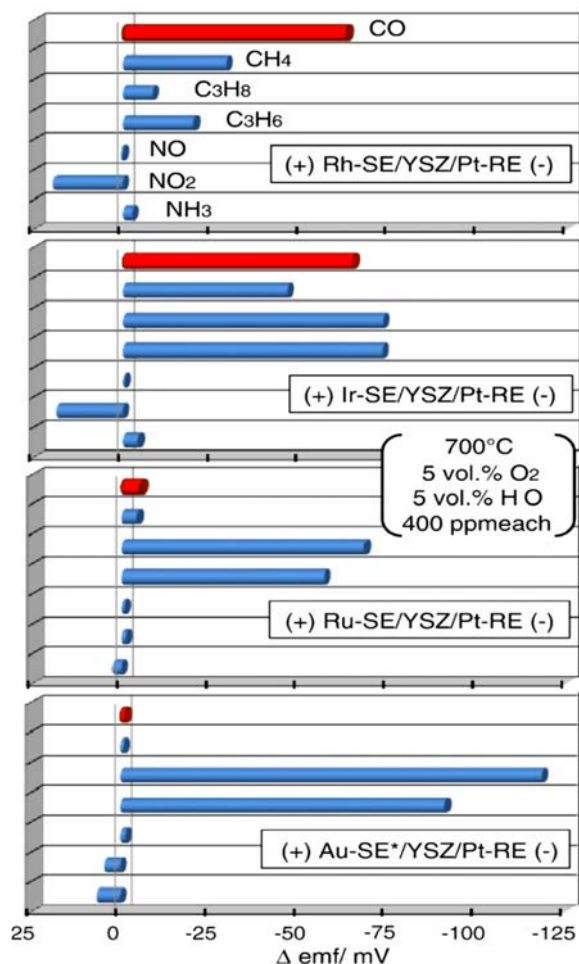
Fig. 7. Selectivity of mixed potential sensors with Rh, Ir, Ru and Au sensitive electrodes (Adapted from [13], Copyright 2011, with permission from Elsevier).

Sensitivity of a mixed potential sensor can be highly improved (Fig. 8) using a special signal conditioning pulsed discharge technique [10-11]. However, despite considerable work over the years by many groups [9] to achieve a high degree of selectivity by manipulation of such factors as working electrode composition, and application of current bias to alter electrode reaction rates, achieving absolute selectivity is still a limitation of the technology.

Cross-sensitivity effects – particularly to hydrocarbons – at present prohibit application in a real combustion process with a wide temperature and pressure variation and highly challenging flue gas chemical composition. Recent efforts to improve mixed potential technology have focused on improving electrochemical interface morphology in order to permit fabrication of stable and reproducible devices.

It has been recently shown [14-15] that once drift and aging effects are eliminated, when arrays (consisting of 3-4 electrode elements) of stable mixed potential sensors are used together with the appropriate response model [14-16], the intrinsic cross-interference behavior becomes a means to isolate the target species in a more complex background gas

mixture to reasonable accuracy (e.g. 1-2 % error). Although this has not yet been demonstrated for CH_4 sensing, recent advancements in automotive mixed potential design and use may prove beneficial to stationary applications.
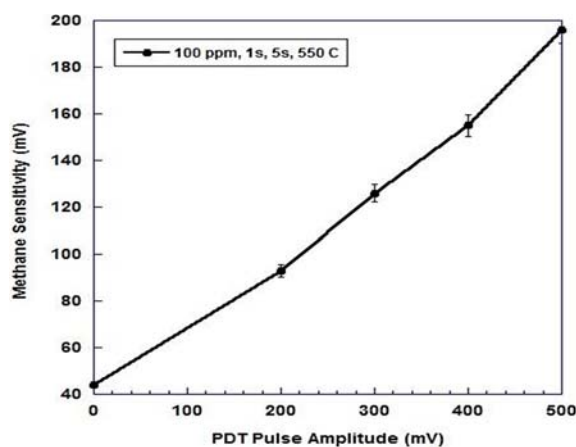

Fig. 8. Mixed potential CH_4 sensor sensitivity using conditioning pulsed discharge technique (Adapted from [12], Copyright 2016, with permission from Elsevier).

3. Calorimetric Catalytic CH_4 Sensor

For extractive combustion analyzers, advanced calorimetric catalytic CO sensors were developed by several analytical corporations utilizing combustible reaction heat on the special selective catalyst film over the resistance temperature detector (RTD) implemented in the sensor package for temperature measurements [17-18].

Calorimetric catalytic CO sensor packaged with protective and thermo-conductive layers over RTD film (Fig. 9) is highly reproducible (Fig. 10) in the flow and temperature controlled extractive measurements environment interference to all other combustion species, including methane (Table 1). The catalyst film was merged with RTD using highly thermally conductive packaging oxide materials to utilize more efficiently the heat transfer of the combustion reaction on catalyst film to RTD.

Table 1. Calorimetric catalytic CO sensor typical cross-sensitivity [6].

Gas of interest	CO sensor cross-sensitivity
H_2	2 : 1
O_2	1 : >10,000
SO_2	1 : >1000
NO_x	1 : >1000
CH_4	1 : >20,000
H_2O	1 : >1000

Conventional catalysts for methane combustion are based on noble metals, i.e., palladium (Pd) or platinum (Pt) deposited on oxides such as cerium oxide (CeO_2)

or metals. Methane's complete combustion reaction is highly exothermic (-890 kJ/mol):

$$CH_4 + O_2 \rightarrow CO_2 + H_2O, \qquad (4)$$
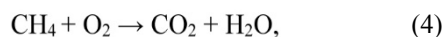
releasing ~25 times more heat compared to partial methane oxidation (conversion) to syngas:

$$CH_4 + O_2 \rightarrow CO + H_2 \qquad (5)$$

So, oxygen sufficiency or even excess would be critical for the calorimetric catalytic CH_4 sensor's reliable performance. Optimized catalytic film would selectively oxidize methane in the presence of other flue gas species. Like the calorimetric catalytic CO sensor implemented on combustion market, the CH_4 sensor would measure temperature and the associated sensor's RTD resistance change in the flue gas with oxygen excess, depending on the methane concentration (Fig. 11).
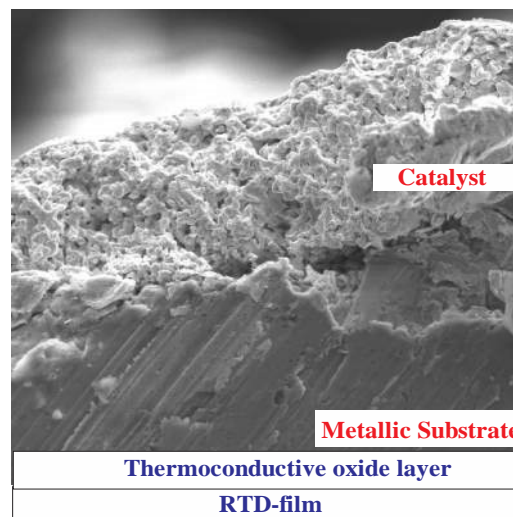

Fig. 9. Scanning electron micrograph of calorimetric sensor catalyst film/metallic substrate interface [6].
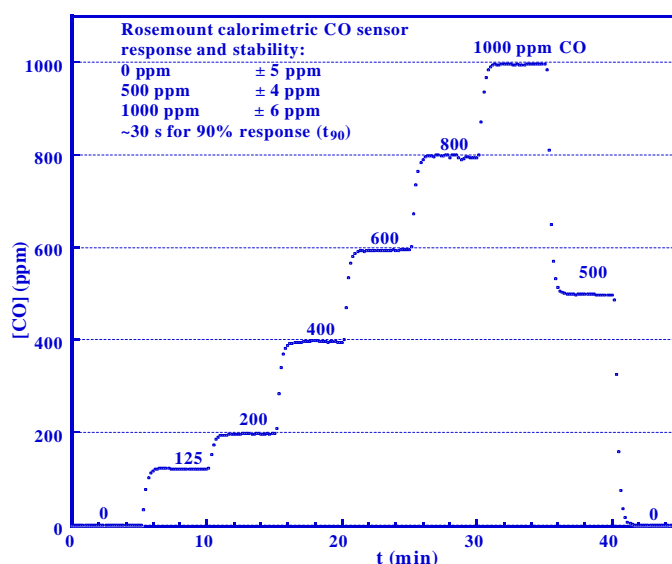

Fig. 10. Calorimetric catalytic CO sensor response and stability [6].
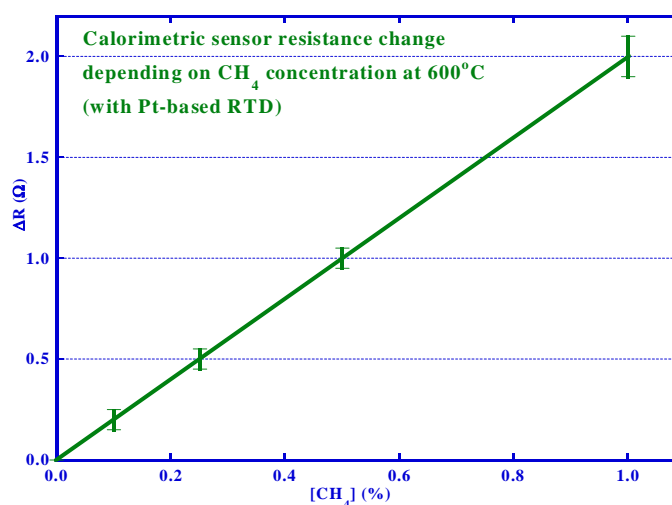

Fig. 11. Calorimetric sensor RTD resistance change dependence on methane concentration.

Catalyst microstructure and sensor temperature optimization would permit quite a reproducible response (Figs. 12-13) and good linearity of the calorimetric CH4 sensor (Fig. 14).
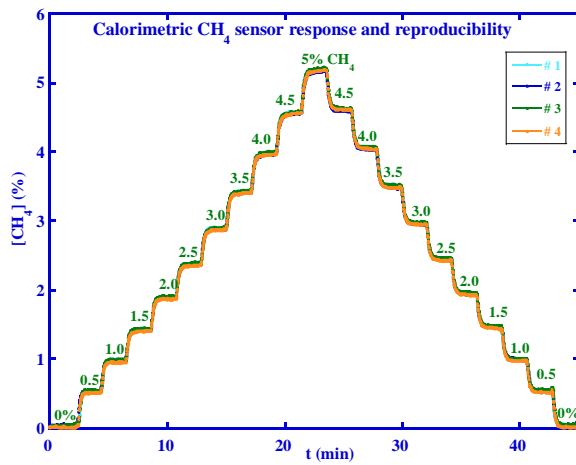

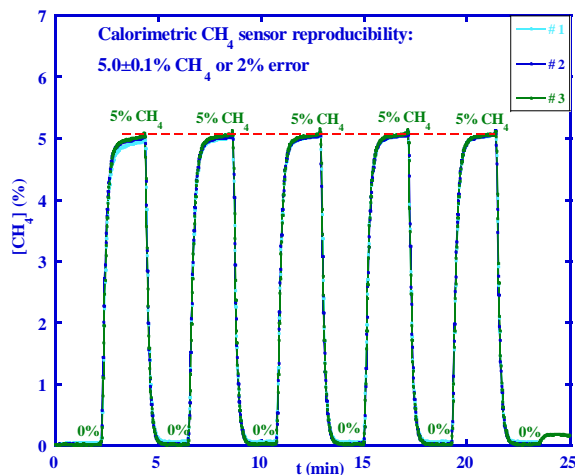**Fig. 12.** Calorimetric CH4 sensor response and reproducibility in 0…5 % CH4 mixture with 10 % O2.

Fig. 13. Calorimetric catalytic CH4 sensor response to 5 % CH4 (mixture with 10 % O2).
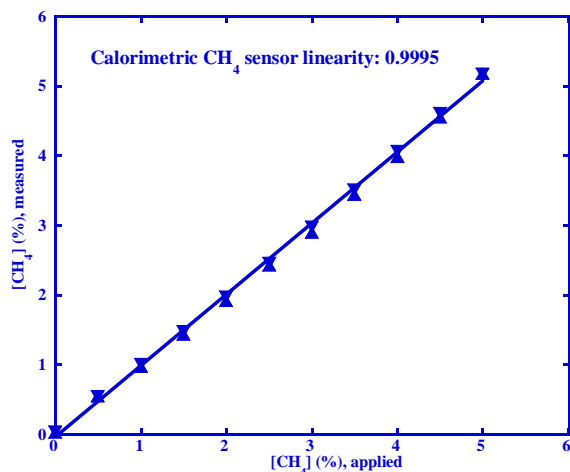

Fig. 14. Calorimetric catalytic CH4 sensor linearity.

A calorimetric catalytic CH4 sensor has a response of ~30 s for 90 % signal (Fig. 15) and the flue gas flow control extractive environment would contribute to CH4 detection accuracy, reproducibility, and reliability in the very challenging temperature, pressure, flow and chemical flue gas combustion environment.
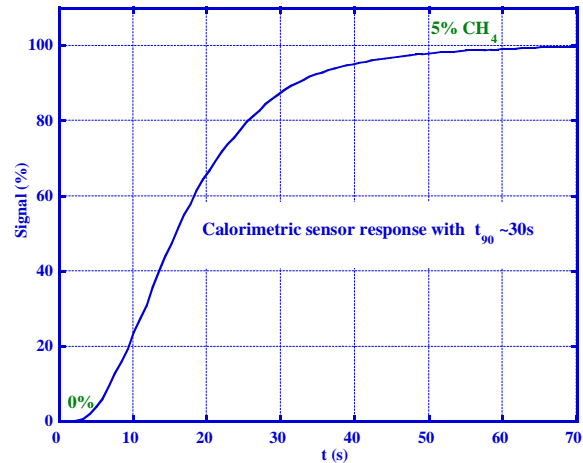

Fig. 15. Calorimetric catalytic CH4 sensor response.

The only calorimetric catalytic CH4 sensor available on the combustion market is quite selective and accurate with ~±5 % of full scale or ±0.25 % CH4 error in extractive methane measurements in flow and temperature-controlled environment.

Typical response of this CH4 sensor is ~40 s for t_{90} and an oxygen concentration variation between 3 and 10 % might bring up to a 0.4 % CH4 error. Some chemicals in combustion like silicon compounds, sulfur oxides, chlorine, and heavy metals might poison catalyst material and will reduce sensor sensitivity and life.

4. Semiconductor CH4 Detector

Metal oxide semiconductor (MOS) based gas detectors, invented in the 1960 s by Taguchi [19], were intensively investigated to detect different reducing gases, including CH4 [20-24], and are used nowadays worldwide for the indoor detection of environmental combustible gases [25].

MOS-type gas sensors change resistance (R) as a result of a change in adsorbed oxygen concentration reducing Fermi level and resistance (Fig. 16). The adsorbed oxygen formed in a clean environment (detector's base line) will be consumed by the reaction with methane or carbon monoxide, resulting in surface resistance reduction related to the concentration of methane, carbon monoxide or any other reducing gas. An MOS detector (Fig. 17) is made of sintered n-type metallic oxide from iron, zinc and thin families with imbedded heater holding the sensor temperature at

~250-400 °C. Control of metal oxide physical-chemical properties, i.e., their stoichiometry, porosity, grain size and shape, as well as the proper addition of dopants or surface catalysts, are all effective tools to tune the sensitivity as well as selectivity [26].
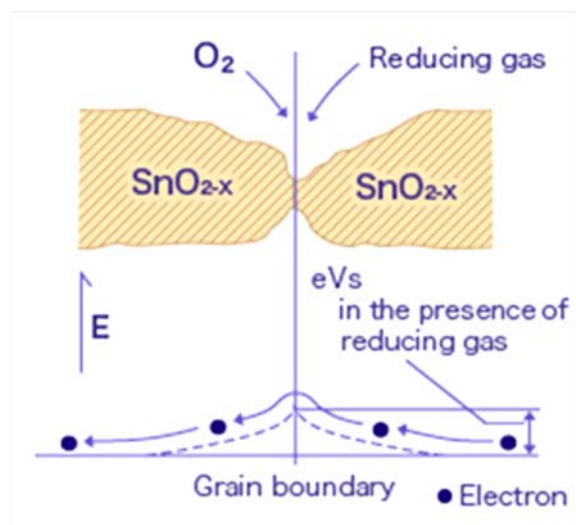

Fig. 16. Semiconductors detector operation diagram [25].

Fig. 17. Semiconductors CH_4 detectors [25].

Unfortunately, the implementation of these semiconducting sensors in the combustion process have been limited due to insufficient selectivity, significant interference to moisture and even oxygen, and long-term stability difficulties. Materials that are more stable at high temperatures based on gallium oxide (Ga_2O_3) have been applied in semiconductor sensors [27], and different physical, catalytic gas conversion filters have been recommended for selective indoor CH_4, H_2 and automotive exhaust gas nitrogen oxides detection [28].
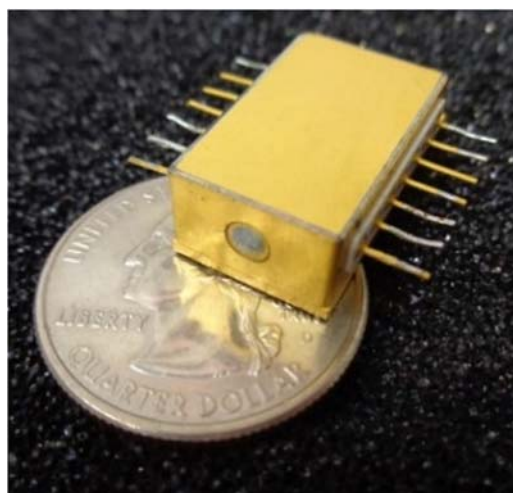
5. Tunable Diode Laser (TDL) and Quantum Cascade Laser (QCL) Spectroscopies

Tunable diode laser (TDL) and quantum cascade laser (QCL) spectroscopies are innovative optical measurement techniques utilizing different lasers (Fig. 18), e.g., tunable diode and quantum cascade, to detect a variety of combustion gases including methane [29-31].

Fig. 18. Tunable diode (A) and quantum cascade (B) lasers.

TDL and QCL spectroscopies are highly distinguished from the conventional process photometry with the laser's ability to be scanned across the narrow CH_4 absorption peaks many times per second by trimming the current through the laser.

With a typical scan in the range of 0.2 to 0.3 nm, the laser would provide much higher selectivity in applications. The IR absorption spectrum of methane (CH_4) is like a fingerprint, providing CH_4 identification at 1.65 µ (TDL) or 7.9 µ (QCL) and measurements in a wide concentration range down to ~0.6 ppm CH_4 (TDL) or even ~10 ppb CH_4 (QCL) as a detection limit. The detection wavelengths and limits of some combustion gases are summarized in Table 2.

The TDL or QCL analyzer would provide extractive measurement across the duct or pipe (Fig. 19) and would serve as a probe (Fig. 20) for single point near real-time measurement.

A series of process adaption application tools were developed for in-situ, extractive or in cross-pipe installations. The probe design would not require a special optical path alignment, but would deliver single point measurement.

Table 2. Combustion gases absorption lines and detection limits.

Target gas	Wavelength (μ)	Detection limit (ppm)
Methane (CH₄)	1.65 (TDL) 7.9 (QCL)	0.15 0.003
Carbon monoxide (CO)	1.57 2.33 4.80	30 0.5 0.01
Oxygen	0.76	8.956
Carbon dioxide (CO₂)	1.96	3
Nitric oxide (NO)	1.8 2.65	60 1
Nitrogen dioxide (NO₂)	0.68	0.3
Water (H₂O)	1.39	0.06

Fig. 19. A typical installation of TDL analyzer across the gas pipe or combustion duct.
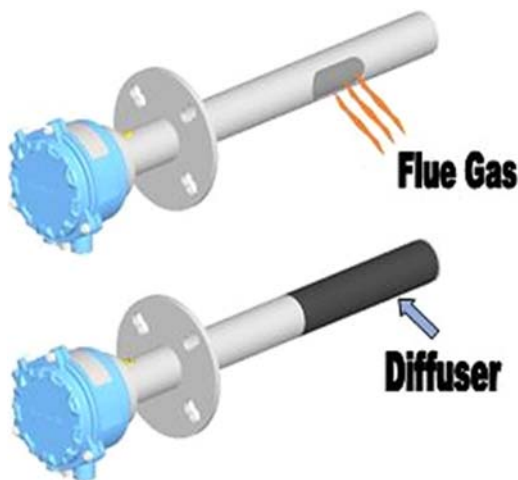
Fig. 20. An in-situ TDL probe with opening for the clean (top) and with diffuser for dusty (bottom) application.

In the probe design the laser source and detector are located in the probe housing with the laser beam being reflected at the probe end, back to the detector by quartz prism, with max operation temperature of <250 °C or by gold mirror with max operation temperature of <430 °C. With a unique folded-path design, the probes can be installed in almost all pipes and stacks with no alignment needed.

Temperature and pressure variation in the process has to be compensated and might cause an additional error in the measurements. IR light reflection at high temperatures, combined with wide background radiation from the fire box and process windows fouling, might bring additional challenges in many applications. There are quite accurate TDL analyzers with ~±4 % or ±0.02 % CH₄ error and sub-ppm detection limits in some applications.

However, TDL analyzers are quite expensive, but considering the combustion process's highly challenging flue gas temperature, pressure and flow variation, an in-situ multipoint temperature measurement [32-33] and an in-situ CH₄ validation would be highly recommended, so these analyzers provide reliability and accuracy. Some of the available TDL/QCL Analyzers on the market are summarized in Table 3.

Table 3. TDL and QCL Analyzers.

Product and Technology	Detection limit, accuracy	Application
TDLS8000 TDLS	N/A ±4 % or ±0.02 % CH₄	Across duct
LaserGas III SP CO (CH₄ optional) TDLS	0.05 % ±1 %	Across duct or extractive
RLGD-100 TDLS	N/A ±10 %	Portable CH₄ detector
SERVOTOUGH MiniLaser 3Plus TDLS	0.2 ppm ±1 %	Across duct or extractive
GM901 TDLS	N/A	Across duct In-situ <430ºC
TDLS GPro 500 TDLS	1 ppm ±2 % of reading or ±1 ppm CH₄	In-situ probe <250°C <600°C with additional thermal barrier
CT5800 QCLS	0.5 ppm ±1 %	Extractive

6. Conclusions

From four available major methane gas sensing technologies, only two – catalytic calorimetric and TDLS/QCLS – have so far found practical application in instrumentation in the combustion market, as they produce quite reliable and accurate (~2...5 % error) extractive or across the stack in-situ methane measurements (Table 4).

Table 4. Performance and application summary of major methane gas sensing technologies.

Technology	Temperature (T) and Pressure (P) effect	Major applications
Calorimetric catalytic, Extractive	Fixed temperature, Minor P effect, Flow sensitive	Power generation, Middle to large boilers, Petrochemical industry
TDLS/QCLS Extractive, across the duct, in-situ	T & P algorithms, T & P fluctuation effect?	Petrochemical industry, High temperature furnaces

Acknowledgements

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