METHANE AND THE FOUR ALCHEMICAL ELEMENTS IN OUR ENVIRONMENT

Anaerobic sewage sludge digesters

Water, earth, wind and fire were regarded by the alchemists as the four classical elements making up our natural environment; methane has a place in each of these. In waste water treatment anaerobic sludge digesters convert biomass to methane, which can be fired in a gas engine to produce electrical power. In landfill sites and natural soils, methanogenic bacteria convert biomass to methane which is released to the air and carried by the wind throughout the troposphere where it is a potent greenhouse gas. Deep in the earth, methane is trapped in coal and rock seams. If this flammable gas accumulates during mining activities, it can create explosive fire balls and gas detection is used to mitigate this risk. So, the monitoring and detection of methane gas is important for safety or environmental management in all four of these alchemical elements.

From an environmental management perspective, carbon dioxide (CO_2) emissions are the main source of global warming gas emissions from the transportation sector and industry. On the other hand, small quantities of methane emissions also contribute to global warming because methane has a global warming potential (GWP) 28 times higher than CO_2. Transportation methane emissions are regarded as diffuse sources of pollution. On the other hand, emissions from power plants, offshore gas rigs, power plants, water treatment facilities and landfill sites are categorised at facility level and methane emissions data for many sites is reported in the European Pollutant Release and Transfer Register (E-PRTR).

Measuring transport methane emissions

Methane is produced in car, bus and truck engines when fuel is not completely burned to form CO_2 and water. This is especially the case during cold-starts, when the ratio of fuel and air in the engine is adjusted by 'choking' the air supply to increase the relative amount of fuel. The change in the reaction stoichiometry causes incomplete combustion of the fuel and slip of hydrocarbons through the engine. Vehicles that run on compressed natural gas (CNG) also have a higher methane emission footprint than vehicles with petrol and diesel engines.

To ensure that methane and other hydrocarbon emissions from transportation are minimised, the development of efficient modern engines and power trains relies on many thousands of hours of engine testing. These tests and the related methane emissions

Deep shaft mining for coal and gold

Water, Earth, Wind & Fire - alchemical elements

limits are governed in Europe by the Euro 6 automotive emissions regulations and in the US through the 49 CFR Regulations for Greenhouse Gas Emissions from Passenger cars and Trucks. The exhaust gas composition is measured under a range of simulated driving conditions from low speeds to high load conditions. A suite of gas analysers is used to measure particles, hydrocarbons, oxides of nitrogen and other pollutant gases in the exhaust. For the detection of hydrocarbons, a flame ionisation detector (FID) is used. In order to differentiate methane from other heavier hydrocarbons, cryogenic traps and molecular sieves can be used with gas chromatography prior to the FID detector. High purity specialty gases and traceable calibration gas mixture cylinders are required to ensure that the gas analysers in these engine testing facilities operate effectively and are calibrated according to the regulations.

The shale gas revolution

In the United States, shale gas has revolutionised the economy and the implications ripple worldwide through the export of products such as ethane shipments to European and Asian Ethylene

Power plant stack emissions

crackers. The USA is now a major hydrocarbon exporting nation in the form of liquefied natural gas (LNG) exports from the Gulf Coast.

Safety at gas terminals, processing stations and LNG storage facilities is often enhanced using open path methane gas detectors. They use infrared light to detect flammable gases that are infrared active, such as methane. These gas detection devices differentiate from each other in the way they compensate for the potential interactions from fog and rain and their resistance to solar interference. Most units have a very rapid response time, reacting within a few seconds and when suitably specified, are generally able to scan across a path of up to 100 metres, so a

Shale gas drilling in the USA

LNG storage terminal

web of these detectors can be used to straddle an LNG terminal comfortably.

The abundance of US shale gas has led to the balance of electrical power generation in the US moving from coal as the staple feedstock to a more even balance of natural gas and coal combustion. Power generation is another area where methane detection is of primary importance.

Natural gas distribution and power generation methane monitoring

Methane emissions monitoring in the natural gas extraction, distribution and power generation sector is essential for environmental management. According to the European Pollutant Release and Transfer Register (E-PRTR), power plants, gas terminals and offshore production platforms, which reported data in the classification of combustion plants, emitted between circa 100 and 1600 Tonnes of methane per facility in 2017.

Research into methane emissions from natural gas fired power plants operating at steady state has indicated that up to 0.2% of the methane fed to the plant is emitted due to incomplete combustion. During start up, this has been shown to increase to a level up to 2.5%. To conduct this study Cavity Ring Down Spectroscopy (CRDS) instrumentation installed in a small aircraft was used to over-fly 14 natural gas fired power plants in the USA[1]. Due to the long path length of the light beam, this laser adsorption analytical technique is one of the most sensitive methods for the detection of trace concentrations of small gas molecules such as methane, carbon dioxide and ammonia which are optically active in the near infrared region.

In the gas distribution sector, gas detectors are being used to improve natural gas pipeline maintenance and reduce methane leaks. Modern wearable natural gas detection units combine location tracking using cell-phone type GPS technology, cloud computing and big-data to enable gas distribution operating companies to monitor and store gas detection data from the devices worn by their employees. Maps can be generated which provide a clear indication of where gas-leak trouble spots exist. This ongoing data gathering is especially effective when used over a long period of time by teams of operators and is highly insightful in urban areas where the gas distribution grid may be aged. Low value data can become highly valuable management information which enables the maintenance and repair of gas pipeline leaks to be prioritised and thereby ensuring cost-effective and safe operations.

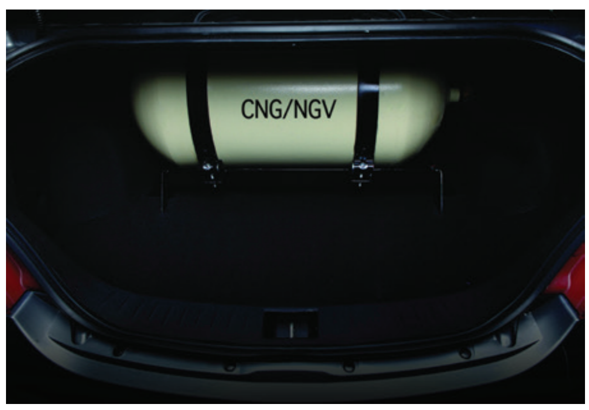
Landfill methane and waste water management

Fixed flammable gas detection system

Onshore and offshore facilities in the hydrocarbon processing sector represent sources of methane emissions. Despite the vast quantities of methane that are produced and transmitted by the natural gas processing sector, methane emission levels from a major site are generally much lower than those from a typical large landfill site.

Adaptations, of the CRDS technique, such as the Off-Axis Integrated Cavity Output Spectroscopy have enhanced its range of applications in environmental detection and these analysers can now be used for permanent landfill gas emissions monitoring where they analyse trace levels of methane and other landfill site greenhouse gas emissions. Perhaps surprisingly, landfill sites are one of the most numerous sources of methane emissions, and according to the data filed with the E-PRTR they can also be some of the heaviest emitters of methane, which is a potent greenhouse gas.

The EU Industrial Emissions Directive and its associated BREF notes have no emissions limit values for methane from gas turbine power plants. On the other hand, BAT 45 of the Large Combustion Plant (LCP) BREF note does specify Best Available Technology Associated Emission Limit values (BAT-AELs) for methane emissions from spark-ignited lean-burn gas engines with a total thermal input greater than 50 MW. Gas engines use positive displacement pistons and work in a similar way to spark-ignition petrol-fired car engines. When compared to large gas turbines, they are suitable for smaller power generation applications typically in the range of 5 to 20 MW. This size range makes them ideal for the combustion of methane produced at biogas facilities or anaerobic sludge digesters in waste-water treatment. Methane leak detection around such equipment can be readily achieved using a fixed gas detection system with fuel cell type detectors: these are readily available, low cost devices.



Automotive CNG tank in car boot

Explosive impact

Methane leakage from the natural gas grid is only one example of the flammability hazard that this gas poses. Methane gas detonation is one of the biggest killers in mining history. It is a common hazard in coal mining and the issue extends into other sub-surface mining operations such as the search for gold. In a case that is sadly not unique, a methane gas explosion killed 18 miners at the world's deepest gold mine, the Mponeng west of Johannesburg in South Africa in July 1999. The mine operator confirmed that "39 men had been drilling a rock face when their gas monitors indicated the presence of methane. They started to evacuate the area but there was an explosion before they were all clear". Sadly, this points to the fact that whilst it is essential to select and wear appropriate gas detectors, they are in themselves no guarantee of safety in harsh and unpredictable underground conditions.

When choosing a gas detector for mining applications several criteria must be met. Firstly, the gases to be detected must comply with the local safety legislation and any additional practices in place in the mine. At a minimum, this would typically involve simultaneous measurement of methane, carbon monoxide, hydrogen sulphide and oxygen. The device must also be intrinsically safe and thereby avoid creating additional ignition risks. Beyond that, many factors come into play such as the robustness of the unit, its weight and battery life. The ease with which the daily functional test using bump-test specialty gas mixtures can be performed and the associated data capture for audit purposes are also key considerations to ensure that an operator can prove to auditing authorities that safety procedures have been correctly adhered to.

The methane gas detection technology available to miners today can help to minimise the risks significantly, but these gas detection devices were not in common usage on the 24th of July 1979 when a massive methane explosion ripped through parts of the Appin coal mine 600m below the surface of New South Wales killing fourteen miners. The judicial inquiry that followed the accident recommended continuous gas monitoring equipment should be used in mines in the future. This was a major turning point in the history of underground gas detection and mining safety. Safety policies, appropriate enforcement and affordable gas detection technologies have all played a tremendous role in the progressive improvement in mine safety.

European Pollutant Release and Transfer Register, 2017

Site	Methane*
Aterro Sanitario da Raposa	5970
3C Waste Limited, Arpley Landfill, UK	3790
Hedeland Deponi, Copenhagen, DK	3130
Equinor Mongstad Refinery, NO	2230
Equinor Refining, Kalundborg, DK	2090
Hempsted Landfill Site, UK	2040
Brae Bravo Platform, UK	1650
Repsol Cartagena Refinery, SP	1190
Hazel Lane Quarry And Landfill, UK	1150
Brae Alpha Platform, UK	1100
Shell Bacton Gas Terminal	855
Perenco Bacton Gas Terminal	663
Henriksdals Reningsverk, Stockholm, SE	663
Hammerfest LNG, NO	650
Foinaven Floating Production & Storage, UK	566
Orlen Południe, PL	488
Gasunie PeakShaver LNG vaporiser Maasvlakte, NL	480
Abfallwirtschaft, Halle-Lochau, DE	452
Captain Floating Production & Storage, UK	358
RWE Pembroke CCGT Power Station, UK	328
Scunthorpe Integrated Iron & Steel Works, UK	282
Klärwerk München, Gut Großlappen, DE	260
Repsol Tarragona Refinery, SP	235
Tata Steel Ijmuiden, NL	228
Ineos Chemicals Grangemouth	203
RWE npower, Staythorpe C CCGT Power Station, UK	196
RWE npower, Didcot B Power Station, UK	176
hanseWasser Bremen, Seehausen, DE	174
ENGIE Zolling Power Station, DE	134
BP Refinery Rotterdam, NL	140
Viridis 178, Nottingham Power Plant	120
Esso Nederland Refinery, NL	114
Total Antwerp Refinery, BE	110
ENGIE Farge Power Station, Bremen, DE	111
RWE npower, Little Barford CCGT Power Station, UK	107
Drax Power Station, UK	106
Rosenheim CHP, DE	102

Landfill site
Natural gas production & processing
Steel production & processing
Waste water treatment
Oil refining
Power generation - gas fired
Power generation - coal/biomass/waste fired

1 Observations of Methane Emissions from Natural Gas-Fired Power Plants, Kristian D. Hajny et al, Environ. Sci. Technol. 2019, 53, 8976–8984

** 2017 Annual methane emissions in Tonnes*

E-PRTR https://prtr.eea.europa.eu/#/pollutantreleases

Table is an extract from the full data base for illustrative purposes

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