Industrial gases support the natural gas production chain

The contribution of industrial gases across the petrochemical processing spectrum is crucial to performance and safety

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For decades, industrial gas companies have assisted producers in the petrochemical landscape to ensure they are able to deliver the levels of product quality and operational safety demanded by changing legislation, environmental regulations and customer requirements.

Industrial gases come into play from the very earliest upstream stage, where offshore exploration equipment is manufactured from steel and special metal alloys. These materials need to be cut, heated, welded and coated with the aid of industrial gases. In particular, many applications associated with drilling equipment now demand the use of higher performance materials. These materials are a world away from what was being used as recently as 10 years ago and, as modern material specifications evolve, metal fabrication companies need to adapt their gases to suit the latest welding processes.

Offshore exploration equipment is often situated in some of the roughest and most inhospitable seas, and has to be able to withstand enormous loads from huge waves and swells and highly corrosive conditions. High-quality steel and the most up-to-date production methods are necessary for exploration operations under such harsh conditions. In this context, welding becomes particularly important, as the huge steel towers and support stilts are manufactured from many individual steel segments. A faulty weld seam on a single component can have catastrophic consequences. Cracks or dangerous salt-water corrosion could lead to a rupture in one or more of the steel components. Performance standards for exploration equipment components, particularly those operating offshore, therefore confront manufacturers with tough challenges.

As more high-strength steels are being specified to manufacture increasingly tough drilling equipment, this has resulted in an extra preheating stage prior to welding in order to safeguard the metallurgical properties of the steel. Preheating prevents failures, such as hydrogen-induced cracking, as well as common failures in the heat-affected zone. As more fine-grained structural steels are being used to construct apparatus and equipment for the oil and gas industry, the importance of preheating prior to the welding process is becoming a focal point.

Welding in this application is a complicated affair. To begin with, the thick metal pieces need to be preheated. If this is not done, the large, cold steel plates will lose heat too quickly and the metal will not be completely melted in the welding zone, making a secure connection impossible. Preheating will also prevent the build-up of cold cracks, which can occur due to hydrogen exposure or internal stress in the component.

This is particularly important when treating high-strength steels. After the weld, these materials must be post-heated for around two to three hours to diffuse any rogue hydrogen atoms in the weld seam. For manufacturers that have to maintain a fast production speed, it is vital that they quickly reach a preheated temperature of greater than 100°C.

In response, special burners for preheating steel before welding are required. Linde has engineered a Lindoflamm acetylene burners for preheating steel before welding takes place. Acetylene provides high heat intensity in the primary

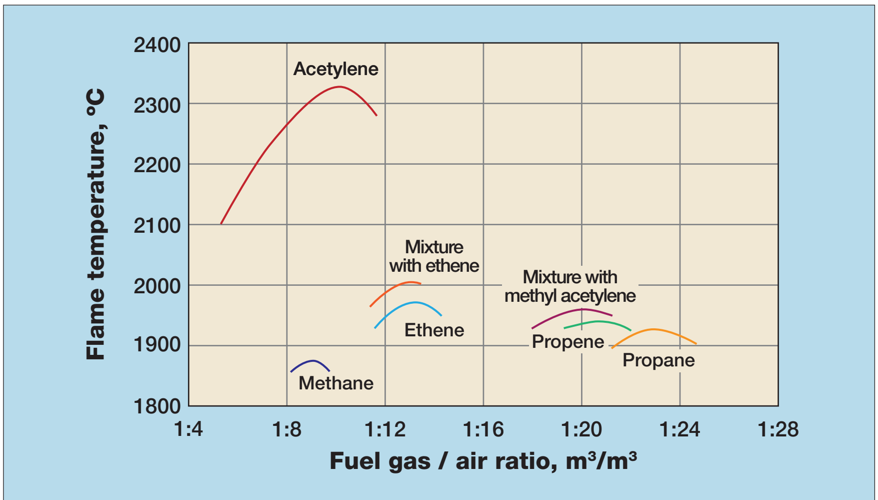

Figure 1 Flame temperatures of hydrocarbon gas/air mixtures

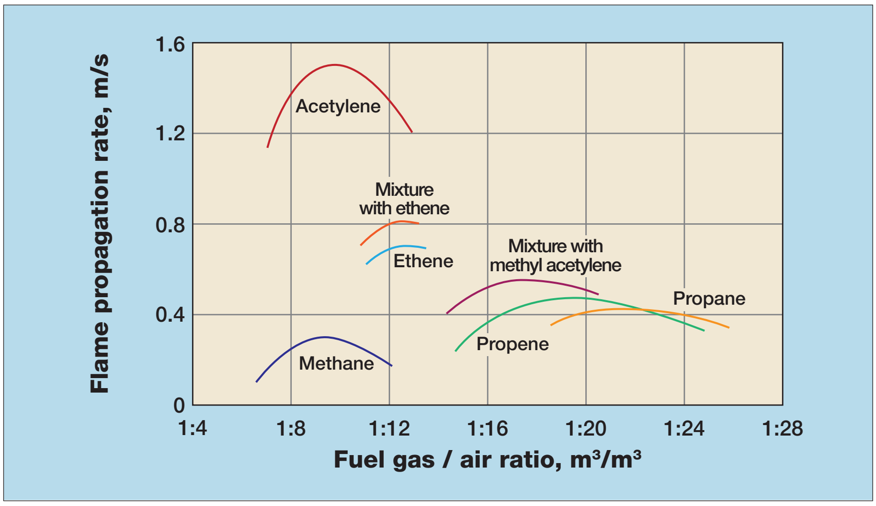

Figure 2 Flame propagation rates for hydrocarbon gas/air mixtures

flame, establishing a focused flame, so that preheating occurs only in the weld area. This results in an increase in the speed at which the weld area is heated — as much as two-thirds faster than that achieved by other fuel gases — plus significant savings on total process cost.

As opposed to a propane gas flame, acetylene gas burns with a very precise, pointed "primary flame cone", which drives the heat directly into the metal. Additionally, flame temperatures that can be reached with the associated acetylene-compressed air torch — approximately 2400°C — are significantly higher than those achievable using other fuel gases in combination with air (see Figures 1 and 2).

Prolonging the lifespan of these offshore assets is another important factor, since equipment lifespan impacts the price of the final product. This issue has led to the development of special coating technologies that lengthen the lifetime of offshore installations. Linde Gases Division has recently developed a state-of-the-art cathodic protection technology as a first line of defence against metal corrosion.

Traditional arc spraying processes involve the use of air to coat metals. However, the enhanced Linspray arc spraying process employs a mixture of nitrogen and hydrogen to avoid oxidation of the applied coating. The new technique provides "active" protection, meaning the coating materials will actively repair the surface as it detects corrosion. Results show it can improve the lifetime of heavy exploration and processing equipment by up to 50%. This is a significant step forward in reducing the number of maintenance intervals required and the associated costs involved.

A critical application of speciality gases within the gas extraction and processing industry is the testing of gas leakage detectors on offshore drilling platforms. With tonnes of natural gas being handled via the platform each day, any leakage could build up rapidly into an explosive atmosphere. Offshore platforms, therefore, have permanent monitors in operation, sniffing for gas seepage, and these gas detectors need continual testing and calibration with speciality gas mixtures.

Human element

During the natural gas exploration phase, a lot of the work takes place under the surface of the ocean, as specialised technical divers undertake oil and gas pipeline construction and maintenance, or maintenance of oil rigs and valves, and so on. Underwater, these divers breathe a range of different gases, depending on the depth at which they need to work.

Recreational divers breathe air, but commercial divers plunging to depths of up to 50 m need specialised mixtures of oxygen and nitrogen in varying concentrations. When divers are required to go down to between 50 and 200 m, helium is introduced into a "tri-mix" with oxygen and nitrogen, or as heliox, which is helium mixed with low concentrations of oxygen.

These mixtures are critical to the well-being of the diver, as at these depths and pressures human blood responds to gas in a different way. The mixtures must be certified safe and need to avoid the presence of dangerous chemical molecules. The gas manufacturing process must be absolutely precise and quality controlled to ensure that no oils, methane or carbon monoxide infiltrate the mixtures. The effects of these substances are amplified at depth and their inhalation could prove fatal.

The human aspect of gas exploration is coming to the fore as gas companies are forced to go further afield to explore for natural gas deposits, frequently in places where the gas is difficult to extract. This means deeper exploratory dives and oil rig maintenance at greater depths.

Extraction and processing

Nitrogen (N_2) and carbon dioxide (CO_2) as bulk gases are used in huge quantities for the extraction and exploration of natural gas with induced hydraulic fracturing, commonly known as fracking. The traditional process for propagating hydrocarbons trapped in underground fractures had required high volumes of water, mixed with foaming agents and friction reducers and injected at high pressure into the fractures, cracking open the shale and creating fissures, allowing gas or oil contained within them to flow freely.

However, some of the issues that have arisen over fracking have been linked to chemicals added to the water to assist in the fracking process. These chemicals are believed to have occasionally contaminated groundwater supplies, with documented cases of seepage into drinking water wells, often through improperly sealed or abandoned drilling wells. There are also places where groundwater is only several hundred feet above gas reserves, where it is at risk of being more easily impacted by fracking. Conventional water treatment is often unable to remove the high concentrations of salts and other toxic and biologically disruptive compounds that can potentially be generated within wastewater from fracking — and if groundwater were to become contaminated, it could take years to clean an aquifer system.

Alternative techniques that can help mitigate water-related issues in fracking include employing CO_2 mixed with alcohol or liquid nitrogen (LIN) in a process known as dry fracking. The CO_2/alcohol mix is also injected at high pressure underground to open up fractures, with the CO_2 expanding as it vaporises, allowing natural gas to flow out through the cracks to be collected and processed.

Liquid nitrogen is used for dry fracking, a fracking process that has eliminated many of the problems associated with hydrofracking and could prove to be more acceptable to people concerned about the environment. It uses very few, or no, chemicals and after fracking the nitrogen is released into the atmosphere, which already comprises 78% nitrogen. Although relatively expensive in comparison to conventional chemical fracking, it is being used extensively for natural gas extraction in areas of high environmental sensitivity.

Air or pure oxygen as an industrial gas is used for sweetening or removal of sulphur compounds from LNG and LPG process streams. This is often done by employing a process called Merox from UOP. The Merox process uses catalysts and caustic soda to extract low molecular weight mercaptans from the refinery gas stream. The mercaptide-rich solvent must then be injected with oxygen from compressed air or industrial pure oxygen — for an enhanced regeneration process — so that the mercaptides present are oxidised to disulphides. The disulphides are subsequently separated from the solvent so that typical mercaptan levels in the gas product are controlled to less than 10 parts per million.

For refiners, throughput of natural gas production can be limited by the speed at which plants can desulphurise natural gas. However, the more stringent the desulphurisation process becomes, increasing Claus plant loadings with hydrogen sulphide and ammonia, the more frequent bottlenecks in the production process also become. Claus plants operating in refineries process concentrated hydrogen sulphide fractions, converting them into elemental sulphur. The technology is also able to destroy pollutants, particularly ammonia.

Although not new, oxygen enrichment technology has now come to the fore as a viable and cost-effective solution for significantly increasing a plant's sulphur handling capacity, as well as addressing problems associated with contaminants such as ammonia and hydrocarbons. Therefore, the use of oxygen debottlenecks the process and enables higher throughput and better returns on capital assets.

Oxygen enrichment of the combustion air significantly increases sulphur handling capacity. Associated benefits include increased productivity achieved without changing the pressure drop, more effective treatment of ammonia-containing feeds and less effort required for tail gas purification (reduced nitrogen flow). Oxygen enrichment is also a highly customisable approach to improving Claus plant yield, with options varying from low-level oxygen enrichment to employing advanced proprietary technology to bring about capacity increases of up to around 150%.

Transport

Once the natural gas molecule has been located in the exploration phase, it must be transported on shore, either through natural gas liquefying stations or through pipelines.

Depending on the corrosive nature of the substance being transported, pipelines are generally manufactured from high-value fabrication materials such as high-alloy or nickel-cladded steels. These are high investment materials, and fabricators are sensitive to the need to work with them appropriately, and sophisticated industrial gases offer protection during the fabrication process. The smaller diameters and prefabricated steel pipes are joined using laser welding, and the bigger items are plasma or arc welded, all of them protected from corrosion through the use of purging gas to prevent deterioration. Gas purging is also environmentally friendly, allowing for a reduction in the use of chemicals to clean up an otherwise oxidised weld.

Where natural gas needs to be transported over long distances, usually by ship, liquefaction takes place, using refrigerant gases such as ethylene, before the liquefied natural gas (LNG) is pumped into isocontainers or specially designed storage vessels on the ship.

Accurate measurement

Industrial gases also play a major role, helping to determine the British thermal unit (BTU) content of natural gas, a measure of how much energy will be liberated when the gas is burned. Speciality gases' calibration standards are made with known BTU values to measure LNG in the system, as this dictates how much the customer will pay for a specific volume of gas.

BTU values are very important when it comes to the transfer of ownership of a natural gas stream from one party to another. Natural gas is a very mobile commodity and can be moved over long distances, often across international borders. At the point where it changes ownership or crosses borders, the calorific value must be measured in an extremely accurate way. These massive quantities of gas are worth billions of dollars and the billing must truthfully reflect the energy value, considering the high cost of error if the calorific value is not precisely measured.

Taxation authorities also base their revenue on the value of the product being distributed. The governments of countries involved in this trade have specified that the BTU measurement must be carried out using high-quality, high-accuracy, accredited gases, which are traceable to international measurement standards.

It is also essential to measure the amount of mercury in natural gas. In oil and gas production and processing plants, the mercury present in natural gas poses a formidable threat to the safety of humans and capital equipment, because of its propensity to amalgamate with the materials of construction used for compressors and high-speed rotating equipment.

For instance, if mercury should amalgamate to pump system components or to the fins of turbine blades, it could cause considerable disruption by throwing these systems out of kilter, and therefore potentially cause immense structural damage. Liquid metal embrittlement (LME), which weakens the original structure of steel, aluminium and other metals in process plants, is the main threat. LME is a form of cracking that occurs when certain molten metals such as mercury come into contact with structural alloys. The most commonly affected materials include carbon steel, low-alloy steels, high-strength steels, 300 Series stainless steel and various alloys — nickel-based, copper, aluminium and titanium.

LME introduces an acute risk to an affected industrial plant. In a worst-case scenario, structural failure could potentially result in a significant explosion in an oil refinery or LNG facility, resulting in catastrophic loss of life, excessive damage to capital equipment and long-term plant downtime.

When natural gas is shipped into a port, samples are taken not only determine the BTU value, but also the mercury levels, which, again, have a bearing on the function of turbines used in the transport process. To support this measurement, Linde produces a mercury gas standard typically between 1 and 60 $\mu g/m^3$, which is the range at which mercury exists in natural gas.

Emissions control, monitoring and analysis

Calibration gas standards are also widely used to monitor emission levels from gas processing or natural gas-fired power plants. With the growing number of fracking operations being initiated, natural gas is becoming a more cost-effective commodity, and an increasing number of natural gas power plants are coming online. Legislation requires close monitoring of emissions from these plants, focusing on the byproducts of the combustion process, sulphur dioxide, carbon monoxide and nitric oxide. Where coal-fired power station emission concentrations are in the 50 to 100 ppm range, natural gas has concentrations around 10 ppm. However, this model is also associated with emissions such as ammonia and nitrous oxide, both of which are considered greenhouse gases, and measurement of these compounds is enabled with high-precision speciality gas mixtures.

When it comes to natural gas combustion control in power generation, plant operators need accurate information about the combustion gases in the system. To avoid overfeeding or underfeeding natural gas into the system, operators rely on BTU values to provide insight and it is therefore imperative to have highly accurate calibration gases made with those specified BTU values in order to monitor the combustion gases and help maintain control throughout the process.

Inside the combustion chamber, it is also necessary to monitor oxygen levels to support fuel and carbon dioxide levels, to control the combustion process and minimise greenhouse gas emissions. These measurements also require speciality gases calibration mixtures to support the instrumentation. Effective monitoring of combustion and optimisation of the process is the key element of emissions reduction.

High-purity "zero" gases are used to zero out the analytical instruments that monitor the output of flue gases from natural gas processing plants. Accurate and pure zero gases are a critical element of monitoring, because any trace amounts of impurities can alter or skew results.

An increasing number of molecules is being analysed and measured to support the growing trade in emissions from natural gas combustion. In the US, there is a strong drive to monitor all the greenhouse gases being emitted from a process, and this trend is likely to go worldwide, bringing under the spotlight emissions of gases such as nitrous oxide, ammonia, hydrogen chloride, formaldehyde, sulphur hexachloride and carbon dioxide.

The future

As the oil and gas industry advances, the more complex the processing of natural gas will become. This maturing value chain is going to demand increasingly high-quality and sophisticated gases. Industrial gases will therefore play a progressively critical role across the entire value chain, helping to ensure that all phases of the process operate effectively and safely, and that environmental impact is minimised.

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