Gas chromatography enabling fair trade in LNG

By Stephen B. Harrison

The Tsunami that led to the Fukushima Daiichi nuclear reactor failure in 2011 transformed the energy market in Japan. Approximately one quarter of the nation's nuclear reactors were taken offline for testing and repairs. Since then, only a handful have returned to service. Gas-fired electrical power generation has grown to substitute the load on these nuclear reactors.

Because of this shockwave, the demand for liquefied natural gas (LNG) in Japan has grown tremendously and the country now ranks alongside China and South Korea as one of the world's top three LNG importers.

In Europe, the dominant method of natural gas export is by pipeline with flows from the North Sea and Russia to Western Europe well established. In Asia the situation is different and LNG transportation by ocean-going tankers is more common. At present, the major sources of LNG for the Asian market are Qatar and Australia.

Sweet and sour

A major boost to the trade of LNG between Australia and Asia took place in December 2018 with the start-up of the Prelude floating liquefied natural gas (FLNG) facility. It processes gas from the Browse Basin off the coast of Western Australia. When natural gas rises from the ocean bed, the methane is laden with heavier hydrocarbons, carbon dioxide, moisture and hydrogen sulfide.

A primary function of the FLNG facility is to separate and liquefy the hydrocarbons into LNG, natural gas liquids (NGL) and condensate. However, before this can take place the 'sour' gas stream must be made 'sweet' by the removal of acid gases such as hydrogen sulfide. The gas stream must also be dried, since moisture would freeze in the LNG processing equipment and cause blockages.

Measurement comes first

As with many process operations, the first step is to quantify the task in hand. Precise measurement of the composition of the gas arriving at the FLNG facility helps to understand the status of the subsea gas field and prepares the gas purification and liquefaction operations for the task in hand. The sample to be analysed contains a diverse mix of chemicals and sophisticated laboratory analysers, such as a gas chromatograph fitted with a flame-ionisation detector (GC-FID) which are ideal to determine the raw gas stream composition.

Operation of such an instrument relies on high purity specialty gases. A carrier gas such as helium or hydrogen is required to move the sample through the chromatography column where the various chemicals are separated. High purity hydrogen and synthetic air are also required to create a high temperature flame that is used to detect the chemicals as they are eluted from the gas chromatography column.

Make or buy?

In a land-based laboratory, cylinder gas supplies are practical. However, delivering gas cylinders on the ocean presents a major challenge! For this reason, generation of the required gases in-situ is desirable.

Heinz P. Schmidlin, Sales & Marketing Manager at the Gas Generator Division of VICI AG International, confirms the point, "The simple choice that analytical instrumentation users have is either to make or buy their high purity gases".

Growth of hydrogen as a carrier gas in chromatography has been strong in recent decades, driven largely by the increasing scarcity of helium and the occasional supply interruptions associated with that situation. Schmidlin adds that "whether it's a bench-top generator for the laboratory or a 19" rack-mounted unit for process control applications, we offer instrumentation engineers and scientists the ability to be more independent."

High purity gas generators are optimised to produce 5.0 grade or 6.0 grade hydrogen and an equivalent grade

> "The simple choice analytical instrumentation users have is either to make or buy their high purity gases"

of purified air. These are self-contained tool-kits for creating the gases required to run a GC-FID set-up for extended periods of time in remote locations. With an eye on safety in un-manned operations, Schmidlin says that, "our VICI generators are always on the look-out for leaks and will automatically stop hydrogen production if an excessive flow is detected. And all our hydrogen generators are equipped with USB ports for seamless integration into distributed control systems."

Consumable and calibration gases

The carrier gas and detector gases run through the GC continuously and are therefore consumed in relatively large quantities. This is one reason that the delivery of these gases in cylinders to an offshore FLNG facility would be expensive and impractical.

On the other hand, calibration gas mixtures are used intermittently and in small quantities. So, a single specialty gas cylinder might last for several years.

The preparation of calibration gas mixtures containing corrosive components such as hydrogen sulfide (H_2S) is a fine art. High-tech gas mixtures preparation and analysis equipment are required. Equal attention must be paid to the cylinder that is used to contain the gas mixture. Sulfur compounds are highly reactive, and it is not acceptable that their concentration decays after the final analysis and certification of the specialty gas mixture.

Steel cylinders are suitable for high purity consumable chromatography gases, such as helium, hydrogen and synthetic air. However, they are not compatible with calibration gas mixtures that contain low concentrations of reactive components such as H_2S. For ▸

these mixtures, aluminium cylinders are required.

Some aluminium alloys have a high strength to weight ratio which makes them ideal for medical applications. However, the elevated copper content in these alloys render them unsuitable for highly sensitive reactive specialty gas mixtures. For these mixtures a different alloy is recommended. Beyond the selection of the appropriate aluminium alloy, preparation of the internal surface of the cylinder is also critical. Stability can be improved using a variety of techniques, such as chemical polishing; sequential vacuum, bake and purge cycles; saturation conditioning with the target gas components or silane passivation processes.

Certified stability

When a high precision calibration gas mixture is to be used offshore for a period of several years, it must be certified with a shelf-life for this duration. One of the advantages of the recently introduced ISO17034:2016 accreditation for reference materials is that it guarantees the stability and homogeneity of gas mixtures over their defined shelf-life.

To achieve this coveted accreditation, the reference material producer must demonstrate that their products and manufacturing processes comply to the most stringent requirements. Coregas, at its specialty gases production facility in Yennora, close to Sydney, achieved this badge of honour late in 2018 through upgrading its accreditation by the National Association of Testing Authorities, Australia (NATA).

Executive General Manager, Alan Watkins, explains what this means for his team. “Our lab has been ISO Guide 34 accredited for many years and we have been one of Australia’s leading producers of accredited specialty gas mixtures in recent decades. The successful transition from the Guide 34 to ISO17034:2016 means that we can continue to occupy our position at the top of the metrological pyramid in the Asia-Pacific region.”

Every cent counts

The monthly value of Japan’s LNG imports is regularly more than $3bn, making the importance of accurate measurement of the gas quality for invoicing during custody transfer clear. A tiny inaccuracy could have a financial impact of millions of dollars.

As shipments are international, harmonisation of measurement across countries is essential to ensure fair trade. These are the drivers for the use of internationally traceable, accredited gas mixtures when calibrating the instrumentation used to measure the quality of the LNG.

The analysers used in this application are generally gas chromatographs which are used to monitor the energy value of the LNG as it is loaded onto the ships and unloaded into the land-based LNG terminals where it is stored. Since these instruments are located on-board the ship, they have specific requirements for vibration tolerance in addition to the need to operate at a wide range of ambient temperatures.

Steve Lakey, Global Product Manager for GC Products at ABB in the US puts the problem into context. “This is not the highly controlled laboratory environment of bench-mounted gas chromatographs, it is the high seas where tropical hurricanes roar,” he says. “At ABB we have made certain that our NGC 8200 series of process gas chromatographs can withstand ambient temperatures from -18°C to 55°C. That’s certainly compatible with the intensity of the Australian climate for example. Furthermore, with Class 1, Division 1 explosion-proof rating, they are suitable for LNG tanker and FLNG applications.”

“The NGC 8200 range is also highly versatile. Changing the GC module within the instrument is a simple 15-minute job, after which you can simply download the relevant software for the new application and the job is done. This means that the initial investment can be paid off several times over with low cost modifications to difference service.”

When it comes to accuracy, modern process gas chromatographs can match many of their laboratory-based cousins. Lakey continues, “In Europe the requirements for a Class A device is an accuracy of plus or minus 0.5%. The NGC 8200 accuracy surpasses these minimal requirements by roughly a factor of 5 (0.1%), as measurement accuracy is really a big deal in this business – every cent counts when we are trading these precious natural resources.” gw

ABOUT THE AUTHOR

Stephen B. Harrison is a consultant at sbh4 GmbH and Principal, Germany at Nexant E&CA. He was previously global head of Specialty Gases & Equipment at Linde Gases.