SENSING THE GAS STATUS

Dr. Philippe Prêtre, Mems AG, Switzerland, outlines the use of gas sensing instruments to assist in the measurement of LNG quality.

LNG is becoming more and more important not only as an easily dispensed energy supply, but also as a fuel on land and at sea in order to achieve the environmental goals set worldwide, such as the reduction of CO_2 and pollutant emissions by the middle of the century. However, LNG is not all the same, as its composition depends on the initial natural gas and the liquefaction process. During transport and storage, LNG changes its composition further due to the so-called boil-off. The efficiency of downstream consumers (ship engines, power generators, see Figure 1) can be increased considerably if LNG quality is measured promptly and reliably. Mems AG supplies instruments that are designed to achieve this in a simple way.

New sensor generation

More and more chip-based, micro-electromechanical systems (MEMS) appear on the market to meet requirements of a new sensor generation, such as ease of operation, robust design, compact size, and low purchase and maintenance costs. Thanks to these characteristics, such sensors are used in places where it was previously not possible to find suitable solutions for on-site gas quality measurement. For the last 15 years, Mems AG has been developing MEMS based gas quality instruments to increase the reliability, efficiency, and environmental compatibility of gas applications against the background of diversified gas supplies. gasQS™ is the unregistered trademark for the technology behind these developments.

Mems AG uses fully integrated micro-thermal hot wire calorimeters for its gas quality instruments. The heart of the calorimeters consists of a sensor chip (3.5 mm × 2.1 mm) manufactured in an industrial complementary metal-oxide-semiconductor (CMOS) process.[1]

The micro-thermal sensor allows analysing a gas mixture for its thermal conductivity as well as heat capacity and, from an associated flow measurement using a sonic nozzle set-up, density. These physical parameters [S] of a gas mixture are used as the input to correlate gas quality factors [Q] such as calorific

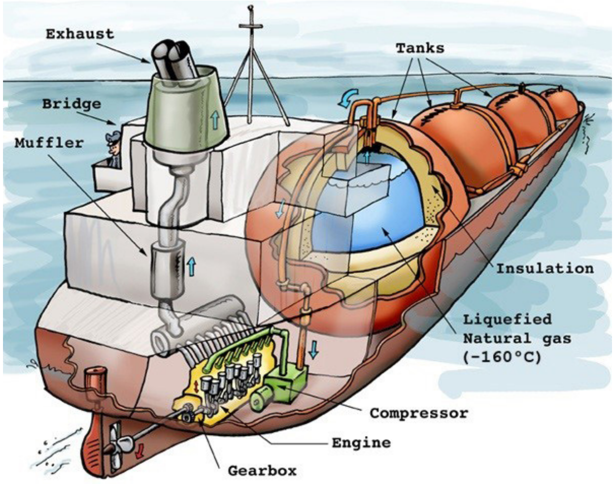

Figure 1. Design of an LNG tanker. Image courtesy of Welleman at Dutch Wikipedia: https://commons.wikimedia.org/w/index.php?curid=1850695.

Figure 2. Left: gasQS™ static. Right: gasQS flonic.

Figure 3. Plug and play measurement system cabinet.

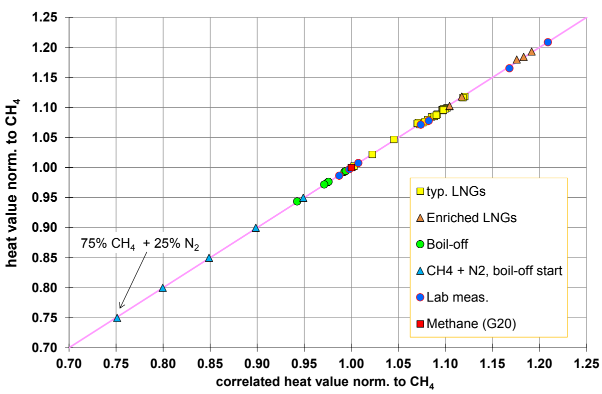

Figure 4. Measured errors for heating value for typical LNGs.

value, methane number (MN), air-to-fuel ratio, compressibility, or Wobbe index of a gas mixture.

Since the correlation scheme of Mems AG is based on physical properties as correlation input, performance is comparable with much more expensive process equipment, together with the advantage that correlation results for a new gas mixture can be predicted from data sheet values of its physical properties. Furthermore, from physical principles there is no restriction on the type of gas to be analysed. However, correlation of an unknown gas mixture works well, as long as it belongs to the same group of gases that the correlation was adapted for.

Two sensor variants in the form of the gasQS static and gasQS flonic are available (Figure 2): as a stand-alone device or as a measurement system that can be installed easily, i.e. like plug and play (Figure 3). gasQS static is optimised for the measurement of binary gas mixtures, such as those found in biogas production, but is also used in pairs in gas mixing processes, e.g. hydrogen in natural gas from power-to-gas production, where the mixing ratio of two gases must be precisely monitored. It is screwed directly into the gas pipe, which enables it to react within a few seconds to changes in the gas. gasQS flonic is used for the determination of complex quantities, such as for the measurement of calorific value and density in gas networks or the determination of the MN for the operation of gas engines. New in this field of application is the possibility to correlate engine specific parameters, such as the optimal ignition angle or the maximum exhaust gas recirculation (EGR) rate, which can be much more meaningful than the MN.[2]

Both sensor types are available for use in ATEX zone 0. Once installed, the devices require very little maintenance: the gasQS static, if installed correctly, requires no maintenance work, whilst a periodic inspection of the inlet filter of the gasQS flonic is sufficient for reliable operation for years.

Correlation

The fundamental principle of correlative methods is that a value of interest might be difficult or too excessive to be measured directly, but that other, more easily accessible physical properties are in a determined relation to the value of interest. Values of interest – for example heating value, Wobbe index or MN – are referred to in the following as gas quality factors.

In order to correlate gas quality factors [Q,] a function f(S) of the measured physical parameters [S] is considered which describes the relation between [Q] and [S] as precisely as possible for a wide range of known gases. This search for f(S) is the more successful, the more independent the physical parameters are from each other and the wider the physical interrelationship between [Q] and the physical parameters [S] is. Once function f(S) has been determined, [Q] is easily correlated from the measured physical parameters [S]. The remaining error constitutes of the correlation error on one hand and the effect of any measurement errors in the physical parameters [S] on the other. The former occurs even when the physical parameters can be measured without error.

In Figure 4, lower heating value is correlated from the sensor output [S] as an example of the gasQS technology. In the case of LNG, the wide range of possible gas compositions is reduced due to the treatment of natural gas on the LNG plant before liquefaction that will remove water, hydrogen sulfide, and carbon dioxide.[3] LNG typically contains more than 90% methane with small amounts of ethane, propane, butane, and nitrogen. The selection of gases in Figure 4 comprises lean and enriched LNGs together with their boil-off gases (BOG). Enriched LNGs have higher contents of higher hydrocarbons due to their origin, weathering, or ageing effects – i.e. when boil-off reduces the amount of methane in the LNG mixture while the higher hydrocarbons are slower to evaporate. Shortly after liquefaction, the boil-off comprises high amounts of nitrogen (N_2), since nitrogen has the lowest boiling point of all constituents of LNG.[4] It is therefore critical to know when the boil-off is rich enough in methane in order to safely start the on-board gas engines of an LNG tanker.

Also shown in Figure 4 are the test gases used to assess sensor system performance in a certified test laboratory.[5] Sensor output values [S] for the correlation have been calculated according to the physical model of the sensor system, that Mems AG developed. It allows for predicting the outcome of the measurement of [S] for any arbitrary gas mixture.

Laboratory test results

Results shown up to this point are all based on model calculations. Measured test results are reported in Figure 5 for typical LNGs covering a heating value range found in many European countries.[5] As expected, total measured errors are larger than correlation errors only. There is also a clear trend of an increase in total error as function of heating value (trend line). This trend allows adjusting the calibration of the gas quality instrument by the inverse. As a result of this readjustment, residual errors are less than ±0.5% over the whole LNG range.

Advantages

Correlative measuring methods are of particular benefit when it is necessary to react quickly to a change in gas composition, or where information about gas quality is needed shortly before launching a particular process. The former refers to, for example, processes in the glass and ceramics industry where the quality of the end product is very susceptible even to only minor changes in the process temperature.[6] Cold start-up of any gas engine, particularly after refuelling, is critical with respect to ignition behaviour (knock, ignition failure) and allowed exhaust gas emissions. A quick gas quality check before first ignition can ensure safe engine operation. Pre-process gas quality measurement can be used for feed-forward control of many applications before gas quality changes affect the process itself.

Technology applications

Initially, the technology was developed for MN determination in natural gas vehicles (NGVs).[7] MN variations were clearly visible but the effective MN after refuelling was hard to predict without sensors due to mixing effects with the residual fuel in the tank. For monovalent NGVs, knowing the gas quality before ignition is indispensable for safe operation, especially during engine start-up. Hence, sensing gas quality prior to combustion is clearly advantageous over exhaust gas measurements.

With the new sensor technology, it is also possible to correlate gas engine-specific parameters which, depending on the engine design, are more meaningful for optimum operation than the traditional MN as a knock index.[2] Figure 6 shows the effect of ignition angle as function of fuel quality.

A gas engine, initially set to best efficiency for M100 (=100% methane), deviates from this optimum when some

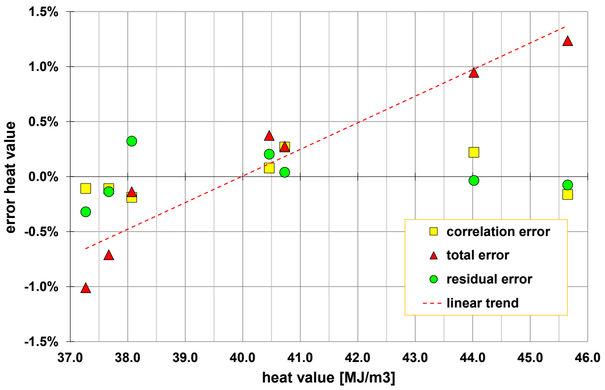

Figure 5. Heating value correlation gasQS flonic for typical LNG.

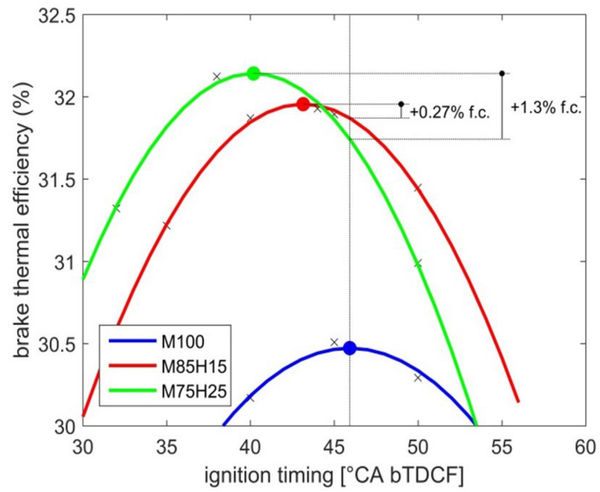

Figure 6. Effect of non-optimum ignition angles on fuel consumption. Image source: see reference 2.

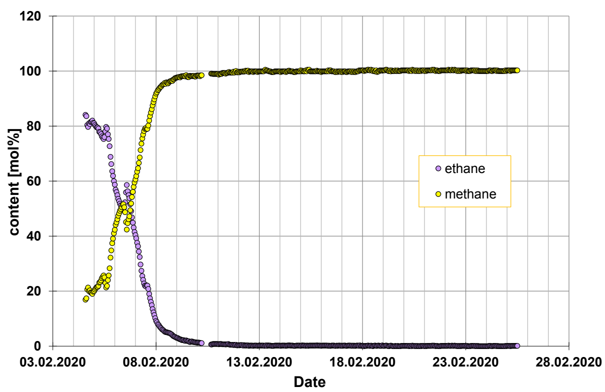

Figure 7. LNG boil-off quality changes as function of residence time in a LNG tank.

hydrogen is added to methane (15% and 25%, respectively). If, due to the lack of information about gas quality, ignition angle is not adjusted to its new optimum value, up to 1.3% higher fuel consumption will be the result. gasQS flonic is able to correlate the optimum ignition angle for many different engine set-ups.

Most recently, the technology was applied to check gas quality in an LNG refuelling station. In this specific case, the boil-off is compressed again and used as compressed natural gas (CNG) fuel for natural gas vehicles. When CNG demand is low, boil-off is reliquefied and returned to the LNG tank. Figure 7 shows the LNG quality over time as a result of the various gas withdrawals from and returns to the LNG tank, as required by the customer's demand of CNG and LNG.

As expected, LNG quality is changing over time due to boil-off. On 3 February 2020, the tank was almost empty and started to heat-up above the boiling point of ethane (-88.6˚C). All lighter components (methane, nitrogen) had boiled off and ethane evaporated as the only remaining component. Beginning on 4 February 2020, the tank was refilled with LNG. Subsequently, the tank cooled down and methane began to evaporate, while ethane liquefied again. The whole process took approximately five days. The measurement also showed that the LNG had an initial, nitrogen free composition. A similar behaviour can be expected onboard an LNG vessel, where the composition of the boil-off changes over time. The knowledge of these changes is of great advantage for an efficient management of the LNG use.

Conclusions

Gas quality instruments are established for most applications where larger and more frequent gas compositional changes affect safety, efficiency, and environmental compatibility. Ease of operation, rugged design, compact size, low acquisition and maintenance costs, are key features of such instruments. With an application-specific calibration, most of the customer requirements can be met with regard to the measurement parameters. In addition, instruments from Mems AG meet relevant standards with regard to safety in use (e.g. ATEX certification). This leaves the field free for a wide range of gas applications. **LNG**

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