Final Publishable JRP Summary for ENG60 LNG II Metrological support for LNG custody transfer and transport fuel applications

Overview

Liquefied Natural Gas (LNG) is the most environmentally friendly fossil fuel and, in the case of long distances, a more economical alternative to pipeline gas. After regasification of the liquid form, the natural gas can be used in power plants, industry and households. Recently LNG has also been used as a more environmentally friendly transport fuel.

All LNG applications require accurate measurements for the 'custody transfer' process i.e. when ownership of LNG is transferred from one organisation to other. However, the current levels of accuracy and uncertainty need improving as they can lead to significant financial loss and discourage LNG use. This project has strengthened the metrological framework for all stages of the LNG distribution chain, and particularly for transport applications. This was done by developing and building new LNG calibration facilities and standards for flow and composition measurements. The project also developed and validated methods to calculate LNG densities and provided a new algorithm to correlate the methane number, (MN; a measure of the fuel quality), to the composition of LNG.

Need for the project

LNG is a cost-effective and greener alternative to pipeline gas, and its potential use as a transport fuel offers a cleaner way to power cars and ships as it has lower carbon dioxide, sulphur dioxide and nitrogen dioxide (CO_2, SO_2, NO_2) and particle emissions. In comparison with other commodities, like natural gas or gasoline, the total uncertainty of measured energy is relatively high for LNG and has been estimated to be up to 1 %. This current lack of direct traceability to SI has delayed introduction of new measurement methods in the LNG business, as well as preventing new users. Therefore a sound metrological framework is urgently required for the development of LNG as transport fuel, as it is one of the pillars of the EU clean fuel strategy.

The delivered energy of LNG is measured indirectly by measurements of its (i) volume, (ii) composition and (iii) density. **Volume** is measured using on-ship level gauging methods i.e. measuring the height of the LNG in tanks, which is an established and accepted, if not particularly accurate, method. For measuring the volume or mass of liquids, flow metering is generally regarded as the most accurate method and is preferable to gauging measuring methods. However, LNG is stored and transported at approximately -162 °C, hence there is a lack of test and calibration standards for LNG flow meters operating at these cryogenic conditions, which is hindering the introduction of LNG to the market.

In order to determine its **composition**, the LNG has to be sampled. Currently, it is difficult to ensure representative LNG sampling as the methane and shorter carbon chain molecules vaporise more readily, meaning gas samples are richer in these. The industry view is that the current standard for sampling of LNG, ISO 8943 Refrigerated light hydrocarbon fluids, falls short of providing practical guidance especially with regards to the demands and uncertainties involved in sampling.

The **density** of LNG is calculated on the basis of the measured composition, temperature and pressure. However, new and more accurate density reference data is needed in order to validate the current density calculation methods that are based on very old reference data.

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Scientific and technical objectives

The previous EMRP project ENG03 LNG I extended primary calibration standards, improved methods for calculating density and developed techniques to validate LNG composition. It also developed a primary standard for the calibration of LNG flow meters for low flow rates. The overall aim of ENG60 LNG II is to further develop the metrological framework for LNG, in order to reduce the measurement uncertainty of LNG custody transfer by a factor two (starting from 1 %) and to develop measurement techniques with lower uncertainties to enable the development of LNG as a clean transport fuel. The goal is to extend traceable flow meter calibration to higher flow rates which are more representative of real world situations. The objectives were:

1. Development and validation of novel and traceable calibration standards of LNG mass and volume flow for vehicle fuel dispensing and ship bunkering. This builds on the work done in EMRP ENG03 LNG I on the flow meter and will increase the flow rates to more realistic levels.
2. Development and validation of novel and improved methods for measuring LNG composition to address online monitoring of LNG quality and issues with sampling LNG.
3. Development of a method for the determination of the MN, including a correlation of the MN to the LNG composition, in support of the use of LNG as transport fuel.
4. Development and validation of an improved model for LNG density prediction and the associated uncertainty evaluation.

Results & Conclusions

The development and validation of novel and traceable calibration standards of LNG mass and volume flow

A world first and unique facility for flow meter calibration and research was constructed in the Netherlands. This mid-scale LNG mass and volume flow facility now runs at up to 200 m^3/h (90 tons/h), compared with 25 m^3/h (11 tons/h) in the previous project ENG03. The construction and pipework was more complex than initially anticipated causing some delays. The equipment was installed at the location and the software for operation developed and tested. A hazard and operability study (HAZOP) for safe operation was also performed. Full validation of the measurement results and uncertainty still needs to be performed. But when in full operation, this facility will benefit end users by providing traceable calibrations for LNG flow meters, and it will serve as a test and research facility for improved flow metering methods and the reduction of uncertainty.

Linked to this, a new ISO Working Group was established: ISO/TC28/WG20 Dynamic measurement of LNG. The new ISO Working Group will enable faster uptake into written standards and a first draft of a new ISO standard for dynamic flow measurements of LNG was written during the project.

A cryogenic Laser Doppler Velocimetry (LDV) standard for flow measurement was developed and accredited for operation under ATEX (explosive atmosphere) conditions. Comparisons with the currently widely used NIST (National Institute of Standards and Technology)/CEESI (Colorado Engineering Experiment Station, Inc) primary standards for flow measurement have demonstrated a measurement uncertainty of 0.3 % for the new LDV standard, which meets the target of reducing the measurement uncertainty of LNG custody transfer by a factor two (starting from 1 %). This LDV standard can be used in the validation process of the new flow meter calibration facility in the Netherlands, as well as, as an independent alternative method for flow measurements of LNG.

The development and validation of novel and improved methods for measuring LNG composition

The project developed a new sampler/vaporiser combination for representative LNG liquid sampling, followed by complete and representative evaporation for composition measurements with gas chromatography. Initially, the results were not satisfactory because of leakage issues, however, these were resolved. The final acceptance tests of the new sampler/vaporiser combination were successfully performed with liquid nitrogen and LNG. The validation of the sampler/vaporiser will be performed after the implementation of the device in the mid-scale flow calibration facility that was developed in objective 1, and will be useful for other LNG plants.

In future work the combination of the new sampler/vaporiser combination with a reference liquefier, is one of the deliverables in the follow-on EMPIR project 16ENG09 LNG III and it is expected that calibration with metrologically traceable LNG composition standards will be made possible.

In addition to the sampler/vaporiser combination, a new prototype LNG sampler was built in order to provide improved insulation and to maintain a representative sample. Additional sampling points were also added to measure the temperature in order to prevent LNG from boiling. The new sampler was used to take samples at an LNG refuelling station to study ageing effects on LNG composition. The composition of LNG can change over time as the lower order hydrocarbons evaporate more readily. LNG composition measurements of samples were taken at two-week intervals and showed no ageing effects for the refuelling station. The project's new sampling method can now be used for other fuel stations and at a lower refuelling frequency in order to determine differences in LNG composition.

The presence of particles is not desirable in LNG as they can cause damage to valves and instruments. Therefore the project's new sampling method was used to facilitate the measurements of particles with an optical particle counter. From this, the project's equipment and methodology are now validated for use in identifing particle concentrations in a gaseous stream of LNG at refuelling stations.

The development of a method for the determination of the MN, including a correlation of the MN to the LNG composition

In order to operate an engine in the most efficient way, it should be run as close as possible to its knocking point i.e. the point during the engine combustion where part of the fuel spontaneously ignites. The MN, together with the engine type and the operational conditions, determines the knocking point. Consequently, in order to run an engine at its most efficient setting, the MN needs to be determined.

A new algorithm for the calculation of the MN from LNG composition was developed based on existing algorithms. The new algorithm includes the effect of higher order hydrocarbons, such as pentane, as these have the potential, because of the ageing effect, to be present in higher concentrations in LNG samples and have a relatively high impact on the MN. The new algorithm has a calculated MN and an uncertainty budget in the range of 0.3 % - 0.8 %, which is lower than for existing algorithms,

Validation of the new algorithm was performed by experiments on two different single-cylinder spark ignition engines, using certified natural gas mixtures of different compositions. The calculated results agreed with the experimental results within the uncertainty of the measurements. However, the results showed a lower measured MN in the low MN range and a higher measured MN in the upper MN range, when compared to the calculated MN. Further experiments are needed to confirm this phenomenon.

Validation was also performed with measurements of the ignition delay time (i.e. a measure of knocking propensity) with a rapid compression machine as an alternative method to the engine experiments. The results were satisfactory for the hydrogen in methane mixtures and for natural gas mixtures, the expected trend was observable, i.e. that the ignition delay time increases at lower temperatures. However, no clear correlation could be found between the experimental results and the calculated MN. It is possible that the variety of chemical reactions during the combustion process was too complex to fit the reaction-kinetics model that was used for the interpretation of the data. Therefore, further measurements are needed on less-complex mixtures such as propane in methane, butane in methane or other binary or ternary mixtures of the lower hydrocarbons in methane in order to improve knowledge on the reaction-kinetics of the combustion process.

The validation and improvement of models for LNG density prediction and associated uncertainty evaluation

The equation of state (EoS) is the relationship between temperature, pressure, volume, internal energy or specific heat, and characterises the state of matter of a material under a given set of physical conditions. A new fundamental EoS, the Enhanced Revised Klosek McKinley Method (ERKM), was developed for LNG using the latest high-precision density data of LNG mixtures, based on the existing Klosek McKinley method, a well-established model for the calculation of saturated liquid densities. The ERKM measurements agreed with the GERG-2008 (the European gas research group) EoS, with the benefit that the ERKM results have a much lower uncertainty. The method and the results were published and a free software tool, based on an MS Excel spreadsheet, including this new EoS together with other existing equations of state was released by the project.

The method has been recognised internationally as an improvement beyond the state-of-the-art and it was implemented in the latest release of the GIIGNL (International Group of Liquefied Natural Gas Importers) handbook in 2017, which is the leading guideline for all LNG measurements

In addition to this, a prototype sensor was developed for on-line density and speed of sound measurements (the key parameter for ultrasonic flowmeters) to transfer metrological traceability to field conditions. Preliminary testing with liquid methane indicate a measurement uncertainty which is a significant improvement over the current state-of-the-art, however tests with LNG still have to be performed. A patenting is in process for the prototype sensor.

A literature study on thermodynamic data was used as the basis for a report and guidelines about the validity, traceability and uncertainty of key parameters for the calculation of energy and enthalpy of different LNG compositions at cryogenic conditions. The guidelines have led to reduced uncertainty levels for liquefaction and regasification processes and are available on the project website.

Actual and potential impact

Dissemination

The project has generated 5 publications in high quality peer reviewed journals, such as The Journal of Chemical Thermodynamics and Fuel Processing Technology and Fuel, and another 4 papers have been submitted. A paper describing the methods and the results for determining the composition of LNG, developed in objective 2, was submitted to the Journal of Natural Gas Science & Engineering. An additional 3 papers were included in conference proceedings. These are all available on the project website www.lngmetrology.info

17 presentations and 5 posters have also been given at international conferences such as the 19th Symposium on Thermophysical Properties (USA, 2015), Flomeko (Austalia, 2016) and the Gas Analysis Symposium (the Netherlands, 2017).

Four stakeholder workshops were hosted by the project and had an attendance of 50-150 participants each. Information and results from the project were presented at the workshop, in combination with presentations by invited speakers from industry and universities.

The ERKM for the prediction of the LNG density was added to the new release of the GIIGNL handbook and is available for end users. A software tool for the implementation of the ERKM and other equations of state is available from the Rühr University of Bochum as part of the work from Researcher Excellence Grants (REG(RUB)). A guideline on the traceability of energy calculations was also written, to ensure the correct use of the relevant physical quantities, and is available on the project website.

Impact on standards

The newly established working group on ISO/TC 28 WG 20 Dynamic measurement of LG, chaired by VSL, has written the committee draft on the new ISO standard for dynamic measurement of LNG. The new algorithm for the calculation of the MN and the results of the engine experiments (objective 3) will be communicated to the new ISO/TC193/WG8 to support a new ISO standard for the assessment of the knock resistance of natural gas fuels.

Early impact

Examples of early impact from the project include:

- Increased knowledge on available instrumentation and their performance at cryogenic conditions. This will improve the calibration and the reliability of such instruments.

- The newly built facility for flow meter calibration will be used for traceable flow meter calibration with high accuracy in the follow-on project 16ENG09. This will enable improved reliable measurement results in the LNG custody transfer chain.
- The ERKM EoS together with the patented speed-of-sound and density sensor, (owned by INRIM) will reduce the uncertainty of density measurements of LNG, which is one of the key parameters for energy content.
- The project's improved sampling techniques will enable more representative determination of quality parameters such as ageing effect and particles in LNG, and is an important step for the realisation of metrologically traceable LNG composition measurements. This will also help the development of new analytical measurement techniques and will support the validation of on-line sensors for composition and MN measurements.

Potential impact

LNG is the cleanest of all fossil fuels and is regarded as a transition fuel to a bio based economy of which the long-term contribution will be towards 'zero' CO_2 emissions. By improving and strengthening the basis for LNG trade, the project's results will have a positive effect on the popularity of this fuel and contribute to a reduction in CO_2 emissions. An improved LNG measurement infrastructure, together with a harmonised method to calculate the MN, will support use of LNG as a fuel and enable truck and ship engine manufacturers to focus more on the development of improved engines using LNG. As the use of LNG grows so more LNG refuelling stations will be built and exploited with a growing acceptance of LNG as a transport fuel. This project took a significant step towards enabling the use of LNG (and bio-LNG) as transport fuel which will lead to a further reduction of CO_2, SO_2, NO_2, particle emissions and noise in land and marine transport.

List of publications

[1]. Development of a special single-sinker densimeter for cryogenic liquid mixtures and first results for a liquefied natural gas (LNG). M. Richter, R. Kleinrahm, R. Lentner, R. Span *Journal of Chemical Thermodynamics 93 (2016), 205 – 221. dx.doi.org/10.1016/j.jct.2015.09.034*

[2]. Density Measurements of Liquefied Natural Gas (LNG) over the Temperature Range from (105 to 135) K at Pressures up to 8.9 MPa. R. Lentner, M. Richter, R. Kleinrahm, R. Span *The Journal of Chemical Thermodynamics, 91, 17-29*

[3]. Enhancement of the Revised Klosek and McKinley Method for Density Calculations of Liquefied Natural Gas (LNG) over the Temperature Range from (100 to 135) K at Pressures up to 10 MPa. C. Tietz, M. Richter, R. Kleinrahm, R. Span *Fuel processing technology 165 (2017), 19-26,* http://www.sciencedirect.com/science/article/pii/S037838201631308X

[4]. Novel algorithm for calculating the methane number of liquefied natural gas with defined uncertainty. Björn Gieseking, Andrew S. Brown *Fuel 185 (2016) 932–940, http://dx.doi.org/10.1016/j.fuel.2016.07.105*

[5]. Density measurements of methane-rich binary mixtures over the temperature range from (100 to 180) K at pressures up to 10 MPa. Lentner, R.; Richter, M.; Kleinrahm, R.; Eckmann, P.; Span, R *Journal of Chemical Thermodynamics 93 (2016), 205 – 221. dx.doi.org/10.1016/j.jct.2015.09.034*

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JRP-Coordinator: Gerard Nieuwenkamp, VSL Tel: +31 152691682 E-mail: gnieuwenkamp@vsl.nl JRP website address: www.lngmetrology.info	
JRP-Partners: JRP-Partner 1 VSL, the Netherlands JRP-Partner 2 CESAME, France JRP-Partner 3 CMI, Czech republic JRP-Partner 4 FORCE, Denmark JRP-Partner 5 INRIM, Italy JRP-Partner 6 JV, Norway	JRP-Partner 7 NPL, United Kingdom JRP-Partner 8 PTB, Germany JRP-Partner 9 RISE, Sweden JRP-Partner 10 Shell, the Netherlands JRP-Partner 11 OGM, United Kingdom
REG-Researcher 1 (associated Home Organisation):	Roland Span RUB, Germany
REG-Researcher 2 (associated Home Organisation):	Peter Eilts TUBS, Germany
REG-Researcher 3 (associated Home Organisation):	Roland Span RUB, Germany
RMG-Researcher 1 (associated Home Organisation):	Jan Sluse CMI, Czech Republic

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