# FINAL PUBLISHABLE JRP REPORT

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# 1 Executive Summary

## Introduction

The LNG II project has significantly contributed to an improved metrological infrastructure for measurements of liquefied natural gas (LNG). The first ever LNG flow calibration facility has been developed and constructed in the Netherlands and samplers and sampling techniques have been developed to improve the measurements of LNG composition and particles and to study the ageing effect of LNG. A new density equation of state has also been developed and adopted in the 5$^{th}$ edition of the International Group of Liquefied Natural Gas Importers (GIIGNL) LNG Custody Transfer Handbook and a new algorithm, validated with engine experiments, has been developed for the calculation of the methane number (MN).

## The Problem

LNG is a cleaner alternative to pipeline gas and it is currently recognised as the only alternative for diesel for heavy duty transport. However, the metrology for energy, composition, methane number and density of LNG is lagging behind. LNG is a liquid mixture at a temperature of 162 $^{o}$C, with a composition that changes over time. These measurements are challenging and not straightforward. Therefore, currently, there is an urgent need from industry and society to improve this metrological infrastructure in order to obtain reliable results with defined and realistic uncertainties thus ensuring fair trade of LNG, reducing the financial risk and improving the performance of LNG as a fuel.

## The Solution

To meet the challenges described above, this project set out to develop new or improved measurement calibration standards and to develop a better understanding of calculation models and algorithms for LNG. The following objectives were defined:

- Design and construction of the first in the world flow meter calibration facility for LNG, and the development of an alternative flow metering technique by Laser Doppler Velocimetry,
- Development of improved LNG sampling and vaporisation devices, including the performance of particle measurements in gaseous LNG,
- Development of a new algorityhm for the calculation of the MN, validated by engine experiments on synthetically prepared gas mixtures,
- Improvement of the measurements and the equation of state for density measurements and preparation of a report on the traceability of thermodynamic data,

The measurement results obtained should be metrologically traceable, including full uncertainty budgets. The results should be communicated to relevant standardisation committees to improve the quality of written standards and to harmonise the measurement methods used for the various properties of LNG.

## Impact

A unique facility for flow meter calibration and research has been constructed in the Netherlands, although initial tests and validation still need to be performed. 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 improvement in flow metering methods and the reduction of uncertainty. Linked to this, a first draft of a new ISO standard for dynamic flow measurements of LNG is being written within the new ISO/TC28/WG20 Dynamic measurement of Liquefied Natural Gas.

The project's new sampling and evaporation techniques have enabled reliable measurements of LNG ageing and the presence of particles, to demonstrate the quality specifications of LNG.

The new and validated algorithm for the calculation of the MN, including measurement uncertainty, will enable LNG users to fine-tune their engines for ships and trucks for optimal performance. Ultimately, this will save significant amounts of money, and as an additional benefit, it will reduce the $CO_2$ emissions from the engines.

A primary method for LNG density measurements was constructed and an improved equation of state for density measurements was developed and has already been included in the 5$^{th}$ edition of the GIIGNL LNG

Custody Transfer Handbook that was released in 2017. The GIIGNL LNG Custody Transfer Handbook provides practical guidance on the equipment and methodology for determining the thermal energy of LNG. It is produced by GIIGNL which has the objective is to promote the development of activities related to LNG, and a membership composed of nearly all the companies in the world active in the import, custody transfer and regasification of LNG.

Finally, the project developed and tested an ultrasonic sensor for density and speed of sound measurements of LNG and a patenting process is pending. This ultrasonic sensor, has been calibrated with a traceable primary method and hence can now be used to transfer its traceability to on-line measurements, resulting in higher reliability and lower uncertainties for LNG measurements.

## 2 Project context, rationale and objectives

### Context

LNG is a strategic, and in the case of long distances, a more economical alternative to pipeline gas. For Europe, a priority of the EC integrated energy policy is an improved infrastructure for LNG which has been motivated by the need to ensure a more diversified and secure energy supply and fair and open trade in natural gas. As addressed in the “Clean Power for Transport package”, the utilisation of LNG and LBG as transport fuels constitute one of the pillars of the European Union clean fuel strategy that was launched in 2013. Taking into consideration the fact that the alternatives to diesel are limited, LNG is particularly suited for long-distance road and water transport. Indeed, LNG implementation enables the stringent pollutant emission limits of future EURO VI standards to be met more cost-efficiently compared to conventional fuels. Engines running on LNG also produce far less noise than diesel-operated engines. Therefore, trucks running on LNG are becoming the preferred choice for deliveries in urban areas in the early morning and late at night (done to reduce the traffic in peak hours). Furthermore, LNG is an attractive fuel to meet the new limits for sulphur content in marine fuels and for NOx-emissions from marine engines.

LNG is also used to transport natural gas from and to locations where no pipeline infrastructure exists. After regasification of the liquid form, the natural gas can be transported to the main end users: i.e. power plants, industry and households.

LNG has become an increasingly important supply source in meeting the world’s energy needs. The total trade has increased nearly five times in the past two decades from 53 million tons in 1990 to over 240 million tons in 2011 and this is expected to further grow to 450 million tons per annum by 2025.

Natural gas, as Compressed Natural Gas and LNG, is the fastest-growing fuel in the transportation sector, with a predicted average annual growth rate of 11.9 % from 2011 to 2040. However, the distribution chain is extending with LNG as transport fuel and it will emerge as a key transportation fuel during the next five years hence doing more to slow oil demand growth than electric cars and biofuels combined. The EU has recently granted funding of approximately €105 million for seven LNG related infrastructural projects. So, while the development of LNG as transport fuel is clearly taking off, a commonly agreed measurement practice and metrological framework needs to be put in place. The roll-out of LNG as clean transport fuel requires the custody transfer measurements to be on a par with traditional fuels. In order to support this, this project has made significant steps by building on the results of the preceding project ENG03 LNG and by addressing newly identified LNG needs.

### Rationale

For billing purposes and to fulfil custody transfer regulations, the amount of LNG in terms of volume flow rate ($m^3$/h) has to be determined. In combination with the density, the amount of LNG in terms of mass flow rate can be calculated, and through measuring the composition, the energy content per mass unit is calculated. 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 1 %. Therefore, the LNG industry needs to improve their measurement accuracies to reduce their financial risks and to improve their mass and energy balances. This can be accomplished through the development of LNG flow calibration standards and accurate models for LNG flow, composition and density measurements. The continuous improvement of measurement systems and the introduction of novel technologies are very important, especially in the development of “small scale distribution” and the application of LNG as a transport fuel, where there is no real alternative to flow metering. However, the lack of traceability leads to delayed introduction of new measurement methods.

For natural gas composition measurements, a well-established metrological infrastructure exists. Comparison and measurement methods are based on gas chromatography, and transfer standards are usually in the form of calibration gas mixtures. In contrast, as LNG is a cryogenic liquid, several issues arise in determining its composition, particularly in the sampling and quantitative vaporisation. LNG consists of a mixture of different hydrocarbons and nitrogen with different vaporisation behaviour. As a result, due to the constant process of the loss of vapour phase (boil off), the composition can change over time. Consequently, there is a need to perform on-line composition measurements across the complete chain of LNG applications. In addition, traceable calibration LNG mixtures to calibrate analytical instruments such as gas chromatographs and Raman spectrometers do not exist. Therefore, the development of novel and improved methods for measuring LNG composition are needed.

One of the potential showstoppers in the roll-out of LNG as fuel is the lack of a commonly agreed MN. The MN is the equivalent of the octane number for liquid fuels. It is a parameter related to the performance of natural gas, LNG and related fuels and the knocking behaviour in combustion engines. Thus, the mix of fuel and air intake in an engine will be tuned on the calculated MN in order to obtain optimal engine performance. Several algorithms to calculate the MN from the LNG composition exist in literature, but all give different results, which has a significant impact on operational costs. A harmonised and accepted method for the calculation of the MN was lacking prior to this project. Therefore, the development of a method for the determination of the MN, including a correlation of the MN to the LNG composition is a crucial element for the roll-out of LNG as a transport fuel.

Further to this, a validated and improved model for LNG density prediction and associated uncertainty evaluation is required as one of the more significant sources of uncertainty in measured energy. The range of density calculation methods used by industry gives variable results and these methods are traceable only to a limited data set with a relatively high uncertainty and potentially significant biases. Part of the dataset was produced several decades ago, occasionally as an extrapolation from measurements on water at ambient conditions rather than on LNG at cryogenic conditions. Therefore, this creates the need for (i) an extended and improved data set, (ii) knowledge of thermodynamic input parameters and (iii) a valid equation of state. A state-of-the-art primary density standard is also needed to establish traceability and to validate on-line measurement techniques in order to transfer traceability to field measurements.

**Objectives**

The aim of this project was to further develop the metrological framework for LNG, both for small and large-scale applications. This should contribute to a reduction of the measurement uncertainty of LNG custody transfer by a factor two and enable the development of LNG as a transport fuel by improved knowledge and reliability in the measurement results and LNG parameters.

Therefore, the project had the following objectives;

1. Development and validation of novel and traceable calibration standards of LNG mass and volume flow for vehicle fuel dispensing and ship bunkering. A mid-scale LNG mass and volume flow facility up to 200 $m^3$/h (90 tons/h) will be built, validated and used for research. This standard will be traceable to the previously developed primary flow standard. It will be cross-validated using a new Laser Doppler Velocimetry (LDV) based standard;
2. Development and validation of novel and improved methods for measuring LNG composition to address the online monitoring of the LNG quality and issues with sampling LNG. An LNG composition calibration system will be developed and integrated into the LNG flow facility. It will be cross-validated with a newly developed reference LNG liquefaction system. The latter will also be used to validate Raman spectroscopy systems;
3. Development of a method for the determination of the methane number, including a correlation of the methane number 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 A new set of measurement data will be created with a 5 times lower uncertainty than existing data and an improved correlation between density and composition will be established. A cryogenic Speed of Sound (SoS) measurement system will be developed to establish an improved correlation between SoS and density.

## 3 Research results

### *3.1 Development and validation of novel and traceable calibration standards of LNG mass and volume flow for vehicle fuel dispensing and ship bunkering;*

LNG flow meters are available and ready to be used for LNG custody transfer, except for two critical missing elements. The first is the availability of calibration standards and the second is the availability of a written standard that can be referred to in industry. Both items are required to achieve trust in the LNG measurement results.

An LNG mass flow calibration standard to provide traceability to the small and mid-scale LNG market therefore needed to be developed. A flow loop has been designed (see Figure 1) which is being constructed (see Figure 2) at a new location in the Rotterdam harbor area in the Netherlands. The design and construction is being performed and/or supported by VSL, FORCE, RISE, Shell and OGM, with significant support from industrial stakeholders. The loop is designed for flow measurements up to 200 $m^3$/h and the results will be traceable to the primary LNG mass flow standard developed by VSL in the preceding project ENG03 LNG.

***Figure 1: Design of the Mid-scale flow calibration facility in the Rotterdam harbor area***


***Figure 2: a photo of the pumps (1), meter cold box including the reference flow meters (2) and a heat exchanger box 930 as installed on-site at the Mid-scale flow calibration facility in the Rotterdam harbor area***

At the final stage of the project the meter under test section (MuT), the diluter, the cold box and the control room have been installed at the location. Software has been developed and tested under the supervision of VSL and RISE, and is ready for the final acceptance tests. HAZOP studies have been performed under supervision by RISE, VSL to ensure the safety during operation. Initial tests and validation of the facility is foreseen to start in early 2018.

The prototype Laser Doppler Velocimeter (LDV) standard developed by Cesame in the preceding project ENG03 LNG as an alternative method for flow metering, has been validated under cryogenic conditions. The final design was made by Cesame with the help of numerical simulations by CMI to find optimum pipe length, venture tube diameter and LDV package size. A comparison was made with liquid nitrogen on the NIST/CEESI facilities in Boulder USA, with very encouraging results (see figure 3). From this it can be concluded that the LDV is consistent with the primary standard of NIST/CEESI.

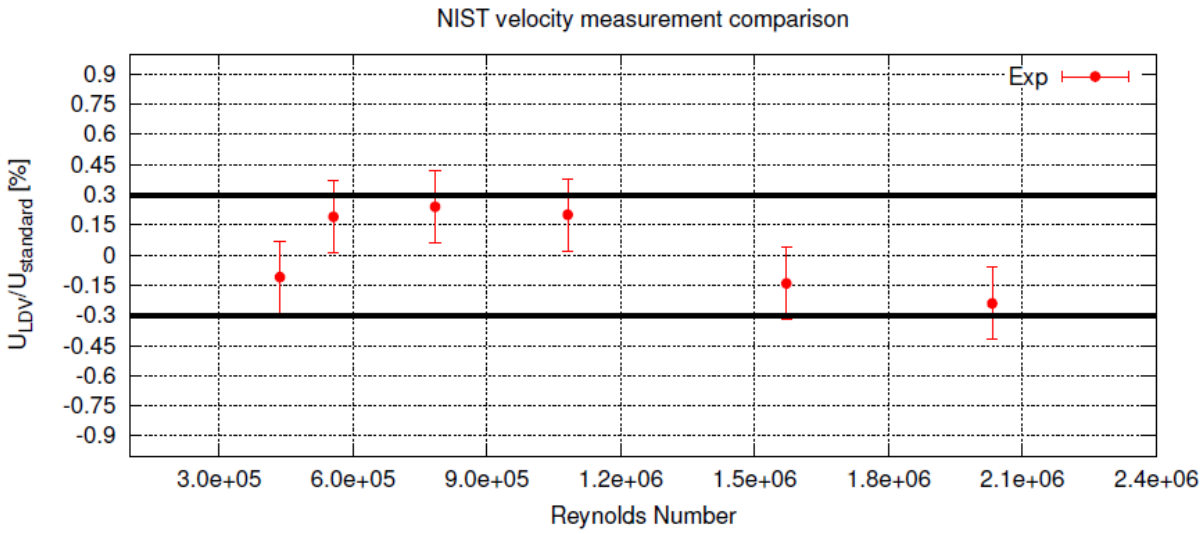



***Figure 3: comparison of the LDV results for liquid $N_2$ with the NIST standards***

Accreditation has been achieved to operate the LDV standard in explosive environments and the first experiments have been performed at an LNG production site. A full uncertainty budget has been calculated for LNG measurements and the first results show a measurement uncertainty of 0.3% relative.

A new ISO working group has been established (ISO/TC28/WG20), chaired by VSL, to work on a new standard for the “Dynamic measurement of Liquefied Natural Gas”. The Working Draft is finished and a committee draft will be presented by the end of 2017.

**Conclusions of 3.1:**

The project partially met its objective to develop and validate novel and traceable calibration standards of LNG mass and volume flow for vehicle fuel dispensing and ship bunkering. A new calibration and research facility for LNG flow meters has been developed and constructed in the Rotterdam harbour area in the Netherlands, in close cooperation with many scientific and industrial partners, although initial tests and validation still need to be performed. The commissioning and validation plans are written and are expected to be executed in 2018. Metrological traceability is obtained by implementation of the primary LNG mass flow standard that was developed in the preceding ENG03 LNG project.

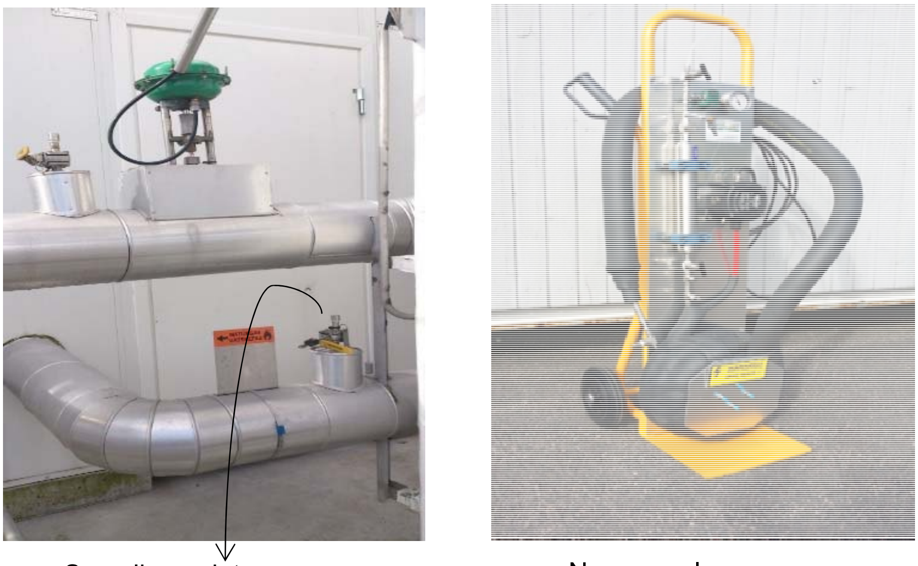
A cryogenic LDV method for an independent cross-validation is developed and accredited for operation under ATEX conditions. Validation results show consistency with primary flow standards.

A new working group (WG20) within ISO/TC28 has been established to ensure the implementation of the gained knowledge into a written standard for dynamic flow measurements of LNG.

### 3.2 Development and validation of novel and improved methods for measuring LNG composition to address the online monitoring of the LNG quality and issues with sampling LNG.

A well-established metrological infrastructure exists for composition measurements of natural gas. Comparison and measurement methods are based on gas chromatography, and transfer standards are usually in the form of calibration gas mixtures. However, as LNG is a cryogenic multicomponent liquid mixture, several issues arise in determining its composition: in particular sampling and quantitative vaporisation, as well as the need for measuring online the composition, preferably with equipment with a low cost of ownership. This creates the need for the development of novel and improved methods for sampling and measuring LNG composition.

LNG is a cryogenic mixture containing a number of hydrocarbons and nitrogen (and some potential other residuals). As the smaller hydrocarbons (methane and ethane) evaporate faster than the heavier hydrocarbons (propane, butane and pentane), the vapour phase above the LNG will be different in composition compared to the liquid phase. This evaporation of the smaller hydrocarbons also implies that the composition and physical properties of the LNG changes over time. The enrichment of heavier hydrocarbons by this evaporation effect is called ageing. As a result of the changing composition, taking a representative sample of LNG becomes very challenging. Figure 4 shows a new design, made by RISE with help of CMI, for a sampler which uses improved isolation to prevent evaporation of LNG and thus prevent the change in composition.



Sampling point New sampler

*Figure 4: the new sampler for LNG as developed by RISE*

The new sampler is used to take samples from an LNG fuelling station within the time interval between refilling of the LNG storage tank. The sampler worked adequately and no ageing effects were observed at the particular station used. In addition, the method can be easily used at other stations, with different LNG composition and different refilling time intervals.

For the measurement of the LNG composition, reference standards are lacking. An ambitious plan in the project was the design and construction of a liquefier to convert natural gas from a known composition into LNG with a known composition. In combination with a new and dedicated sampler/vaporiser, such prepared LNG samples could be used as a reference materials for the calibration of analytical instruments such as gas chromatographs and Raman spectrometers.

Early on in the project, NPL concluded that the construction of a liquefier was not feasible within the budget and time frame of the project.

However, the construction of a new sampler/vaporiser combination was continued. The sampler/vaporiser has been constructed (figure 5) and the final acceptance tests have been 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 (from objective 1).

*Figure 5: the new sampler/vaporiser for LNG composition measurements*

During the project, the potential presence of particles in the gaseous phase of the LNG became a topic of growing importance. Therefore, the project focussed on this instead of the work on the liquefier. The project developed an appropriate online method for measuring particulates in a stream of gaseous LNG. The method was to enable real-time measurement of the particles at, for example, a compressed natural gas station or during transfer/injection into the grid.

An optical particle counter (OPC) was identified as a candidate analyser to meet this measurement challenge. The following issues for when using an OPC for measurement of particles in LNG were taken into account:

- The OPC uses an internal pump which is unsuitable for flammable gasses such as gaseous LNG;
- The OPC is not intrinsically safe (ATEX rated), as required by LNG filling stations;
- The OPC head operates at nominally ambient pressure.

A sampling system was designed by NPL to overcome these issues. Due to the fact that the OPC head has no electrical or mechanical components it was accepted that if only this part was exposed to the LNG then there would be no risk of ignition. Therefore, by purchasing two 30-meter fibre-optic cables the OPC head could be considered as a separate intrinsically safe instrument (as only light passes between the head and the body of the instrument). The instrument could therefore be used on an ATEX rated site with the measurement head in the flammable area and the instrument body up to 30 meters away in a safe area (see figure 6). The sampler that was developed was used to study the ageing effect of LNG and has been used in a joint measurement campaign by RISE and NPL.

*Figure 6: Online Particle measurements with the OPC*

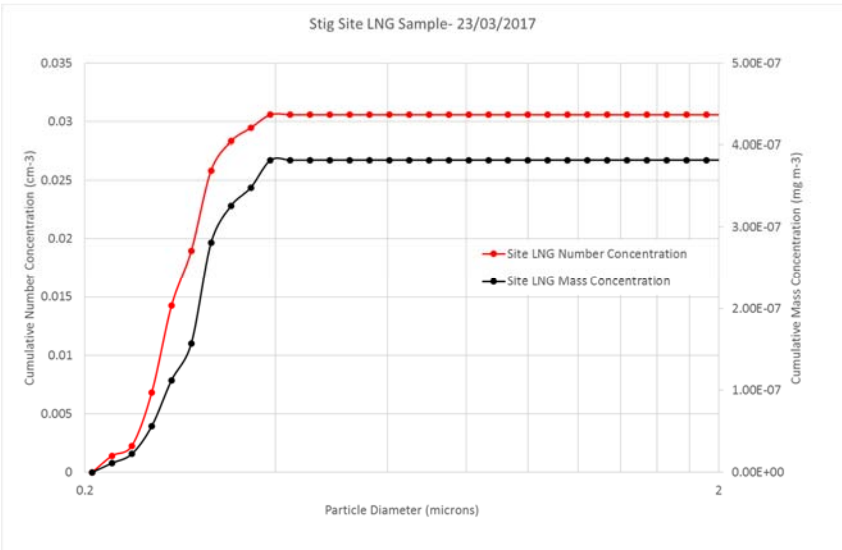



*Figure 7: Results of the on-site particle measurements in LNG with the OPC*

The particle number concentrations, expressed as particles per cubic centimetre, peaked at nominally 0.03 $cm^{-3}$ for both days. There was no contribution from particles above 0.5 microns in diameter (see figure 7).

The equipment and the methodology can be used to identify particle number concentrations in a gaseous stream of LNG at refuelling stations in the future. The measurement system and detector were shown to work reliably in the field. The larger particles were expected to be removed within the sampling system due to impaction. The smaller particles, however, in particular those of nominally 0.3 µm and below, have a higher penetration efficiency through the system. These 0.3 µm particles could potentially be used as a ‘canary species’, to indicate the presence of larger particle fractions which may have been removed by the sampling system.

**Conclusions of 3.2:**

The project partially met its objective to develop and validate novel and improved methods for measuring LNG composition to address the online monitoring of the LNG quality and issues with sampling LNG. An improved sampling method has been developed and tested for representative composition measurements. The sampler is used in combination with an OPC for measurement of particles in the gaseous stream of LNG as a quality indicator. A liquefier for the production of traceable LNG reference compositions was not produced according to the initial plan of this project, but this activity has been incorporated in the 16ENG09 LNGIII project. A cryogenic sampler/vaporiser was developed and tested with LNG to enable adequate calibration of analytical composition measurement instruments such as e.g. gas chromatography with the traceable reference LNG samples prepared with the liquefier. The validation of the sampler/vaporiser and the calculation of the measurement uncertainty still have to be performed.

### 3.3 Development of a method for the determination of the methane number, including a correlation of the methane number to the LNG composition, in support of the use of LNG as transport fuel.

One of the potential showstoppers for the roll-out of LNG as a transport fuel is the lack of a commonly agreed MN. The MN is a parameter related to the knocking behaviour of natural gas in combustion engines. The MN is used in the quality specifications of the LNG and to finetune the engine performance for optimal operation. At the start of the project, different algorithms are used to calculate the MN, and they showed a significant variation of results.

Within the project, a new algorithm has been developed by NPL including the implementation of the effect of higher hydrocarbons, such as pentane, as these components are expected to be present in higher concentrations in LNG samples and have a relatively high impact on the MN. The algorithm comes with an uncertainty budget, which is an improvement over the existing algorithms. The algorithm is programmed in a user-friendly Microsoft Excel spreadsheet and has been validated by experiments with a selection of certified gas mixtures on two different Spark Ignition engines and a Rapid Compression Machine.

Figure 8 shows the comparison of the results for the calculation of the MN from the composition with the project's new algorithm versus two commonly used algorithms, i.e. the DGC and the MWM for LNG compositions originating from different production locations.

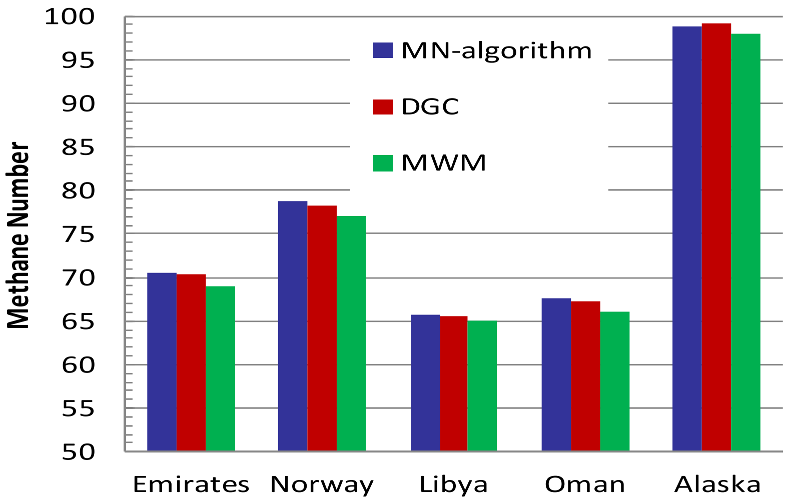



***Figure 8: Comparison of the results with the new algorithm (in blue) versus two commonly used algorithms, i.e. the DGC and the MWM for LNG compositions originating from different production locations***

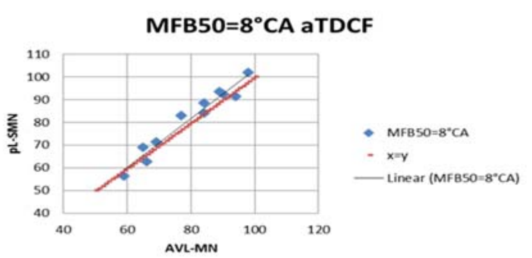
The set of test gas mixtures consisted of a selection of natural gas mixtures, representing LNG compositions from bigger global production sources. Also, a number of n- and iso-pentane in methane mixtures were included to study the influence of pentanes in the fuel on the MN. A set of five hydrogen in methane mixtures were used to calibrate the instruments and to relate the experimental results to other algorithms.

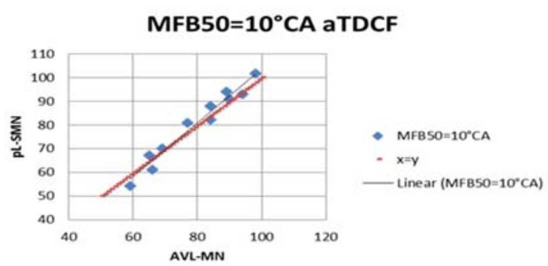
VSL, NPL, a Researcher Excellence Grant (REG) at (TUBS) and PTB performed a literature study for the MN experiments and selected a set of gas mixtures. Table 1 gives an overview of the nominal compositions of the selected gas mixtures that were used for the experiments. After the experiments, samples of the mixtures (taken by REG(TUBS) and PTB with a new developed sampler) were certified against VSL's and NPL's primary reference gas standards for their exact composition and uncertainty.

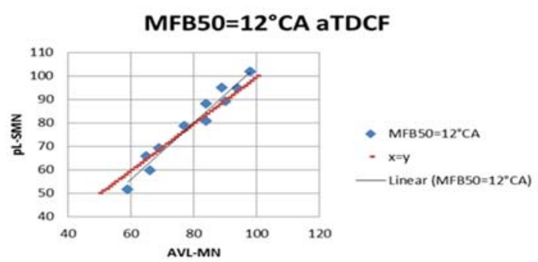
***Table 1: Overview of the gas compositions, expressed as amount-of-substance fractions (cmol/mol) and their calculated MNs***

| Component | $CH_4$ | $C_2H_6$ | $C_3H_8$ | n-$C_4H_{10}$ | i-$C_4H_{10}$ | n-$C_5H_{12}$ | i-$C_5H_{12}$ | n-$C_6H_{14}$ | $N_2$ | $CO_2$ | $H_2$ | MN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mix 1 | 78.80 | 14.0 | 3.40 | 0.90 | 1.10 | 0.15 | 0.15 | | 1.5 | | | 59 |
| Mix 2 (Emirates) | 84.52 | 12.9 | 1.50 | 0.21 | 0.22 | 0.03 | 0.02 | | 0.6 | | | 69 |
| Mix 3 (Norway) | 91.80 | 5.70 | 1.30 | 0.15 | 0.17 | 0.04 | 0.04 | | 0.8 | | | 77 |
| Mix 4 (Libya) | 81.69 | 13.38 | 3.67 | 0.27 | 0.28 | 0.01 | 0.01 | | 0.69 | | | 65 |
| Mix 5 (Oman) | 87.89 | 7.27 | 2.92 | 0.71 | 0.65 | 0.10 | 0.11 | | 0.35 | | | 66 |
| Mix 6 (AVL 6) | 95.01 | 2.62 | 0.73 | 0.20 | 0.15 | 0.06 | 0.09 | 0.22 | 0.54 | 0.38 | | 82 |
| Mix 7 | 97.876 | 1.00 | 0.50 | 0.21 | 0.18 | 0.016 | 0.018 | | 0.2 | | | 90 |
| Mix 8 (Alaska) | 99.68 | 0.09 | 0.03 | 0.01 | 0.01 | 0.005 | 0.005 | | 0.17 | | | 98 |
| calibration MN50 | 50 | | | | | | | | | | 50 | 50 |
| calibration MN60 | 60 | | | | | | | | | | 40 | 60 |
| calibration MN70 | 70 | | | | | | | | | | 30 | 70 |
| calibration MN80 | 80 | | | | | | | | | | 20 | 80 |
| calibration MN90 | 90 | | | | | | | | | | 10 | 90 |
| calibration MN100 | 100 | | | | | | | | | | | 100 |
| Pentane test 1 | 99.4 | | | | | 0.3 | 0.3 | | | | | 84 |
| Pentane test 2 | 99.6 | | | | | 0.2 | 0.2 | | | | | 89 |
| Pentane test 3 | 99.8 | | | | | 0.1 | 0.1 | | | | | 94 |

The experimental MN also known as the service methane number (SMN) of gas mixtures 1-8 (natural gas type mixtures) and the three pentane test mixtures were also measured by REG(TUBS) in a series of engine tests. In these tests, the intake manifold pressure was used as a measure for the knocking propensity of the gases. Four different centres of combustion were used in the tests :8°CA (=Cranck Angle), 10°CA, 12°CA & 14°CA, which yielded different service methane numbers for each mixture.



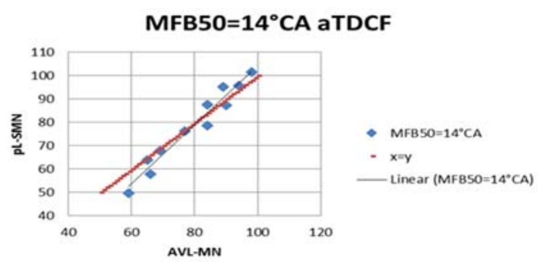



*Figure 9: Results of the experimental service MN on a 600 cc single cylinder Spark Ignition engine.*

The charts in figure 9 show plots of the SMN against the MN calculated for the 11 mixtures tested for a 600 cc single cylinder SI engine.

To study the knocking propensity of different LNG mixtures with a second method, the set of test mixtures shown in table 1 was also used by the PTB for experiments with a Rapid Compression Machine. The LNG mixtures were premixed with oxygen and a constant amount of diluent gases (nitrogen/argon), allowing the measurements in a similar temperature range at an equivalence ratio of $\phi$=0.4/$\lambda$=2.5. The measurements were extended to an equivalence ratio $\phi$=1.2/$\lambda$=0.83 in order to cover a fuel-rich situation and thus a deeper insight into the ignition behaviour of LNG mixtures. Each measurement was performed at a minimum of 3 different temperatures within a temperature range from ~870-1100 K. Ignition delay times were determined for two different pressures (20 bar and 40 bar). Each test series (LNG-Mix) was repeated three times to minimise the uncertainty of the experimental data and averaged to extract the value for the ignition delay time. Figure 10 shows the determined ignition delay times for the LNG mixtures at different pressures at different stoichiometric conditions.

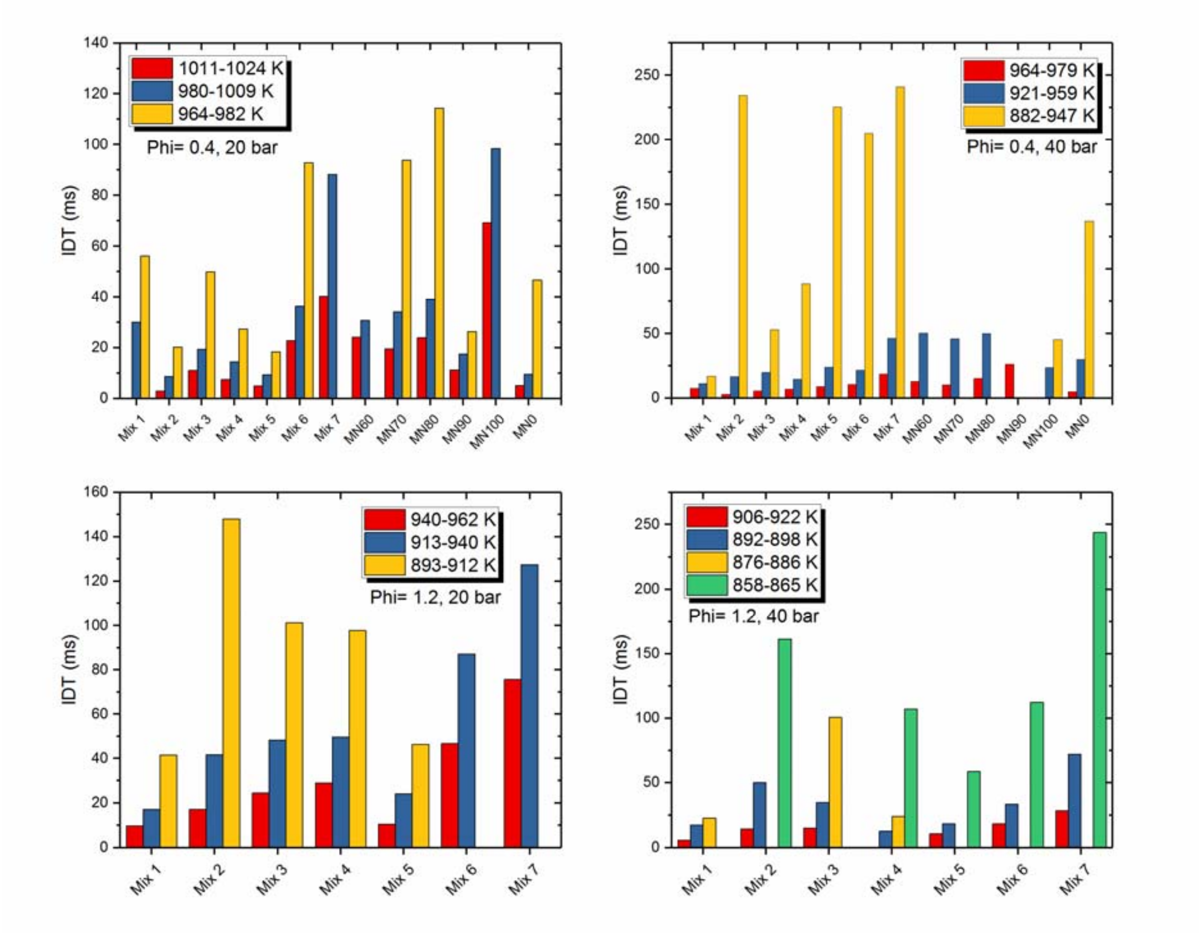



***Figure 10: Determined ignition delay times for the LNG-mixtures at two different pressures and with two different stoichiometries. The bars' colour code indicates similar temperatures***

The algorithm shows similar results (Figure 8) to other existing algorithms. The expanded uncertainty was calculated to be in the range of 0.3 % - 0.8 % relative, depending on the uncertainty in the input parameters. The results were confirmed by the experimental results on the Spark Ignition engines within the uncertainty of the measurements. However, the correlations (Figure 9) show a “tilted” line of the experimental results versus the calculated MN. This results in a lower measured MN in the low range and a higher MN in the high range. Further experiments are needed to confirm this phenomenon.

The results with the ignition delay time measurements were satisfactory for the hydrogen in methane mixtures. For the natural gas mixtures, the expected trend was observable i.e. that the ignition delay time increases at lower temperatures (Figure 10). However, no clear correlation could be found between the experimental results and the calculated MN. A conclusion is that the variety of chemical reactions during the combustion process is too complex to fit the reaction-kinetics model that was used for the interpretation of the data. Therefore, it should be recommended that measurements are performed on less-complex mixtures such as e.g. propane in methane, butane in methane or other binary or ternary mixtures of the lower hydrocarbons in methane.

The algorithm and the results will be offered to the new ISO/TC193 WG8 “Knock Resistance”, to support the production of a harmonised method to calculate the methane number from the composition of the LNG. Further experiments are foreseen in the follow-on project 16ENV09 LNGIII.

**Conclusions of 3.3:**

The project met its objective to develop 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. A new algorithm has been developed, based on a literature study of existing algorithms in combination with specific issues for LNG, such as e.g. potential higher pentane concentrations. The calculated MN is accompanied by a measurement uncertainty, which is not the case for the existing algorithms. Validation of the algorithm has been performed by studying the knocking behaviour during the combustion of a selected set of eleven multicomponent gas mixtures and five hydrogen in methane compositions on two different spark-ignition engines. Validation was done by ignition delay time measurements with a Rapid Compression Machine. However, the experimental results indicate that more experiments (on less complex mixtures) and increased knowledge on the reaction kinetics are required.

### 3.4 Development and validation of an improved model for LNG density prediction and the associated uncertainty evaluation.

A validated and improved model for LNG density prediction and associated uncertainty evaluation was urgently needed since this is still one of the more significant sources of uncertainty in the measured energy. The range of density calculation methods used by industry gives variable results. In addition, these methods are traceable only to a limited data set with a relatively high uncertainty and potentially significant biases. This created the need for an extended and improved data set using the state-of-the-art primary density standard developed as part of the preceding project ENG03 LNG.

The state-of-the-art primary density standard from ENG03 was modified for the density measurements of binary mixtures. To avoid decomposition of the binary mixtures, all measurements in the supercritical region were carried out at least 1 MPa above the cricondenbar. Moreover, to avoid vaporisation of the binary mixtures in the measurement cell, all measurements in the liquid region were carried out at pressures at least 0.1 MPa above the calculated vapor pressure $p_{sat}$. The modified primary density standard was then used to carry-out new experiments by a Researcher Excellence Grant (REG) at RUB on a set of seven binary gas mixtures (see table 2) along four isotherms. A temperature range from $T$ = 100 to 160 K, at pressures up to 9.7 MPa, was used. For the (methane + isobutane) mixture, two additional isotherms at $T$ = (170 and 180) K were investigated.

***Table 2: Gravimetric compositions (mole fraction) and average molar mass M of the studied mixtures***

| Component | methane<br>ethane | methane<br>propane | methane<br>isobutane | methane<br>pentane | methane<br>nitrogen | methane<br>nitrogen | methane<br>nitrogen |
|---|---|---|---|---|---|---|---|
| Composition | 0.75040<br>0.24960 | 0.88030<br>0.11970 | 0.97007<br>0.02993 | 0.99014<br>0.00986 | 0.98998<br>0.01002 | 0.96998<br>0.03002 | 0.69791<br>0.30209 |
| $M/(\mathrm{g \cdot mol^{-1}})$ | 19.543 | 19.400 | 17.302 | 16.596 | 16.162 | 16.402 | 19.659 |

The relative combined expanded uncertainty ($k$ = 2) for the reported density data was estimated to be 0.02 %. Comparisons to the GERG-2008 equation of state revealed relative deviations between −0.573 and –0.003 % for the methane + isobutane mixture and between 0.402 and 0.507 % for the methane + n- pentane) mixture. All other binary mixtures, as listed in Table 1, agree very well with the GERG-2008 equation of state; deviations are within a band of approximately ±0.07 % and, thus, well within the uncertainty of the equation of 0.1 to 0.5 % for $T \leq 140$ K.

A comparison of the experimental binary density data with relevant mixture models led to the development of a new fundamental Equation of State: the Enhaced Revised Klosek McKinley method (ERKM). Figure 11 shows the improvements with respect to the Revised Klosek McKinley method (RKM).

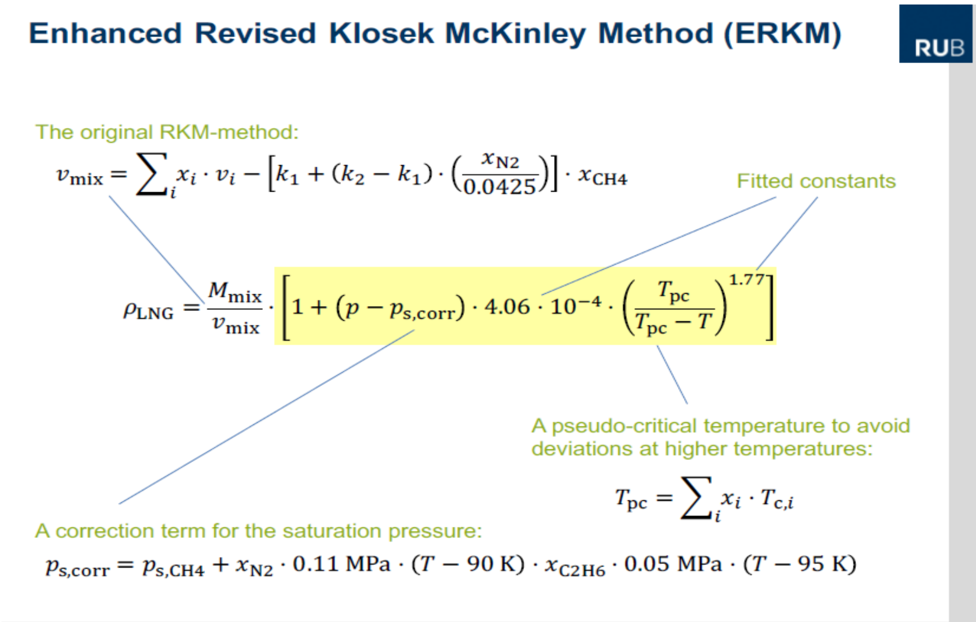



***Figure 11: Schematic overview of the Enhanced Klosek McKinley method (ERKM)***

The calculation of the density and other parameters were implemented in a software tool called TREND. Section 5 contains the contact details for how to get a free copy of the software. The results have also been published in the journal Fuel processing technology and the new ERKM Equation of State will be implemented in the 5th release (2017) of the GIIGNL handbook provided by the International Group of Liquefied Natural Gas Importers http://giignl.org/system/files/giignl_cthb_5.0.web_.pdf.

To implement the improved density prediction into field measurements, an ultrasonic densimeter suitable for obtaining simultaneous measurement of speed-of-sound (SoS) and density in cryogenic flowing liquids was developed by INRIM with support from REG(RUB). Figure 12 shows a picture of the first prototype ultrasonic densimeter that was tested at atmospheric pressure and at a temperature of 20 °C with fluids with a density in the range of 600 to 1000 kg/m$^3$. Modifications to the first prototype ultrasonic densimeter were made and a second prototype ultrasonic densimeter was developed and tested with liquefied methane at a temperature of 100-150 K and pressures up to 10 bar. (A picture is not included due to the patenting process of the second prototype). Tests with LNG still have to be performed on the second prototype ultrasonic densimeter, but based on the preliminary results, a measurement uncertainty of less than 0.1 % relative is expected.

***Figure 12: First version of the ultrasonic densimeter prototype***

The ultrasonic densimeter can be calibrated with a traceable primary method, such as the hydrostatic weighing device which was used by REG(RUB) to optimise the Equation of State. Based on this the ultrasonic densimeter can be used to perform on-line measurements and/or to calibrate other commercial sensors.

As well as predicting the density of the LNG using of thermodynamical models, one of the tasks in the preceding ENG03 project was to calculate the calorific values and enthalpies of formation of typical LNG samples. The results showed a difference between the LNG in the real liquid state (at a temperature of -160 ºC and several bars of pressure) and at pipeline reference conditions (ambient temperature and atmospheric pressure). Another conclusion from the ENG03 project was the lack of uncertainty for many input quantities for calculations, such as heat capacities or enthalpies of formation. Following on from these ENG03 results, a report was produced by PTB, based on a comprehensive literature survey. The report, included an overview of the current available data and a statement how this data can be classified in the sense of traceability. A guideline on the traceability of energy and enthalpy calculations waswritten, to ensure the correct use of the relevant physical quantities. The guideline is available on the project website.

**Conclusions of 3.4:**

The project met its objective to develop and validate an improved model for LNG density prediction and the associated uncertainty evaluation. A new fundamental EoS, the enhanced revised ERKM, has been developed based on experiments with a primary cryogenic densimeter. The method has been published and a free software tool including this new EoS together with other existing equations of state was released. The method has been recognized internationally as an improvement beyond the state-of-the-art and it has been implemented in the latest release of the GIIGNL handbook in 2017.

A prototype sensor has been developed for on-line density and speed of sound measurements to transfer the metrological traceability to field operation. A patenting process for the sensor is pending.

A literature study on thermodynamic data has been the basis for a report and a guideline about the validity, traceability and uncertainty of key parameters for the calculation of energy and enthalpy of different LNG compositions at cryogenic conditions.

## 4 Actual and potential impact

Metrological achievements

A unique flow meter calibration and research facility was designed by the project. All critical elements have been realised and full assembly of the facility is scheduled for by the end of 2017. When operational, this facility will enable calibration with traceable results with an established uncertainty. As there are currently no facilities available world-wide for LNG flow and composition, this facility is an important step for realising trust and confidence in (small scale) LNG trade. The facility also enables the study of the effects of flow-profiles (turbulence, swirl) caused by bends and/or elbows in the upstream or downstream pipeline, two-phase flow and insulation and the inclination of flow meters. This is an important breakthrough and will facilitate reducing the uncertainty in field measurements and improving the reliability of LNG measurement results.

The project's LDV device from objective 1 has been validated to perform flow measurements under cryogenic conditions. The LDV device can be used for on-site flow measurements and will be of great support in the validation of e.g. the new LNG flow calibration facility.

The project's new sampler/vaporiser combination from objective 2 has been successfully tested with liquid methane and LNG and it is a step forward in the production of traceable LNG composition reference standards. The new sampler/vaporiser in combination with a liquefier, can be used to validate and traceably calibrated analytical instruments used for the measurement of the composition, such as e.g. gas chromatography and Raman spectroscopy. Research studies of alternative techniques can also benefit from the metrological anchor point, provided by the LNG composition reference materials.

A new algorithm has been developed by the project for the MN calculation (objective 3), based on a literature study of existing algorithms. This is the first algorithm that is accompanied by a full description of the uncertainty budget and thereby a step towards the incorporation of the MN calculation in a metrological infrastructure. The algorithm was validated by MN measurements with two engines and a Rapid Compression Machine, performed on a series of gas mixtures with traceable compositions. A paper about the new algorithm has been published, and the new algorithm and the experimental results can be used as the basis for a new harmonised standard for the MN calculation.

The revised equation of state for the LNG density calculation and the report and guideline for the traceability of thermodynamically data for energy and enthalpy calculations (objective 4) strengthens the metrological framework for reliable calculations under cryogenic conditions.

Description of dissemination activities

### *Publications*

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. In addition, another 5 papers are, or soon will be, submitted. A list of these papers is provided in section 6. Also, three papers have been submitted to be implemented in conference proceedings.

### *Conferences and presentations*

Results and outputs from the project have also been presented at numerous conferences. A total of 17 presentations and 5 posters have been presented mainly in Europe e.g. the International Gas Analysis Symposium & Exhibition GAS 2017, but also to a number in countries with a high interest in the production or use of LNG, such as the 19th Symposium on Thermophysical Properties in the USA, Singapore and 18th International Conference & Exhibition on Liquefied Natural Gas (LNG18) and the 17 International Flow Measurement Conference (Flomeko 2016) in Australia.

### *Stakeholder engagement*

The project has engaged with stakeholders in a variety of ways. The project received feedback from its advisory board, which included more than 20 stakeholders and collaborators from end user companies such as (in alphabetic order) Emerson, Enagas, Endress+Hauser, Fluxys, Gas Natural Fenosa, GE sensing (chair), Kaiser optical systems, Krohne and Mustang sampling. Members of the advisory board were also present and invited to the project's progress meetings to be informed about the status of the project.

### *Workshops*

A total of six days of training/workshops were given, spread over 4 occasions:

1. In May 2015, a workshop on Metrology for LNG was organised in Copenhagen, Denmark
2. In June 2016, a workshop and a training day for Metrology for LNG were organised in London, UK
3. In April 2017, a two-day Metrology for LNG workshop/conference was organised in Noordwijk aan Zee, the Netherlands
4. In August 2017, a one day workshop/training for LNG was organised in Delft, the Netherlands.

Presentations at these meetings were given by partners, collaborators or stakeholders from the LNG industry. The meetings were attended by 50-150 participants each.

### *Standards*

A new ISO working group (WG20) has been established in ISO/TC28 to prepare a new standard for "Dynamic measurement of Liquefied Natural Gas". One of the partners, VSL was selected as the chairperson of this working group. A working draft of the standard has been written and a committee draft for the new standard will be presented for voting at the end of 2017.

The work that has led to the ERKM equation of state has been communicated to GIIGNL. As a result, the ERKMK will be included in the new 2017 revision of the GIIGNL handbook.

The work on the MN was supposed to form the basis of a New Work Item Proposal for a revised ISO standard in ISO/TC193/WG8, to realise a harmonised method for the MN calculations. A paper describing the algorithm has been published and can form the basis of this NWIP. Due to delays in the project, the realisation of a new ISO standard for MN will be implemented as one of the deliverables in the follow-on EMPIR project 16ENG09 LNGIII.

### *Effective cooperation between partners*

The design of the mid-scale flow calibration facility was a joint effort by VSL, OGM, Shell, FORCE, RISE and JV, with significant support from industrial or municipal stakeholders. In this way, an independent metrological calibration facility has been established that would have otherwise been far beyond the capabilities of a single National Metrology Institute.

The design and validation of the LDV for cryogenic flow measurements was performed by CESAME with important support from CMI for numerical simulations for an optimal design. An additional Researcher Mobility Grant was granted to CMI for further support in this work.

The sampler constructed by RISE and the OPC method developed by NPL have been used in a joint measurement campaign for on-line particle and composition measurements on an LBG plant in Sweden.

VSL, NPL, TUBS and PTB worked together on a literature study to map the state-of-the-art in MN measurements and calculations. Together they decided on a set of mixtures to be used in the experiments and in cooperation, a sampling technique was designed to sample the gases from 50L cylinders into smaller cylinders during the engine experiments at REG(TUBS). The smaller cylinders were sent to PTB for Rapid Compression Machine experiments and to VSL and NPL for composition measurements.

REG(RUB), PTB, INRIM, VSL and RISE have shared the know-how on the LNG behaviour under cryogenic conditions. This was important for the design of the ultrasonic densimeter prototype and the samplers and vaporiser for the composition measurements.

VSL and JV cooperated in a successful effort to establish a new ISO Working Group for the realisation of a new ISO standard for dynamic measurement of Liquefied Natural Gas.

Examples of early impact

The construction of the mid-scale calibration and research facility has attracted a high number of industrial and economical stakeholders, who have supported the construction of the facility. Hereby, a platform has been created to combine the knowledge from research companies, production companies, instrument manufacturers, etc., and to make a joint effort to fulfil the needs in the LNG market.

The Committee Draft for the new ISO standard for “Dynamic measurement of Liquefied Natural Gas” will be ready by the end of 2017. Improved and more comparable measurement results can be expected.

The sampler for LNG is ready and validated and can be exploited for e.g. the study of ageing effects in LNG storage tankers at fuelling stations.

A method for the measurements of particles in LNG has been completed and can provide additional quality specifications for LNG and to prevent potential damage caused by the presence of particles.

The ERKM equation of state for the prediction of LNG density under cryogenic conditions has been implemented in the new revision of the GIIGNL handbook, which is seen as “the Bible” for LNG users and producers. This will improve the reliability of LNG density results and lead to a lower uncertainty in the calculated amount of energy.

The ERKM Equation of State has been implemented in a freeware Microsoft Excel spreadsheet called TREND. The program gives the opportunity to calculate density and other related quantities by using a variety of Equations of State. USB sticks with the program were given to the participants of the workshops in London (2016) and Delft (2017). A free copy of the software can be obtained from RUB and for contact details see section 5. This will improve the quality of the cryogenic density measurements worldwide.

Potential impact

The good cooperation between REG(RUB) and INRIM has led to a successful design for a prototype for an online ultrasonic densimeter that is currently undergoing a patenting process. This will enable high quality online density measurements with metrological traceability.

The LDV is ready to be implemented as a valid alternative for flow measurements.

The improved knowledge on the MN calculation and the potential to create a harmonised standard will be very attractive for the transport industry. Knowledge of the MN will enable the operation of ship- and truck engines in a more effective and economical way, saving money and reducing greenhouse gas emissions. The upcoming trend to use LNG as a fuel for cruise ships and small vessels especially in harbour areas will be supported by this and hence can be adopted in other areas. In addition, the number of truck refuelling stations is growing and will profit from the reliability of measurements in the LNG chain. A publication of the new ERKM algorithm has been published and this will support the realisation of a harmonised standard.

Finally, the report and guideline for the traceability of energy and enthalpy values will be submitted to ISO TC193 (WG13 and WG18), to be used in new revisions of relevant standards

## 5 Website address and contact details

A project website has been set up, which details information about the project, including its objectives, publications, events and presentations. The website address is: http://www.lngmetrology.info

The contact person for general questions with respect to the project is Gerard Nieuwenkamp from VSL: gnieuwenkamp@vsl.nl

The contact person for the construction and the state of the art of the Midscale Calibration Facility at the Dutch Rotterdam harbor area is Dr. Peter Lucas from VSL: plucas@vsl.nl

The contact address for the TREND software tool and the ERKM equation of state for density measurements is TREND@thermo.rub.de

The contact person for the impact of the project is Dr. Kianoosh Hadidi from JV: kih@justervesenet.no

## 6 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*