3.2.1 (REG(TUBS) D3)	Validation protocol for the calculation of the MN from the LNG composition	**VSL**, NPL, PTB, REG(TUBS)	Protocol	Sep 2014	D3.1.2
3.2.2 (REG(TUBS) D4)	Set of at least 4 characterised gas mixtures with traceable composition	**VSL**, NPL, PTB, REG(TUBS)	Samples	Nov 2014, May 2015	D3.2.1
3.3.1 (REG(TUBS) D5)	Service methane number as a function of gas composition for test engine A for well-defined LNG samples over a complete operating range	**REG(TUBS)**	Datasets	May 2015	D3.2.1, D3.2.2
3.3.2 (REG(TUBS) D6)	Service methane number as a function of gas composition for test engine B for well-defined LNG samples over a complete operating range	**REG(TUBS)**	Datasets	Sep 2015	D3.2.1, D3.2.2
3.3.3	Ignition delay measurements using an RCM for well-defined LNG samples	**PTB**	Datasets	Nov 2015	D3.2.1, D3.2.2
3.3.4 (REG(TUBS) D7)	Report on the determination of knocking resistance for characterised LNG samples using SI engine and RCM techniques	**PTB**, REG(TUBS)	Report	May 2016	D3.3.1 to D3.3.3
3.4.1 (REG(TUBS) D8)	Updated model for the calculation of the MN from the LNG composition	**NPL,** VSL, PTB, SP, REG(TUBS), Shell	Model	Nov 2015	D3.1.1, D3.1.2, D3.3.1 to D3.3.3
3.4.2 (REG(TUBS) D9)	Measurement uncertainty for the calculation of the MN from the LNG composition	**NPL,** VSL, PTB, SP, REG(TUBS), Shell	Uncertainty budget	Jan 2016	D3.4.1
3.4.3	Report on the validation of a calculation for the MN from the LNG composition and the correlation of the MN to the LNG composition	**VSL**, NPL, PTB	Report	Sep 2016	D3.3.4, D3.4.1, D3.4.2

C4 WP4: Density, Enthalpy and Calorific Value

*(**PTB**, INRIM, NPL, VSL, REG(RUB))*

Start month: Jun 2014, end month: Feb 2017

The aim of this work package is to provide an improved model for LNG density prediction and uncertainty analysis. The work package consists of 4 Tasks. In Task 4.1 a LNG densimeter (developed as part of the preceding JRP, ENG03 LNG) will be further developed and density data of different LNG samples will be determined. A selected Equation of State (EoS) for LNG will be improved in Task 4.2. In Task 4.3 a LNG densimeter will be constructed which applies to speed of sound measurements and operates with an alternative physical principle compared to the densimeter in Task 4.1. Uncertainties and the traceability of enthalpy and calorific value calculations will be examined in Task 4.4.

The work of this technical work package will lead to the submission for publication of at least four peer reviewed paper. These papers are included in WP5 as D5.1.7, however the resource is included in this WP.

C4.a Description of Work

Task 4.1: LNG density measurements (REG(RUB), VSL, NPL)

(Start Jun 2014, end Dec 2015)

The aim of this task is to further develop a LNG densimeter (developed as part of the preceding JRP, ENG03 LNG) and use it to determine density data of different LNG samples.

A LNG densimeter was developed in the preceding JRP, ENG03 LNG, based on the single-sinker buoyancy principle. This principle was combined with a separate vapour-liquid equilibrium cell (VLE) cell, which allows for liquid-density measurements at cryogenic temperatures without change of the composition of the liquid-phase. Together with a new way of operation (supercritical filling) of the apparatus, this allowed measurements which are much less effected by uncertainties of the liquid-phase composition.

In JRP ENG03, measurements on pure fluids and two LNG samples proved that the principle of the LNG densimeter worked well and the obtained results were consistent and reproducible. However, the force transmission error was unacceptably large at magnetic suspension coupling temperatures below 150 K with a steep increase below c.130 K. Previously, magnetic suspension couplings had never been operated at such low temperatures and in such conditions, as LNG densities can only be measured relative to liquid methane or liquid nitrogen densities. But for methane and nitrogen the temperature dependent force transmission error can be determined by comparison with reference EoS, with an uncertainty of calculated liquid densities of approximately 0.02 %. Therefore, in this way LNG densities can be measured with an uncertainty of approximately 0.05 %.

Currently, RUB is working on a better understanding of temperature dependence and the size of the force transmission error so that either proper models for the correction of the force transmission error can be established or cell materials with smaller low-temperature force-transmission error can be found by the start of ENG60-REG1 REG(RUB). This should lead to a reduction in the uncertainty LNG density measurements to 0.02 %.

Description of activities:

- REG(RUB), with input from VSL, will produce a report on the current understanding of temperature dependence and the size of the force transmission error in LNG density measurements. The report will include whether models for the correction of the force transmission error or cell materials with smaller low-temperature force-transmission error exist. The report will be used to decide whether relative or absolute density measurements are most appropriate and whether a reduction in the uncertainty of LNG density measurements to 0.02 % is possible. (REG(RUB), VSL) (D4.1.1)
- Based on D4.1.1, REG(RUB), with agreement from NPL and VSL will select at least 4 LNG compositions for density measurements with the LNG densimeter from JRP ENG03. REG(RUB) will then use the LNG densimeter from JRP ENG03 to measure the density of the four LNG compositions; with at least six isotherms for each composition. Measurements will include saturated liquid densities and homogeneous liquid states at pressures up to 8 MPa in order to describe the compressibility of LNG (a property often neglected in LNG density calculations). A report on the results of the LNG density measurements will be produced, which will include the level of uncertainty. (REG(RUB), NPL, VSL) (D4.1.2, D4.1.3)

Major facilities to be used:

Thermodynamics laboratories REG(RUB),

Sample mixture preparation and analysis facilities (NPL, VSL)

Task 4.2: Improvement of a selected EoS for LNG density (REG(RUB), VSL)

(Start Nov 2015, end Feb 2016)

The aim of this task is to improve a selected EoS to calculate the saturated liquid density of LNG. Density is crucial for the custody transfer of LNG and currently, density is predominantly calculated according to the 'LNG Custody Transfer Handbook' of GIIGNL (International Group of LNG Importers – Paris, France) using the revised Klosek and McKinley Method. The revised Klosek and McKinley Method is a pressure-independent equation used to calculate saturated liquid densities within the temperature range relevant for

LNG custody transfer ($T < 115$ K). However, the equation is in need of improvement with regard to uncertainty.

Description of activities:

- REG(RUB) with input from VSL will compare the density measurements from D4.1.2 with existing data and relevant EoS in order to determine which EoS should be improved. Following the selection of the EoS, REG(RUB) will fit the experimental data from D4.1.2 to the EoS and determine the improvements required, such that the selected EoS can be used to calculate the saturated liquid density of LNG. REG(RUB) will then improve the EoS accordingly. The results of the data comparison and EoS improvements will be written in a report (REG(RUB), VSL) (D4.2.1, D4.2.2)
- Using the improved EoS from the previous activity, REG(RUB) will develop a software tool for LNG density calculations. The software specifications will be agreed with VSL and will most likely be in the form of an 'add in' (macro) for Microsoft Excel. Following development of the software REG(RUB) will validate it using the density measurements from D4.1.2. Then, when validated, the software will be provided to VSL for further testing and validation. (REG(RUB), VSL) (D4.2.3, D4.2.4)

Major facilities to be used: none

Task 4.3: Speed-of-sound and density sensor for LNG (INRIM*)*

(Start Jun 2014, end Feb 2017)

The aim of this task is to produce a sensor for simultaneously determining the density and speed-of-sound (SoS) of LNG samples in liquid phase at different cryogenic temperatures (91 < (T/K) < 110). A sensor and method independent of the approach used with the LNG densimeter in Task 4.1, will be used in order to allow a mutual validation of the experimental results of each. The measurement data could also be used indirectly to check and support the improvements of the EoS in Task 4.2.

Description of activities:

- INRIM will develop an SoS sensor which works on the principle of the double pulse-echo technique ($\Delta w/w$ in the order of 0.5 %) at cryogenic temperature and a closed-loop cryostat suitable to thermostat the sensor. This design differs from commercial ultrasonic flow-meters as the cell is immersed into the LNG. Furthermore, the new SoS sensor will be adapted to support a piezoelectric transducer, coupled to the cell by means of a buffer rod. In this configuration, it should be possible to obtain the density of the LNG sample, by measuring its acoustic impedance Z and the sound velocity w, $\rho = Z/w$. INRIM will begin by designing and constructing the new SoS sensor. (INRIM) (D4.3.1, D4.3.2)
- Based on the design for the new SoS sensor D4.3.1, INRIM will design and construct a new cryostat for use with the SoS sensor D4.3.2. (INRIM) (D4.3.3)
- INRIM will validate the new SoS sensor D4.3.2 with fluids of which the SoS and densities are known, firstly at non-cryogenic temperatures and then at cryogenic temperatures using pure liquids (in the LNG range) and the newly constructed cryostat D4.3.3. (INRIM) (D4.3.4, D4.3.5),
- The results from D4.3.5 will be supported by an estimated uncertainty according to the "Guide to the expression of uncertainty in measurement" (GUM) to ensure they are fully traceable. INRIM will perform uncertainty analysis for the density and SoS measurements. The level of uncertainty aimed for the speed of sound is 0.5 %. (INRIM) (D4.3.6)
- Using the new SOS sensor D4.3.2 and the associated cryostat D4.3.3, INRIM will perform measurements on at least four LNG like mixtures at cryogenic temperatures. The LNG-like mixtures will be the same four samples used in D4.1.2 and measurements will be determined in liquid phase ($\Delta\rho/\rho$ in the order of 0.2 %). (INRIM) (D4.3.7)

Major facilities to be used:

Thermophysical Properties, Fluids Density and Viscosity laboratories (INRIM)

Task 4.4: Uncertainty of enthalpy and calorific value calculations (PTB)

(Start Dec 2014, end Nov 2016)

The aim of this task is to examine current data used in enthalpy and calorific value calculations with respect to the uncertainties and to check the traceability of the data. As well as density and the total amount of transferred LNG, the energy content per mass or mole will be determined for LNG samples. In the preceding JRP, ENG03 LNG, one of the tasks was to calculate the calorific values and enthalpies of formation of typical LNG samples. The result showed a difference in energy content between the LNG in the real liquid state (-160 °C, several bar pressure) and at pipeline reference conditions (15 or 25 °C, atmospheric pressure).

Another conclusion from the previous JRP ENG03 was the lack of uncertainty for many input quantities for calculations, such as heat capacities or enthalpies of formation. Therefore, some of these uncertainties are estimated, including the uncertainty for the calorific values of pure LNG components. This task will contribute to a firmer basis for these values in accordance with the GUM (Guide to the expression of Uncertainty in Measurement).

This Task is linked to ISO TC193 WG13 and WG18 (responsible for preparing an update of ISO6976 'Natural gas – Calculation of calorific values, density, relative density and Wobbe index from composition' and results of the Task will be shared with these committees as part of Task 5.1 (D5.1.8).

Description of activities:

- PTB will identify and then examine current data used in enthalpy and calorific value calculations with respect to the uncertainties and will check the traceability of the data. The calculations of enthalpies and calorific values will be investigated according to relevant physical quantities, e.g. heat capacities and enthalpies of formation. A report on the study will be produced. (PTB) (D4.4.1, D4.4.2)
- Using input from the previous activity, PTB will produce a guideline on the traceability of energy and enthalpy calculations. The guidelines will highlight the physical quantities requiring scientific investigation in order to ensure traceability in enthalpy and calorific value calculations. It will also include the current status of the traceability of the relevant physical quantities for energy and enthalpy calculations and recommendations for improvement. (PTB) (D4.4.3)

Major facilities to be used: none

C4.b Labour Resources for WP4

	1- VSL	2- CESAME	3- CMI	4- FORCE	5- INRIM	6- JV	7- NPL	8- PTB	9- SP	10- Shell	11- REG(RUB)	12- REG(TUBS)	TOTAL
WP4	3.0				24.0		1.0	5.0			13.5		46.5

C4.c Summary of Deliverables for WP4

Deliverable number	Deliverable description	Participants (Lead in bold)	Deliverable type	Delivery date	Dependent on
4.1.1 (REG(RUB) D2)	Report on current methods for dealing with low-temperature dependence and the size of the force transmission error in LNG density measurements	**REG(RUB),** VSL	Report	Nov 2014	
4.1.2 (REG(RUB) D3)	LNG density measurements for at least 4 LNG compositions using the LNG densimeter from JRP ENG03	**REG(RUB)**, VSL, NPL	Datasets	May 2015 Oct 2015	D4.1.1

4.1.3 (REG(RUB) D4)	Report on the results of the LNG density measurements in D4.1.2 including the uncertainty for the measurements	**REG(RUB)**, VSL, NPL	Report	Dec 2015	D4.1.2
4.2.1 (REG(RUB) D5)	Selection of the EoS for improvement for calculation of the saturated liquid density of LNG	**REG(RUB)**, VSL	List	Dec 2015	D4.1.2
4.2.2 (REG(RUB) D6)	Report on the improvements of the selected EoS for calculation of the saturated liquid density of LNG	**REG(RUB)**, VSL	Report	Jan 2016	D4.2.1
4.2.3 (REG(RUB) D7)	Specifications for the software tool for LNG-density calculations	**REG(RUB),** VSL	Document	Jan 2016	D4.2.1
4.2.4 REG(RUB) D8)	Validated software tool for LNG-density calculations	**REG(RUB),** VSL	Software	Feb 2016	D4.1.2, D4.2.3
4.3.1	Design for a new SoS sensor for simultaneously determining the density and SoS of LNG samples in liquid phase at different cryogenic temperatures	**INRIM**	Design	Nov 2014	
4.3.2	SoS sensor based on the design in D4.3.1 constructed	**INRIM**	Device	May 2015	D4.3.1
4.3.3	Cryostat suitable for use with the SoS sensor D4.3.2	**INRIM**	Device	Nov 2015	D4.3.1, D4.3.2
4.3.4	Validation of the SoS sensor D4.3.2 at non-cryogenic temperatures with pure liquids	**INRIM**	Datasets	Jan 2016	D4.3.2
4.3.5	Validation of the SoS sensor D4.3.2 at cryogenic temperatures with pure fluids	**INRIM**	Datasets	Jul 2016	D4.3.2, D4.3.3
4.3.6	Uncertainty analysis of the SoS sensor for simultaneously determining the density and SoS of LNG samples in liquid phase at different cryogenic temperatures	**INRIM**	Uncertainty budget	Nov 2016	D4.3.5
4.3.7	Measurements of density and SoS of LNG samples in liquid phase at different cryogenic temperatures using the SoS sensor	**INRIM**	Datasets	Feb 2017	D4.1.2, D4.3.2, D4.3.3
4.4.1	Identification of current data used in enthalpy and calorific value calculations	**PTB**	List	May 2015	
4.4.2	Report on the relevant physical quantities and current data used in enthalpy and calorific value calculations	**PTB**	Report	May 2016	D4.4.1
4.4.3	Guideline on the traceability of energy and enthalpy calculations	**PTB**	Guide	Nov 2016	D4.4.2