

CALORIC QUANTITIES AND DENSITY MEASUREMENT OF NON-CONVENTIONAL GASES

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Abstract – This article presents a general description of the technical program of a work package related to the EMRP joint research project (JRP) ENG01 GAS supported by EURAMET and the European Commission as part of the targeted programme Energy (2009). The JRP “Characterisation of Energy Gases” proposes to put in place the necessary metrology infrastructure to enable the “inter-changeability” of energy gases so that gaseous fuels from non-conventional sources can access gas grids across the EU. Four-funded European JRP partners participate to the work package dedicated to direct measurement of the energy content of non-conventional gases as biogas or coal bed methane by calorimetry. Energy content measurements with calorimetry ensure validation of the indirect method (gas chromatography) generally adopted by operators for on-site gas control. A reference gas calorimeter and different field calorimeters will be used to measure the energy content of real samples of non-conventional gases. Results will then be compared with indirect measurements. The work package will also focus on development of novel methods for density (needed for Wobbe index calculation) and thermophysical property as heat capacity of these gases.

Keywords: gas calorimetry, calorific value, non-conventional gases, thermophysical properties

1. INTRODUCTION

The EU aims at generating 20 % of its primary energy use from renewable sources by 2020 and it is estimated that approximately one third of natural gas use will be exchanged to biogas. The introduction of biogas, mixed natural gas and coal bed methane in the European gas network needs to meet the performance requirements requested by operators and European regulation.

Because of the numerous and the diversified origins of the biomass products and others non-conventional gases, the compositions are different from one site to another and are dependant of the source (household and industrial waste, sewage sludge from industrial effluents or residues in agricultural products, coal bed methane or coal mine

methane). The resulting calorific value¹ is not constant and can vary from approximately 8 MJ/kg to 50 MJ/kg.

By now invoicing the gas transactions in energy units, the energy content of the gas is of prime importance. In most cases, calorific value measurements cover only natural gases and are determined by the indirect method using the gas composition from gas chromatography coupled with references calorific values issued from a standard (ISO 6976:2005 [1]). For renewable gaseous fuels, this method has to modify its prerequisite spec for accurate calorific value measurements by a validation with gas calorimetry (direct method).

Jointly supported by the European Commission and the participating countries within the EURAMET (European Association of National Metrology Institutes), the European Metrology Research Programme (EMRP) was dedicated in 2009 to energy field. One of the selected projects, the JRP ENG01 “Characterisation of Energy Gases” proposes to put in place the necessary metrology infrastructure to enable the “inter-changeability” of energy gases so that gaseous fuels from non-conventional sources can access gas grids across the EU [2]. Composed with 15 funded European institutes, the project began in June 2010 for three years and consists in four work packages dedicated to alternative fuel gases. We present here a detailed description of one work package (WP2) entitled “Direct measurement of the calorific value of non-conventional gases” where four national metrological institutes are involved. It is devoted to accurate calorific value measurements of renewable gaseous fuels by direct method with primary and field calorimeters and development of novel methods for density and heat capacity measurements of these gases.

2. SCIENTIFIC AND TECHNICAL OBJECTIVES

2.1. The JRP ENG01 of the EMRP: “Characterisation of Energy Gases”

The work programme is organised in four technical work packages [2]:

¹ Calorific value is defined as a quantity of energy released by a complete combustion of a volume, molar or mass unit of a gas

- WP1: New methods for the measurement of the composition of non-conventional gases
- WP2: Direct measurement of the calorific value of non-conventional gases
- WP3: New primary and reference humidity facilities
- WP4: Evaluation and comparison of novel and existing techniques for humidity sensing in energy gases

Work packages 1 and 2 focus on new and improved methods for determining the energy content and other physical properties of non-conventional and alternative gaseous fuels. The determination of the calorific value and related thermodynamic properties is the main focus of these WPs. The comparison of the indirect (composition measurement) and direct (calorimetry) methods for the calorific value is one of the key elements in these work packages.

The following diagram shows the inter-relationship between work packages [2]:

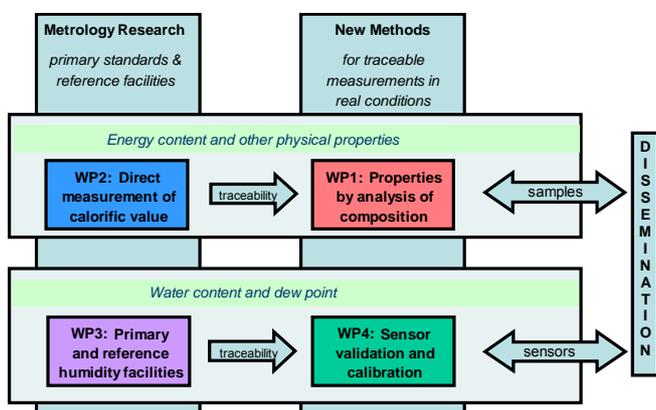


Fig. 1. Diagram of the inter-relationship between the four work packages

2.2. WP2 “Direct measurement of the calorific value of non-conventional gases”

This work package “Direct measurement of the calorific value of non-conventional gases” aims at developing and validating the results of a primary reference calorimeter able to produce very low uncertainty on calorific value (CV) measurements of non-conventional gases in accordance with the principles of the “Guide to the Expression of Uncertainty in Measurement” (GUM) [3]. It concerns also the development and validation of field calorimeters for calorific value measurements of the same gases. Novel methods for density (needed for Wobbe index calculation) and heat capacity will also be developed for non-conventional gases (synthesized and real). The non-traditional energy gases likely to be traded are derived from bio-digestion, coal bed methane, coal mine methane, natural gas-type mixtures such as natural gas with added hydrogen, landfill gas etc. and will have compositions and physical properties differing from traditional natural gas.

Only direct method by calorimetry can guarantee highly accurate CV measurements. For non-conventional gas mixtures, there is a pressing need to develop gas

calorimeters, so that the interchangeability of these gases in pipeline networks can be ensured.

Four national metrology institutes are involved in the work package: LNE in France, PTB in Germany, CEM in Spain and BRML in Romania. Each institute has adapted accuracy equipments to realise measurements.

The primary and field calorimeters will first both be validated by determining the calorific value of reference materials (primary gas mixtures) developed in WP 1. The results obtained by direct measurements (calorimetry) will be compared with indirect measurements (GC composition analysis and use of equations of state). These calorimeters will then be used to carry out measurements of ‘real’ non-conventional gases. These measurements are particularly challenging as even low levels of impurities, odorant species, moisture and process by-products all have effects on the calorific value of the mixture.

In parallel with these activities, research will also be undertaken to develop novel methods for the density and heat capacity of non-conventional gases. A gas densimeter with a magnetic suspension float and a microbalance is being developed to determine the density of non-conventional gases. (Density, which enables Wobbe index to be calculated, is a key parameter when ensuring interchangeability). Heat capacity will be determined via speed of sound measurements undertaken using a novel spherical acoustic resonator.

Four tasks within the work package have been listed:

- 1- Development and validation of a primary reference calorimeter for non-conventional gases
- 2- Validation of field calorimeters for non-conventional gases
- 3- Application of the newly developed primary and field calorimeters to real samples of non-conventional gases
- 4- Identification and determination of thermophysical properties for indirect calorific value measurements of non-conventional gases

3. WP2: DESCRIPTION OF THE WORK AND CURRENT STATUS

For accurate determination of calorific values of non-conventional gases, different calorimeters will be used including field calorimeters and a reference gas calorimeter.

To allow traceability of the energy content measurements with field calorimeters used in this WP, a primary calorimeter has been developed at LNE (partner in the project) for the analysis of non-conventional gases. It is based on Rossini principle [4] initially operating with pure gases. Calorific values (CV) are determined with very low uncertainty (0.1% for pure gases). Fig. 2 presents an overview of the set-up and figure 3 shows the gas container pressurized up to 25 bars.

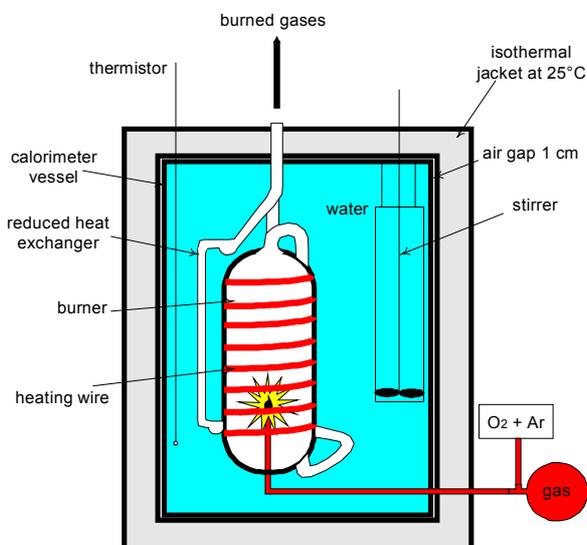


Figure 2: Scheme of the reference gas calorimeter at LNE for renewable gases.

For the CV measurements of non-conventional gases, the reference gas calorimeter has been modified to avoid damages of elements as gas burner or connection tubes. Materials have been provided for the purpose of CV determination of sulphured gas mixtures including safety equipment as safety cabinet for pressurize gas cylinders, masks and sulphured compound detectors.

New input parameters for the reference calorimeter have been studied to allow accurate GCV measurements: inlet flow, drying process, inflowing gas temperature...

The heating wire in red in fig. 2 represents the electrical resistance used to calibrate the calorimeter by Joule effect.



Figure 3: pressurized gas container

Although traceable field calorimeters are currently commercially available for the on-site measurements of natural gases (to determine calorific value for billing purposes), these instruments have not been tested nor validated for the applicability to non-conventional gases.

PTB (Germany) and BRML (Romania), partners in the project, will arrange and validate field commercial calorimeters. One of them, used by both institutes, is presented in figure 4. No arrangement of the gas is necessary to measure CV of non-conventional gases with this analyser from *Union Instruments*.

In a first part of the project, field and reference calorimeters will be validated and tested with these reference materials, and the results will be compared with calorific values determined by the indirect (composition) methods developed in WP1.



Figure 4: Union Instruments CWD 2000 calorimeter

These reference gas mixtures are presented in table I and reproduce the main components of real non-conventional gases that will be analysed further in the project.

The H₂S concentrations traduce the different purification steps for biogas use; the last one is narrow H₂S concentration in raw biogas that can make high damages in flanges and pipelines in wet environment.

TABLE I. Compositions of the reference gas mixtures

Binary mixtures	60% CO ₂ + 40% CH ₄
	40% CO ₂ + 60% CH ₄
	20% CO ₂ + 80% CH ₄
Ternary mixtures	36 ppm H ₂ S in 50% CO ₂ / 50% CH ₄
	720 ppm H ₂ S in 40% CO ₂ / 60% CH ₄
	2876 ppm H ₂ S in 30% CO ₂ / 70% CH ₄

Research is also required to develop and validate novel method for other thermodynamic properties of non-conventional gases in order to solve problems derived from their purification, transport and distribution. In collaboration with the University of Valladolid, CEM (Spain) developed and adapted the methods in order to measure density and heat capacity of non-conventional gases. The University de Valladolid collaborates with CEM to perform the measurements thanks to their equipment and their valuable expertise in the field.

Density measurements are carrying out using a gas densimeter consisting of a magnetic suspension float and a microbalance [5]. Heat capacity determination takes place via the measurement of the speed of sound in the gases using a spherical acoustic resonator [6].

Results will be compared to literature data. The magnetic suspension densimeter and the spherical acoustic resonator are schematised in fig. 5 and fig. 6.

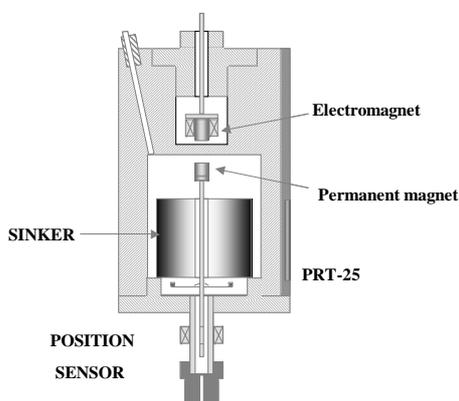


Figure 5: Magnetic suspension densimeter principle

Density measurements can be performed for gases in real conditions circulating in gas network, i.e. at pressures up to 20 MPa and temperatures from 250 K to 400 K. Approximately, the same experimental conditions are in use for the heat capacity determination via the speed of sound measurement.

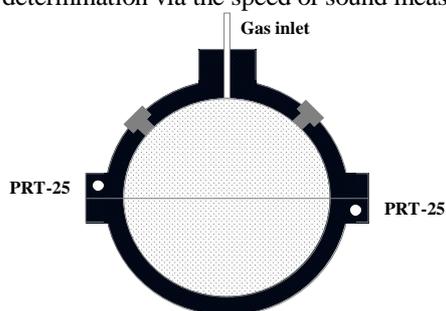


Figure 6: spherical acoustic resonator for heat capacity measurements

The nature of the gases to be studied here will be part to those considered for CV measurements (by direct and indirect methods).

4. CONCLUSION

Due to the growing injection of non-conventional gases in the European gas network and the existing numerous interconnection points in it, the energy content of gas requires continuous measurements of a number of parameters as calorific value, Wobbe index, water content or sulphured compounds to better control cost of the transported and distributed gas. In the state of the art, energy content is measured with instruments adapted to the needs of the natural gas industry. A joint research project entitled "Characterisation of Energy Gases" is carrying out with funding by the European Union and EURAMET and focuses on energy characterisation of gaseous fuels from renewable sources in order to improve their inter-operability in the European gas grids.

A general description of a work package program of the JRP dealing with accurate direct measurements of calorific values, heat capacity and density was here presented. The technical program and objectives of the work package are here highlighted with equipments and specifications.

ACKNOWLEDGMENTS

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