Publishable JRP Summary Report for ENG54 Biogas Metrology for biogas

Background

To support the use of green gas, the European Commission has issued mandate M/475 to CEN, the European Organisation for Standardisation, concerning the specifications for biogas and biomethane for injection into natural gas grids and for use as transport fuel. This mandate was issued to facilitate the market penetration of biomethane through the development of a European Standard for a quality specification for biomethane. CEN has been given the mandate to develop, as a first step:

a) A European Standard for a quality specification for biomethane to be used as a fuel for vehicle engines,

b) Technical Specifications or EN standards for quality specification for biomethane to be injected into natural gas pipelines transporting either High calorific-gas or Low calorific-gas. The specifications and standards shall include a method (such as gas chromatography-mass spectrometry, ^{14}C-isotope analysis or equivalent) to determine the volume fraction biogenic methane in the pipeline.

For the implementation of such specifications, metrologically traceable methods and reference materials are required to ensure that measurements of the relevant properties of biogas are robust and reliable. For a substantial number of parameters, such methods and reference materials are lacking. Reliable measurement results with stated measurement uncertainties are a prerequisite for assessing conformity with the aforementioned specifications for biogas. This conformity assessment is a prerequisite for the trade and use of biogas and biomethane.

Need for the project

As natural gas resources are declining and the EU depends increasingly on imported natural gas, diversification of the European natural gas supply is underway as required by the Renewable Energy Directive 2009/28/EC and EC targets, which specify that 20 % of EC energy consumption should come from renewable sources by 2020, and that biofuels should provide at least 10 % of transport petrol and diesel consumption by the same year. There is now an urgent need to significantly increase the amount of biogas which is injected into natural gas networks.

To promote the use of biomethane as required by the EC Directive concerning common rules for the internal market in natural gas (2003/55/EC), specifications have been developed for the injection of biomethane into the natural gas transport and distribution grids and for use as transport fuels. Access to the natural gas grids and fuelling stations is essential for the promotion of biomethane. This project aims to develop new and novel methods for measuring these specifications. Without the results of the work in this JRP, the growth in the use of biogas is effectively stopped as it will be uneconomic to transport, and the objectives concerning the diversification of gas resources and the increased use of renewable fuels cannot be met.

Scientific and technical objectives

This JRP aims to develop and validate methods for determining key impurities, moisture, particulates, calorific value, and density:

- novel traceable methods for the measurement of the contents of key trace-level impurities in biogas and biomethane namely: total silicon and siloxanes, sulphur-containing compounds, aromatic hydrocarbons, halogenated hydrocarbons, ammonia, hydrogen cyanide, hydrogen chloride and carbon monoxide.

EMRP European Metrology Research Programme Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

- robust analytical capabilities for the measurement of the particulate content and water content / dew point of biogas and biomethane.
- methods for the measurement of the calorific value, heat capacity, and density of biogas and biomethane.
- a traceable method for determining the concentration of biomethane in samples of blended biomethane and natural gas.
- robust methods for sampling biogas and biomethane in the field, and to enable the biogas industry to perform robust and traceable quality assessment measurements.

The results of this JRP will enable the National Metrology Institutes (NMIs) to provide services that enable the gas industry to reliably measure key properties of biogas and biomethane. The work undertaken will be discussed with CEN TC408 on biogas and it will support the efforts of this TC and other committees in setting up specifications for biogas and biomethane as well as in developing test methods for key parameters.

Expected results and potential impact

Traceable methods for key impurities

Two methods have been developed for total silicon content, one based on an acidic impinger method and another using gas chromatography (GC). Assessing this method with gas mixtures containing siloxanes revealed that the recovery of the impinger method is 80 %. The GC-method uses ICP/MS. The LoD (limit of detection) of the method is 0.5 mg/m^3, without preconcentration, which is being further improved.

For sulphur containing species, the stability of these components in gas mixtures has been determined. In general, these species are less stable in moist gas, especially hydrogen sulphide, the mercaptans (thiols), and tetrahydrotiophene (THT). For other sulphur-containing species the differences are less pronounced.

The work performed on benzene, toluene, ethylbenzene and xylenes (BTEX) has led to the development of a variety of GC-methods. In some cases, differences were observed between gas mixtures using biomethane and upgraded biogas as the matrix and mixtures in nitrogen. A relative expanded uncertainty of 3 % on the mole fractions of the components was achieved.

For the halogenated volatile organic compounds (VOCs), 5 components with a wide variety of boiling points were selected. However, one of these was banned so the following gas mixtures were prepared in passivated cylinders containing dichloromethane, tetrachloroethylene, m-dichlorobenzene and trichloro-trifluoroethane.

In the measurement of ammonia in biomethane and upgraded biogas, three different optical methods were developed. For one of these, there were interferences due to the presence of carbon dioxide and methane in the biomethane and upgraded biogas. Decreasing the pressure in the measurement cell of the spectrometer appreciably reduced such interferences. After optimisation, the effect of the residual interference was quantified. In the measurement of the ammonia content, the background is subtracted from the spectrum before quantifying the ammonia content. A linearity test confirms the adequacy of this approach. The stability of the ammonia content in passivated gas cylinders was within approximately 5 %.

For hydrogen cyanide, calibration gas mixtures are prepared dynamically using a permeation tube containing pure hydrogen cyanide. The mass flow of hydrogen cyanide is then mixed with a flow of the desired matrix gas, e.g., nitrogen, biomethane and dry biogas. In spectral regions, the interference of the methane and carbon dioxide present in biomethane and upgraded biogas is very limited. A relative expanded uncertainty of approximately 5 % is expected to be achievable.

For the hydrogen chloride content in biomethane and upgraded biogas, spectroscopic methods have been developed. The specification for the content is 1 ppm HCl. The spectroscopic method has been validated for the analysis of HCl down to 100 ppb. One of the spectroscopic methods developed is also able to discriminate between the stable isotopes in chlorine, i.e., H^{35}Cl and H^{37}Cl. In composition measurements, the signals of both isotopes are added. There are appreciable interferences from the methane and carbon dioxide present in biomethane and upgraded biogas. Work is being done to reduce these effects and to quantify these by subtracting the infrared active background. The analysis of 10 ppm gas mixtures in cylinders underlines the importance of proper gas handling to deal with, e.g., adsorption effects.

For carbon monoxide, upper limits are set at 0.1 % in the specification of EN16723-1. A GC-method has been developed for measuring the amount-of-substance fraction carbon monoxide in biomethane and upgraded biogas. The method is largely based on ISO 6974-1 and ISO 6974-2. The instrument configuration had to be chosen carefully, to enable the separation of carbon monoxide from, e.g., nitrogen, oxygen and argon. For (very) low levels of carbon monoxide, spectroscopic methods have been made available. Using the developed laser spectroscopy method, the range covered is from 10 ppm to 400 ppm (as amount-of-substance fraction). Below 50 ppm, the reproducibility of the measurement method gets poorer because of optical fringes.

Capabilities for particulate and water content

The facilities for measuring the water dew point and water content are being improved for use with biomethane and upgraded biogas. The emphasis in this work lies on determining the absolute enhancement factors for water in biomethane and upgraded biogas. In the meantime, relative measurements of the enhancement factor of water in biomethane and upgraded biogas have been performed. A suite of commercially available moisture sensors and hygrometers have been tested. The results underline the significance of the matrix effect of using such sensors in biomethane and upgraded biogas matrices. Also the pressure and temperature affect the dew point temperature obtained from such sensors. Relevant differences are observed for different types of sensors.

Particulate content measurements have been performed on both biomethane and untreated biogas. Measurements with a scanning electron microscope show particles containing aluminium oxide and carbonated elements. An electrical low pressure impactor was used to determine the particle concentration in various matrices. The particle concentration in raw biogas sampled in a gas cylinder was very low ~ 100/cm^3. Onsite measurements indicate higher, but still low levels ~ 10^3/cm^3, which is less than one tenth of the particle concentration of ambient air. Commonly applied filters in biogas processing lead to low particle concentrations downstream of the filter.

Capabilities for calorific value, heat capacity and density

For the experiments concerning the calorific value of biomethane and upgraded biogas, field samples were obtained. A practical issue was the low pressure (5 bar) of some of the samples. Sufficient quantities could be obtained. Eventually one biogas and three biomethane samples were obtained Complementary to these experiments, synthetic mixtures were prepared to cover a very wide range of calorific values, densities, Wobbe indices, and gas viscosities in order to accurately calibrate both field calorimeters. The direct measurements are compared with the indirect method, involving composition analysis by gas chromatography (ISO 6974) followed by calculating the gas properties (ISO 6976). With raw biogas, agreement was demonstrated between the reference and field calorimeters within the respective uncertainties. Such agreement was not demonstrated for the first biomethane sample with both reference calorimeters. Improvement of the experimental conditions has led to agreement between the results on calorific value measurements for the second biomethane sample.

Substantial work has been done on the density measurements. For several reference systems (e.g., methane, nitrogen, carbon dioxide and water) high-accuracy measurements were performed to characterise thermodynamic properties such as the density, the heat capacity and the speed of sound as a function of temperature, pressure and composition. A comparison between two laboratories has been done for the gas density measurement of a biomethane sample showing equivalence of results. The reference data obtained in the project is being used to validate equations-of-state used for calculating, e.g., the density of biomethane and biogas.

Traceable method for biogenic methane content

Substantial progress has been made in the development of a traceable method for biogenic methane content. Using a spectroscopic method, absorption line pairs have been selected for the measurement of the isotope ratios ^{2}H/^{1}H and ^{13}C/^{12}C. The measurement of the latter is more challenging than the former. The linearity of the method has been assessed and found to be satisfactory. The first experiments on blends of natural gas and biomethane have been performed and the results look promising.

Sampling methods

An overview of sampling methods has been prepared and published. Most experience exists with sampling biogas for the determination of the volatile organic compounds (VOCs) content, and there is little to no existing experience for components like ammonia, hydrogen chloride and hydrogen cyanide. Experiments with selected passivated cylinders, sample bags and adsorption tubes show good results for the cylinders and tubes with respect to the short-term stability of siloxanes. The heavier siloxanes show adsorption over time in bags. The results for sulphur-containing components show the same trend. Also for BTEX, there are differences. In particular sampling bags perform less well than Tenax TA adsorption tubes. The results enable us to identify suitable sample containers. For the other components, experimental work is ongoing.

A biomethane sampler has been built and successfully used for sampling biomethane for the work on calorimetry. A best practice guide related to sampling and sample collection has been prepared. ISO/TC193/WG20 is interested in these results in view of the revision of ISO 10715 (Natural gas -- Sampling guidelines) to make the standard suitable for sampling biomethane and upgraded biogas for impurities.

Specifically, this JRP generates impact by creating an infrastructure for delivering calibration services and certified reference materials (CRMs) for the contents of key impurities (siloxanes, sulphur-containing components, aromatic hydrocarbons, halogenated VOCs, ammonia, hydrogen cyanide, carbon monoxide and hydrogen chloride) in biomethane and upgraded biogas at relevant content levels with established metrological traceability and known uncertainty. Laboratories can use these services and CRMs for developing and delivering measurement services to the industry for the conformity assessment of biomethane and upgraded biogas in accordance with EN16723-1 and prEN16723-2. The methods for particulate matter and water content enable laboratories to deliver corresponding services to the biogas producers and upgraders.

Further impact is being created with respect to standardisation, e.g., by submitting the best practice guides on sampling and sample preservation to ISO/TC193/WG20 in view of the revision of ISO 10715. This written standard is being updated and extended to cover, among others, the sampling of biogas, biomethane and upgraded biogas for, e.g., impurities. The experience on working with dynamic methods for calibration gas mixture preparation is being shared with ISO/TC158/WG5 in view of the further development of the ISO 6145-series of standards.

The work on field calorimetry enables biogas producers and grid owners to use field calorimeters with known performance as an alternative to gas chromatography. This creates impact, especially for small biogas producers, as the costs of ownership of gas chromatographs is deemed to be too high.

The dedicated models and methods for water dew point enable the industry to rely on measurement results with similar accuracy to those in conventional natural gas. The water content will be measured more reliably and accurately than currently possible. This in turn will enable the gas treatment to be optimised so that the water dew point specification can be reliably met, without drying the raw biogas any more than is needed.

The work in the project as a whole allows authorities and inspection agencies to assess the content of biogenic methane in natural gas networks and stores for fiscal purposes and the fight against fraud. Taxation schemes supporting the use of biogas will be enforceable and claims of biogas content in networks can be verified, as well as the conformity with prEN 16723.

JRP start date and duration:	1 June 2014 (36 months)
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The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union