Final Publishable JRP Summary Report for ENG54 Biogas Metrology for biogas

Background

To support the use of green gas, the European Commission 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, or authority to carry out a policy, was issued to facilitate the market penetration of biomethane through the development of a European Standard for a quality specification for biomethane, and is for the development of:

a) A CEN 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 of biogenic methane (or biomethane) in the pipeline.

This project developed the traceable methods and reference materials needed to ensure that measurements of the properties of biogas are robust and reliable.

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.

Biomethane is produced from organic waste, by cleaning biogas, and it is a 100 % renewable energy source. Its properties are similar to those of natural gas, making it suitable for use as a vehicle fuel and in heating applications.

To promote the use of biomethane, as required by the EC Directive concerning the 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. EN 16723-1:2016 contains specifications for gas grid injection, and EN 16723-2:2017 for use as transport fuel. A specification for liquefying biomethane is currently under consideration as new work item in CEN/TC408.

Reliable traceable methods and reference materials are needed for the implementation of the specifications to ensure that measurements of the relevant properties of biogas are robust and reliable. This conformity assessment is a prerequisite for the trade and use of biogas and biomethane.

Prior to this project, there was a lack of traceability and poor comparability between results from different laboratories, and there was a need for new and novel methods for measuring these specifications. Without these, the growth in the use of biogas would be effectively stopped as it would be uneconomic to transport, and the diversification of gas resources and the increased use of renewable fuels could not be met.

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Scientific and technical objectives

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

1. 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.
2. Robust analytical capabilities for the measurement of the particulate content and water content / dew point of biogas and biomethane.
3. Methods for the measurement of the calorific value, heat capacity, and density of biogas and biomethane.
4. 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 project 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.

Results and conclusions

1.1 Traceable methods for silicon and siloxanes content

Silicon, predominantly present in the form of siloxanes, forms after the combustion of biomethane deposits of SiO_2 (silicon dioxide) in the natural gas transmission infrastructure and in end user appliances. Methods were developed for determining the total silicon content and the siloxanes content. The latter methods enable calculating the total silicon concentration to be calculated from the concentrations of the siloxanes and their molecular formulae. The aim of this task was to develop and validate methods for the analysis of the total silicon content of biogas, supported by the preparation and analysis of high-accuracy reference gas mixtures of siloxanes in cylinders. This aim was achieved by preparing measurement and transfer standards using static gravimetry. The preparation presented some problems in that siloxanes are reactive species, and substantial losses were recorded initially and over time. The gas mixtures contained the most prevalent siloxanes at the sub-ppm mole fraction levels, as these are the most relevant in view of the specification (between 0.3 mg/m^3 and 0.1 mg/m^3).

Different instrumental configurations were used to determine the contents of the siloxanes. In parallel, two methods were developed for total silicon content. The different methods provided comparable results.

All analytical methods have the potential to be developed further as standardised test methods, and demonstrated how equipment can be reliably calibrated. The expanded uncertainties varied between 3 % and 10 %, depending on the concentration level of the silicon or siloxanes.

1.2 Traceable methods for sulphur content

The sulphur content in biomethane and upgraded biogas is generally very low. Scrubbing biogas (a technique for upgrading biogas to biomethane) eliminates carbon dioxide, hydrogen sulphide and other sulphur containing compounds. When injected into the natural gas grid, biomethane and upgraded biogas has to be odorised again, which often involves the addition of a sulphur-containing odorant. For commonly encountered sulphur-containing components, as well as for sulphur-free odorants, measurement standards and calibration methods exist. The aim of this task was to assess the stability of reference gas mixtures containing parts-per-million levels of sulphur-containing compounds in the presence of water, in order to simulate biogas and biomethane.

This aim was achieved by preparing gas mixtures with nominally 1 µmol/mol of the sulphur-containing components. The mixtures without the addition of water were stable within 2 % over 30 months. Much greater instability was observed for the mixtures with 5 µmol/mol and 50 µmol/mol of added water.

1.3 Traceable methods for aromatics content

The aim of this task was to develop novel reference materials for the measurement of the monocyclic aromatic hydrocarbons (BTEX, *i.e.* benzene, toluene, ethylbenzene, and *ortho*-, *meta*- and *para*-xylenes) in biogas, and to study whether existing methods for the measurement of polycyclic aromatic hydrocarbons (PAHs) in matrices such as workplace air can be applied to the analysis of PAHs in biogas. Depending on the feedstock used for the production of biomethane and biogas, varying concentrations of BTEX and PAHs were encountered.

The aim was achieved for BTEX by preparing reference gas mixtures and analysis methods. A relative expanded uncertainty of 3 % on the mole fractions of the components was achieved. The stability of certified reference materials of these components in biomethane and biogas matrices is similar to that of corresponding mixtures in nitrogen or air, as known from air quality measurements.

For PAHs, a method was developed and validated by spiking solutions onto thermal desorption tubes using a calibration solution loading ring (CSLR) apparatus and sweeping them with the aid of an air stream. Once the method was developed and validated, the effect of other compounds found in biogas and biomethane was investigated using a gravimetrically prepared biogas mixture. The results provide a basis for future studies to develop a standard method.

1.4 Traceable methods for halogenated VOC content

Halogenated volatile organic compounds (halogenated VOCs) are widely found in the environment and hence are also found in biogas and biomethane. The aim of this task was to develop methods for the analysis of trace levels of halogenated hydrocarbons in biogas. This aim was achieved as follows. A literature survey revealed that 38 different compounds are encountered. Due to the large variety of compounds, the determination of all species in a single analysis is almost impossible in routine analysis. A further practical issue is that some of these compounds have been banned, which makes it impossible to develop corresponding calibration reference materials for quantitative measurement. From the 38 identified compounds, 5 were chosen for the preparation of reference gas mixtures and method development.

A method based on thermal desorption-gas chromatography with flame ionization/mass spectrometry detection was then developed. For the sampling, three different sorbents were tested, showing that none of the sorbents tested here were fully suitable for the selected halogenated VOCs. Large discrepancies in recoveries were observed in some cases and/or large biases were obtained when analysing the reference gas mixtures. The method needs to be further developed to be suitable for measuring the total chloride and fluoride content in biomethane and biogas.

1.5 Traceable methods for ammonia content

The European specification for biomethane EN16723 sets an upper limit for the ammonia concentration in biomethane and upgraded biogas of 0.1 mg/m^3. In response to this measurement need, three traceable analytical methods and reference standards for the analysis of trace (ppb) amount fractions of ammonia in biogas were developed. For one of these, there were spectral interferences due to the presence of carbon dioxide and methane in the biomethane and biogas, which could be eliminated during method development. In the measurement of the ammonia content, the background was subtracted from the spectrum before quantifying the ammonia content. A linearity test confirmed the adequacy of this approach. The stability of the ammonia content in passivated gas cylinders was within approximately 5 %.

1.6 Traceable methods for hydrogen cyanide content

The aim of this task was to develop a method for the analysis of trace levels of hydrogen cyanide (HCN) in biogas. For HCN, calibration gas mixtures were prepared dynamically using a permeation tube containing pure

hydrogen cyanide. The mass flow of hydrogen cyanide was 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 the biomethane and upgraded biogas was very limited. A relative expanded uncertainty of approximately 5 % was expected to be achievable, but it could not be confirmed because of issues with the dynamic gas mixture preparation system. The work done is pivotal for the further development of a metrological infrastructure targeted at certifying calibration gas mixtures, proficiency testing and the production of certified reference materials.

1.7 Traceable methods for hydrogen chloride content

The aim of this task was to develop an analysis method for the measurement of trace levels of hydrogen chloride (HCl) in biogas. This goal was achieved as follows. The specification for the content is 1 ppm HCl. The spectroscopic method developed was validated for the analysis of HCl down to 100 ppb. One of the spectroscopic methods developed was 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 were added. There were appreciable interferences from the methane and carbon dioxide present in the biomethane and upgraded biogas, which could not be satisfactorily eliminated. The analysis of 10 ppm gas mixtures in cylinders underlined the importance of proper gas handling to deal with effects such as adsorption. Notwithstanding these problems, this work greatly enhanced the measurement of the HCl content in nitrogen and air, and contributed to better quality measurements for monitoring air pollution and emissions. Further work is needed to make the method suitable for biomethane and biogas.

1.8 Traceable methods for carbon monoxide content

For carbon monoxide, the upper limits are set at 0.1 % in the specification of EN16723-1. The aim of this task was to develop measurement methods and standards for the determination of the carbon monoxide content in biogas. A method based on ISO 6974 was developed, for measuring the mole fraction of carbon monoxide in biomethane and biogas. For (very) low levels of carbon monoxide, spectroscopic methods were developed. Using the developed laser spectroscopy method, the range covered was from 10 ppm to 400 ppm (as an amount-of-substance fraction). Below 50 ppm, the reproducibility of the measurement method becomes poorer due to the presence of optical fringes.

At the level of the specification, a relative expanded uncertainty of 0.5 % was readily achievable. For lower levels, a relative expanded uncertainty of 1 %-2 % was achieved. The methods developed for carbon monoxide content are now ready to be standardised and disseminated to laboratories involved in the conformity assessment of biomethane and upgraded biogas.

1.9 Traceable methods for biogenic methane content

The aim of this task was to develop and validate techniques for determining the biogenic methane concentration in a mixed gas sample. Isotopic composition carries information about the origin of methane. For the determination of the biogenic methane (or biomethane) content, two approaches were followed, one based on the $^{14}CH_4$ content and one on the isotopic composition of the stable isotopes of hydrogen and carbon. The instrumental techniques used were mass spectrometry (for both) and spectroscopy for the stable isotopic composition. This work has contributed to the development of methods for determining the isotopic composition of biomethane and upgraded biogas, which enables the determination of the fraction of biomethane in blends of natural gas and biomethane.

2. Capabilities for particulate and water content

The aim of these actvities was to develop robust analytical capabilities for the measurement of the particulate and water content / dew point of biogas and biomethane. These goals have been achieved as follows. The facilities for measuring the water dew point and water content of biomethane and upgraded biogas were improved. A suite of commercially available moisture sensors and hygrometers were tested. The results show the significance of the matrix effect (components of a sample other than the analyte of interest), and that

pressure and temperature affect the dew point temperature obtained when using these sensors. The facilities for measuring the water dew point and water content of biomethane and upgraded biogas were improved.

Particulate content measurements were performed on both biomethane and untreated biogas. Measurements with a scanning electron microscope showed particles containing aluminium oxide and carbonated elements. The particle concentration in raw biogas sampled in a gas cylinder was less than one tenth of the particle concentration of ambient air. These methods are ready to be disseminated to the aboratories involved in the conformity assessment of biomethane and upgraded biogas.

3.1 Capabilities for calorific value

The aim of this task was to perform calorific value measurements on real biogas and biomethane samples using the calorimetric technique and then to compare the results obtained from all of the calorimeters used and to compare the results obtained by the direct and the indirect methods. One biogas, three biomethane field samples and synthetic mixtures were prepared to cover a wide range of calorific values, densities, Wobbe indices, and gas viscosities in order to calibrate two field calorimeters. Direct and indirect methods were compared, involving composition analysis by gas chromatography (following the methods in ISO 6974) followed by the calculation of the gas's properties (following ISO 6976). Agreement, within the uncertainties, was demonstrated between the reference and field calorimeters for both raw biogas and biomethane.

Two different field calorimeters were configured for use with biomethane and biogas, and they were operated following the gas analysis methods in standards DIN 51899 and ISO 6143. Seven calibration gas mixtures with different thermophysical properties (focusing on calorific value, density and viscosity) were used. The results achieved demonstrate that field calorimetry is a good alternative to the use of a field GC (gas chromatograph) to determined the calorific value, provided that the field calorimeter is adapted and optimised for use with biogas; for biomethane, such an optimisation is generally not necessary, as its properties are close to those of natural gases.

3.2 Heat capacity and density

The aim of this task was to experimentally characterise the thermophysical behaviour of binary mixtures and biogas and biomethane synthetic mixtures in addition to real biogas samples in order to validate the use of the widely used equations of state. This aim was achieved by performing high-accuracy measurements to characterise thermodynamic properties such as density, heat capacity and the speed of sound as a function of temperature, pressure and composition for a number of reference systems (e.g. methane, nitrogen, carbon dioxide and water). A comparison between two laboratories for the gas density measurement of a biomethane sample showed good agreement. The reference data obtained in the project is being used to validate the equations-of-state that are used for calculating, for example, the density of biomethane and biogas. The density and heat capacity measurements were used to evaluate the performance of commonly used equations of state, such as AGA8 and GERG2008.

In order to validate current equations-of-state for natural gas for their use with biogas and biomethane, the thermophysical behaviour of selected binary mixtures, as well as multicomponent biogas and biomethane synthetic mixtures were studied in addition to real biogas samples. The results obtained were within the limits of uncertainty claimed by the GERG-2008 equation of state. However, for mixtures with a high content of carbon dioxide, the deviations from the equation of state can be higher, but only at the temperature of 275 K and at pressures around 10 MPa.

The speed of sound behaviour of the biogas-like mixtures is closer to that modelled by GERG-2008 at intermediate temperature and pressure ($p \approx 6$ MPa and $T = 300$ K), but it tends to disagree at low temperature and high pressure ($p \approx 12$ MPa and $T = 273$ K). The same can be seen at high temperature and low pressure ($p \approx 1$ MPa and $T = 325$ K). Measurement results are mostly within the limits of uncertainty stated by the GERG-2008. This work underlines the issues with using equations-of-state for biogas; for biomethane, the current models were shown to be valid within the stated measurement uncertainty.

4. Sampling methods

The aim of these activities was to develop and optimise sampling methods for biogas and biomethane. One of the greatest challenges was to collect biogas samples so that the composition of the samples did not change

between the sampling time and the analysis. Losses of gas components, especially impurities, during sample collection can give rise to incorrect conclusions in the conformity assessment and trade.

To achieve these goals, an overview of sampling methods was first prepared and published. Most available information is for sampling biogas for the determination of the volatile organic compounds (VOCs) content, and there is little to no existing information for components such as ammonia, hydrogen chloride and hydrogen cyanide.

A biomethane sampler was built and successfully used to take the biomethane samples for the analysis of both impurities and physical properties. The samples of biomethane were sent from Sweden to other partners, in accordance with the Transportable Pressure Equipment Directive 2010/35/EU, and they were analysed for the main components (methane, carbon dioxide, nitrogen). The composition was found to be in good agreement with that determined at the plant where the gas was produced.

Sampling for the purpose of analysing the main components in biogas is similar to the sampling of natural gas so ISO10715 (Natural gas – sampling guidelines) is applicable. The standard recommends the use of stainless steel. Results from this project show that the standard should be extended to include additional compounds and sampling vessel coatings in order to make it fully applicable to biogas and biomethane.

A literature survey was conducted to investigate what had already been done for identifying suitable sample collection vessels. Based on this survey, an experimental programme was designed, taking advantage of the measurement methods developed in this project, to assess the performance of various vessels. The following recommendations can be made:

- For sampling siloxanes, either Silconert® 2000, Silonite or Tenax adsorbent should be used. The siloxanes species in these samples will remain stable for at least 10 days.
- For sampling sulphur-containing compounds, sulfinert and siliconite passivated cylinders perform well. Other sampling means show different performance for different components, and most of them are not suitable for all sulphur-containing components.
- For sampling BTEX compounds, different adsorbents (Tenax, Carbotrap 300, Carbopack X) perform well.
- For sampling halogenated hydrocarbon compounds, Tenax TA performs well for the compounds with boiling points over 50 °C. Methods need further development for compounds with low boiling points.
- For sampling ammonia, cylinders (sulfinert treated and not) are suitable vessels.
- For sampling carbon monoxide, both multi-layer sampling bags and sulfinert-treated cylinders perform well.

These recommendations were documented in a best practice guide on sampling and sample collection, which also summarises the major outcomes of the short-term stability studies run on the various sample vessels.

Impact

Dissemination

32 presentations on calorimetry, calorific value, density and heat capacity were given at conferences such as the International Congress of Metrology, Conference of the European Biogas Association and Biogas Science. Fifteen articles were published in peer-reviewed journals such as The Journal of Chemical Thermodynamics and Analytica Chimica Acta.

An e-learning course entitled ‘Metrology for Biogas’ was developed, and this aims to make the work of the project more accessible to industry and end users such as biogas producers and transmission companies, helping them to comply with regulations. The course is available on the NPL website.

Four training courses on various aspects of biogas analysis were run for external delegates from industry, higher education and public research organisations.

Early impact

This project created 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 will be able to use these services and CRMs provided by the partners 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 will enable laboratories to deliver corresponding services to the biogas producers and upgraders.

Companies and other organisations will be able to use the new measurement capabilities at NMIs to test and validate instruments, processes and methods. This will mean that calibration work based on the new measurement capabilities will be available at NMIs/DIs as a result of the project.

The work on field calorimetry will enable biogas producers and grid owners to use field calorimeters with known performance as an alternative to gas chromatography. This provides benefit, especially to small biogas producers, as the costs of ownership of gas chromatographs is high.

The dedicated models and methods for water dew point will 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 is 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.

Contribution to standards

The work of the project provided input to the following draft documentary standards:

- ISO/C 158 Analysis of gases
- NEN 310 408 Biomethane (Netherlands Standards Institute)

A new working group WG25 Biomethane was formed by the consortium, CEN/PC 408 and ISO/TC193/SC1, to work on the standardisation of test methods for the conformity assessment of biomethane and upgraded biogas. It will use the work on impurities (siloxanes, sulphur-containing components, aromatic hydrocarbons, halogenated VOCs, ammonia, hydrogen cyanide, carbon monoxide and hydrogen chloride) to develop ISO-methods, supporting the European specification EN 16723.

A best practice guide (available from the project website) about sampling and sample collection was written. ISO/TC193/WG20 is interested in using these results to feed into the revision of ISO 10715 (Natural gas -- Sampling guidelines). 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 preparation for the further development of the ISO 6145-series of standards.

Future potential impact

The standardisation committees, will benefit through project reports, method descriptions and other building blocks that foster standardisation of measurement methods to support the specification for biomethane.

Equipment manufacturers will benefit from the project's results in that the novel measurement methods will direct their research and development activities towards new or improved technological solutions for measuring biomethane quality.

The Member States of the EU will benefit from this project in particular through the improved access of green gas to the national natural gas grids. This access is a prerequisite for the expansion of the biogas-producing community in order to meet the targets of the Renewable Energy Directive. The increased use of biogas adds to the diversification of sources of natural gas from non-conventional sources, which has a stabilising effect on both the supply and the natural gas price, because of a reduced dependence on imported gas.

The increased use of biogas and biomethane will help to reduce the emission of greenhouse gases, as biogas is produced from renewable sources, such as organic waste, landfills, or manure. Biogas does not compete with food and feed production with regard to its feed stocks. It can be transported in an environmentally friendly way through existing natural gas grids.

This project output will allow producers to reduce biogas upgrading costs by optimising these processes so that they are adjusted to what is actually needed to meet the specifications, thereby optimising revenues. A reduction in the production and upgrading costs of between 10 % - 30 % is possible. These developments will foster growth in the production of non-conventional energy gases from renewable sources by 50 % over the next 5 years. This growth in turn will reduce the dependency of the EU on imported natural gas and it will have a stabilising effect on energy prices for industry and consumers.

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JRP-Coordinator: Dr. Adriaan M.H. van der Veen, VSL, Tel: +31 15 2691500 E-mail: avdveen@vsl.nl JRP website address: http://projects.npl.co.uk/metrology-for-biogas/	
JRP-Partners: JRP-Partner 1 VSL, the Netherlands JRP-Partner 2 CEM, Spain JRP-Partner 3 CMI, Czech Republic JRP-Partner 4 IMBIH, Bosnia and Herzegovina JRP-Partner 5 LNE, France JRP-Partner 6 MIKES, Finland JRP-Partner 7 MKEH, Hungary	 JRP-Partner 8 NPL, United Kingdom JRP-Partner 9 PTB, Germany JRP-Partner 10 SMU, Slovakia JRP-Partner 11 SP, Sweden JRP-Partner 12 TUBITAK, Turkey JRP-Partner 13 HCP, Taiwan
REG-Researcher (associated Home Organisation):	Cesar Chamorro Funge, Spain
REG-Researcher (associated Home Organisation):	Francois Lestremau INERIS, France
RMG-Researcher (associated Home Organisation):	Fernando Pérez Sanz Funge, Spain

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