Calorific value of biomethane: Comparative measurements using reference gas calorimeters

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Abstract. The first comparison of traceable measurements taken using two reference gas calorimeters was performed by LNE and PTB. The super calorific values (SCVs) of three different biomethane samples were within the assessed uncertainties of approximately 0.1 %.

1. Introduction
The European Metrology Research Programme (EMRP) is promoting the usage of ‘green gas’ in its three-year ‘Metrology for Biogas’ project. The project specifies the chemical and physical properties of biogas and biomethane, including the development and validation of traceable methods for determining key impurities, moisture, particulates, calorific values, and density. LNE and PTB, as part of the European Consortium working on this EMRP project, have determined and compared superior calorific values (SCVs) of real biomethane samples with reference-gas calorimetry. The uncertainties of the SCVs are approximately 0.1 % and fulfil the target uncertainties of the EMRP project (0.1 to 0.4 %).

2. Reference gas calorimeters
The Rossini-type calorimeters that were developed and set up at LNE and PTB are isoperibolic gas calorimeters with a stirred water bath in which approximately 1 g of gas is burned in an open flame and the temperature rises by approximately 3 K [1]. Both of the reference-gas calorimeters of LNE and PTB have been used to measure the SCVs of methane [2-4]; LNE’s calorimeter has been used to measure non-conventional fuel gases and compare these measurements to those of commercial calorimeters [5].

The calorimeters are calibrated with an electrical heater to ensure traceability of the energy measurement. Both laboratories analysed the exhaust gas. At LNE, Tedlar bags were used to collect the gases during their combustion; FID and FTIR analysers were installed in series at the output of the combustion chamber. PTB used also an FID in addition to an infrared detector (methane) to perform an in-situ measurement of the unburned fuel gas leaving the calorimeter during combustion. The LNE calorimeter is different to the PTB calorimeter in several technical aspects – for example, the geometry of the burner and the fact that the mass of the fuel gas to be burned is weighed with a mass comparator.

3. Samples
Three real biomethane samples were tested by means of calorimetry, and calorific values were calculated from measurement series. Two biomethane samples were collected from household waste sources; one biomethane sample was collected from manure and slaughterhouse waste. Table 1 presents the

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characteristics of all biomethane samples. The typical composition of the Bio3 biomethane sample, for example, was 96.4 mol% methane, 2.35 mol% carbon dioxide, 0.93 mol% nitrogen, 0.28 mol% oxygen and traces of ethane.

Table 1. Characteristics of biomethane samples.

| Production site          | Sample identifier | Raw sources                                      |
|--------------------------|-------------------|--------------------------------------------------|
| Lille (France)           | Bio1              | Household waste, food and wood waste             |
| Falköping (Sweden)       | Bio2              | Household waste, professional kitchen            |
| Vårgårda (Sweden)        | Bio3              | 90% manure (cow, pig, fowl) and 10% slaughterhouse waste, silage |

Two 5 L gas bottles with a maximum pressure of 200 bar were used for the Bio1 biomethane sample and four 300 mL cylinders with a maximum pressure of 100 bar were used for the Bio2 and Bio3 biomethane samples. The Swedish biomethane samples were prepared by Göteborg Energi, while Metropole in Lille, France provided the French biomethane sample. A tightness problem in the third biomethane sample was observed with the 0.3 L cylinders, leading to discrepancies in the calorific values (see Section 4.3).

4. Results of the calorific value measurements

4.1 Biomethane 1 (Bio1) Sample

For the Biomethane 1 sample prepared in the urban community of Lille (France) and two 5 L bottles were filled 50 bar (Bio1.1 and Bio1.2). The sample mass was varied to ensure reproducibility of the measurement values. The average SCV of the Bio1 sample ($H_s \approx 44.5 \text{ kJ/g}$) was approximately 20% lower than the SCV of pure methane ($H_s \approx 55.5 \text{ kJ/g}$). In one series of combustion experiments, the standard sample mass of a pure methane combustion (1 g) was burned and an adiabatic temperature rise $\Delta T_{ad} \approx 2.4 \text{ K}$ was recorded. To match the further general experimental parameter of a Rossini-type combustion calorimeter (i.e., an adiabatic temperature rise of 3 K for a combustion of 1 g of pure methane), the mass of the Bio1 samples was increased to 1.26 g.

Table 2. Calorific value and uncertainty results for biomethane samples from Lille (Bio1).

| Property            | Bio1.1            | Bio1.2            | Bio1.1            | Bio1.2            |
|---------------------|-------------------|-------------------|-------------------|-------------------|
| $H_s$(mean) / Jg$^{-1}$ | 44 246.5          | 44 296.6          | 44 800.6          | 44 854.7          |
| $\sigma$ / Jg$^{-1}$ | 17.8              | 34.2              | 18.0              | 16.4              |
| $u$(GUM) / Jg$^{-1}$ | 17.8              | 18.2              | 15.6              | 17.7              |
| $u_c$ / Jg$^{-1}$    | 25.2              | 38.7              | 23.8              | 24.1              |
| $U_{c,rel}$ / % ($k = 2$) | 0.11              | 0.17              | 0.11              | 0.11              |

It should be noted that it was not necessary to adjust the experimental parameters for the different SCVs of the biomethane samples, in contrast to the combustion conditions of pure methane. For example, the settings of the mass flow controllers (fuel gas, oxygen and argon) remained the same, while the effective gas flow of the fuel gas increased because of the sensitivity of the controller unit of a mass flow controller to the amount of heat transported by the biomethane gas mixtures.

During each combustion experiment, the carbon monoxide content of the exhaust gas was monitored. Most of the carbon monoxide was produced at the ignition point; its total amount had to be used as a correction (approximately 1 J/g) for the SCV. No significant difference was observed in the CO produced in a biomethane combustion when compared to a combustion of pure methane.

Table 2 presents the results of the gas bottles that contained the biomethane from Lille, which are identified as Bio1.1 and Bio1.2. The properties in Table 2 are the average SCV of the same sample $H_s$(mean), the standard deviation $\sigma$ of the average SCV and the uncertainty $u$(GUM) assessed in
accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) [6], as well as previous publications by the authors concerning the uncertainty estimations of calorific values measured using reference gas calorimeters [2, 7, 8]. The combined uncertainty \( u_c \) (coverage factor \( k = 1 \)) is calculated as the root of the squared sum of \( \sigma \) and \( u(GUM) \) in Table 2; \( U_{c,rel} \) (\( k = 2 \)) is the relative uncertainty of \( u_c \).

The calorific values \( H_s(\text{mean}) \) of the Bio1 biomethane sample (Table 2) are within their expanded total uncertainties. The combined uncertainty \( u_c \) of the LNE result for the Bio1.1 sample has a higher value because of the smaller number of combustion experiments performed. For both samples, a constant deviation of 50 Jg\(^{-1}\) was observed; this may indicate a systematic bias. Further investigations are advisable.

### 4.2 Biomethane 2 (Bio2) Sample

Three different biomethane samples from Falköping, Sweden (see Table 1) were investigated within the scope of this project. Only the Bio2.2 biomethane sample was used in a round robin test on the sample cylinder in both reference calorimeters, which is identical; the Bio2.2 sample was also used in a gas chromatographic (GC) analysis performed by the Van Swinden Laboratory (VSL, The Netherlands). In accordance with the calculation in ISO 6976, and assuming non-consideration of both the compression factor and the correlation coefficient (for uncertainty calculations), the SCV of the Bio2.2 sample taken using the physical unit of mass as its basis was calculated as \( H_s = (50\,952.7 \pm 48.3) \text{ Jg}^{-1} (k = 2) \).

![Figure 1](image)

**Figure 1.** Superior calorific values and corresponding uncertainties \((k = 2; \text{ units Jg}^{-1})\) for Bio1 and Bio2 biomethane samples.

Figure 1 and Table 3 present gross calorific values with expanded total uncertainties for biomethane 2 (three sample cylinders) obtained at PTB and LNE, including a comparison on the same cylinder (Bio2.2). The perfect agreement between the calorific values determined at PTB and those determined at LNE for the Bio2.1 and Bio2.3 samples could be explained by the fact that both cylinders were filled in a short period of time (a few minutes) between two samplings with no change in composition. Values obtained using the direct method (LNE and PTB reference calorimeters) agree with the value calculated using the indirect method (GC analysis in line with CMC capabilities at VSL) within the expanded uncertainties, as shown in Figure 1.

As mentioned above (see Section 3, ‘Samples’, and the results of the Bio1 biomethane sample), taking two biomethane samples at a production site within one hour cannot guarantee that the composition of the samples will be identical; thus, the calorific values measured will be from non-identical biomethane samples. The resulting calorific value difference between both cylinders (Bio2.1
and Bio2.2) of the PTB results is 0.17 %, which is greater than the total expanded uncertainty calculated. Nevertheless, the results in Table 3 indicate only a moderate variation of the sample composition during the sampling process.

The combined uncertainties are approximately 0.1 % for both the LNE and PTB calorific value measurements and agree with the initial objective of the project (between 0.1 and 0.4 %, \(k = 2\)). For the Bio2.2 sample exchanged between PTB, LNE and VSL, the results are still in agreement within their combined uncertainties, with a slight discrepancy of absolute values. It should be noted that only two experiments were performed at LNE for the comparative measurements; this fact is reflected in a higher standard deviation of the SCV mean value in Table 3.

### Table 3. Calorific value and uncertainty results of biomethane samples from Falköping (Bio2).

| Property       | Bio2.1          | Bio2.2          | GC analysis | LNE     | LNE     |
|----------------|-----------------|-----------------|-------------|---------|---------|
| \(H_s\) (mean) | 50 993.1        | 50 909.2        | 50952.7     | 50 984.2| 50 995.5|
| \(\sigma\)     | 7.3             | 11.9            | -           | 22.9    | 25.9    |
| \(u\) (GUM)    | 19.4            | 18.0            | 24.1        | 20.7    | 21.2    |
| \(u_c\)        | 20.8            | 21.6            | 24.1        | 30.9    | 33.5    |
| \(U_{c,rel}\)  | 0.082           | 0.085           | 0.09        | 0.12    | 0.13    |

### 4.3 Sample Biomethane 3 (Bio3)

LNE and PTB received sample cylinders that had lost much of their initial filling pressure (11 and 30 bar, compared to 80 bar at the sampling site) and fairly different calorific values were measured by LNE \((H_s = (52 453.5 \pm 75.5) \text{ Jg}^{-1}, k = 2)\) and PTB \((H_s = (51 712.8 \pm 36.9) \text{ Jg}^{-1}, k = 2)\). A contamination of the samples by air at the sampling site or during the transportation process might be a possible reason.

### 5. Conclusions

Using gas calorimeters, LNE and PTB measured the superior calorific values (SCVs) of three biomethane samples within the scope of ‘Metrology for Biogas’, an EMRP project. The traceable measurements are within the assessed uncertainties of 0.1 % and represent the first comparative measurements performed using reference gas calorimeters. Nevertheless, some apparent systematic differences are revealed (Bio1 sample) and require additional investigation.

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