NEW FRENCH REFERENCE CALORIMETER FOR GAS CALORIFIC VALUE MEASUREMENTS

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The direct measurement of gross calorific value (GCV) of gas with the lowest possible uncertainty can be performed with a reference gas calorimeter. LNE is currently developing an isoperibolic reference gas calorimeter. An exhaustive description of this calorimeter (set up and raw data analysis) for natural gas calorific value measurements is here described. A repeatability study of GCV of methane performed with a prototype version and first tests to reduce the unburned methane dragged with the burned gases are also presented. Calculation method of GCV is detailed and the improvements carried out on the different parts of the calorimeter (burner, vessels, sensors, etc…) are highlighted.

Keywords: *calorific value, isoperibolic calorimeter, methane, natural gas*

Introduction

The application of European directives for opening the gas market to competition leads to a supplying from various gas resources and to an increased number of interfaces in European networks. Thus, the natural gas composition flowing in the European pipes is no longer constant and varies in a large proportion. The currently method used to determine the energetic characteristic (gross calorific value or GCV) of a natural gas is based on gas chromatography (indirect method) and is no more relevant. Calorific value is defined as a quantity of energy released by a complete combustion of a volume, molar or mass unit of a gas. This indirect method implies the use of the calorific values given in the ISO 6976 standard [1] and which were measured from 1930 to 1970 with unknown modus operandi.

Since the thirties and the work completed by Rossini [2–6] and more recently by Pittam and Pilcher from the University of Manchester in the early 1970's [7], it is undeniable that the isoperibolic technique represents the most accurate means to achieve lowest uncertainty on GCV.

In this context, the European Gas Research Group (GERG) began few years ago the development of a combustion reference calorimeter for natural gas [8, 9]. The uncertainty target for the GCV is ±0.05%. Partner and scientific contributor on uncertainty calculations on GCV in the GERG project, LNE engaged in parallel the development and the characterization of a French reference gas calorimeter in order to meet the requirement of a metrological redundancy. This calorimeter, which allows calorific values measurements of pure gases and natural or synthetic gas mixtures, is currently under development and the uncertainty purpose joins the GERG project target. Even if existing reference gas calorimeters are both based on Rossini and Pittam and Pilcher design and works [2–7], many improvements, done by LNE, are here described. Thus, research centre of GDF-Suez performed a specific thorough modelling including the complete calorimeter geometry and the evaluation of the heat flux sources. This modelling whose aim was to reproduce the thermal behaviour of the water bath in the calorimeter led to modifications of the French calorimeter [10, 11].

This paper presents an exhaustive description of the French isoperibolic reference calorimeter. First methane GCV values were obtained with a prototype version of the calorimeter. Experimental results are presented with special attention to the temperature measurement system. Determination of the temperature rise of the water bath is here described and unburned methane analysis is also implemented in order to evaluate precisely the concentration of methane during combustion.

Determination of the gross calorific value

This calorimetric technique consists in burning a given quantity of gas in a combustion chamber totally immersed in a coolant fluid (water bath). The whole system is maintained at constant pressure. The heat released during combustion is transmitted to this

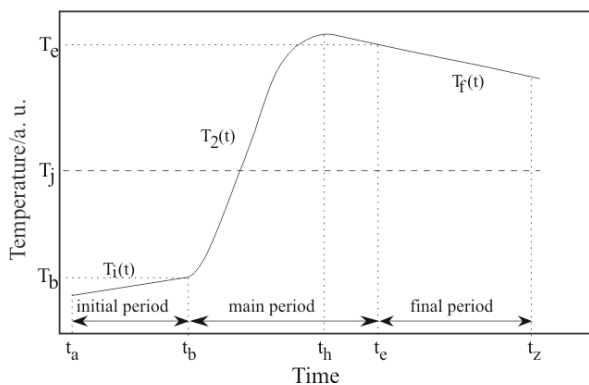*   Author for correspondence: frederique.haloua@lne.fr

Fig. 1 Temperature–time curve feature with the isoperibolic calorimeter

stirred water bath whose transient temperature is recorded as a function of time. Figure 1 shows a typical water bath temperature time curve obtained with the isoperibolic reference calorimeter from combustion or electrical calibration run. The curve can be divided into three periods of 20 min each where the water bath is continuously stirred: two quasi-stable phases with no heat input (also called the initial and the final periods, $T_i(t)$ and $T_f(t)$) and a main period of heat input from electric or combustion run $T_2(t)$, during which the main temperature rise occurs.

The water temperature rise, calculated for an ideal adiabatic case $\Delta T_{ad,comb}$ allows an evaluation of GCV according to Eq. (1):

$$GCV = \frac{C_{cal} \Delta T_{ad,comb} + K}{m_{gas}} \qquad (1)$$

where C_{cal} (J K^{-1}) is the heat capacity of the calorimeter determined by electrical calibration, $\Delta T_{ad,comb}$ (°C) is the water bath temperature rise issued from the heat released during combustion in an ideal adiabatic case, K (J) represents the different energetic corrections inherent to the calorimeter and occurring during an experiment and m_{gas} (g) is the burned mass of gas.

The mass of the gas is determined by the double weighing method with a mass comparator adapted for this purpose. The Dale *et al.* [12] approach adopted this method while GERG calorimeter selected the continuous measuring method of the methane mass [8]. This method involves technical difficulties that do not require such a commitment when assessing the relative uncertainty contribution of the mass m_{gas} on the overall uncertainty that is around 10%.

The K correction factor

The K correction factor consists of a sum of different heat sources forwarded to the water bath and having not as origin the combustion or the electrical heating as:

- Electrical ignition energy (E_i) released during electrical spark between the platinum electrodes
- Energy due to water vapour leaving the calorimeter during the experiment (E_w)
- Energy due to the difference of the in and out flowing gases temperatures (E_g)

Energy E_i can be determined by measuring the water bath temperature during extended time of electrical spark. Energy E_w is calculated by weighing the water vapour produced by the combustion and trapped in the absorption tubes, the temperatures of the in and out flowing gases, currently measured with 100 Ω Pt resistance thermometer, have to be corrected to 25°C to reach E_g.

The heat capacity of the calorimeter C_{cal}

The heat capacity of the calorimeter C_{cal} is determined during an electrical calibration. This calibration consists in releasing the same amount of energy than during the combustion by electrical heating. A heating resistance wire is coiled around the burner wall and provides Joule effect dissipation power of 46 W. The electrical energy is defined as the sum of the products of voltage drop, current of the heating wire and the time interval t_i. The current is measured through a standard resistor of known value installed in series with the heating resistance wire:

$$E_{cal} = \sum_i U_{heati} \, i_{refi} \, t_i = \sum_i U_{heati} \frac{U_{refi}}{R_{ref}} t_i$$
$$= \frac{\sum_i U_{heati} \, U_{refi} \, t_i}{R_{ref}} \qquad (2)$$

The heat capacity of the calorimeter is consequently the electrical energy (Eq. (2)) divided by the temperature rise in an adiabatic ideal case resulting from the electrical heating here called $\Delta T_{ad,cal}$:

$$C_{cal} = \frac{E_{cal}}{\Delta T_{ad,cal}} \qquad (3)$$

The temperature rise in an adiabatic ideal case $\Delta T_{ad,comb}$

In the ideal case of an adiabatic calorimeter, the jacket temperature is adjusted continuously to the calorimeter bath temperature in order to avoid the heat exchanges between the calorimeter bath and the surroundings (zero thermal leakage). Consequently, the two stabilization periods $T_i(t)$ and $T_f(t)$ are horizontal baselines and then the water temperature rise is merely $\Delta T_{ad,comb} = T_e - T_b$. Temperatures T_b and T_e are respectively the temperatures at the beginning (at time t_b) and at the end (at time t_e) of the main period. Adiabatic conditions are difficult

to realize and thermal leakages generally happen. It is consequently easier to maintain the jacket at constant temperature (isoperibolic technique) and to apply a thermal correction δT for heat transfers occurring with the surroundings to get the adiabatic temperature rise $\Delta T_{ad,comb}$.

$$\Delta T_{ad,comb} = T_e - T_b - \delta T \qquad (4)$$

Time t_b is easily determined as the time when the main period begins i.e. opening of the fuel gas valve (combustion) or starting of electrical dissipation (calibration) and time t_e is a calculated time corresponding to the end of heat transfer from the burner to the water bath (Fig. 1). Time t_e is calculated using a step by step backwards method with a linear regression procedure of final period data points converted in moving averages. This method, based on works of Borrell [13], was optimised at LNE with a Matlab® program. The parameters T_e, T_b and δT are calculated according to the Newton's law of cooling (Eq. (5)) and to its boundary conditions.

$$g = \frac{dT}{dt} = u + k(T_j - T) \qquad (5)$$

Term u expresses constant heating released by stirring and the self-heating of the temperature sensors, k is the cooling constant of the calorimeter due to thermal leakage with the jacket. After infinite time, the temperature of the calorimeter would reach a convergent temperature T_∞. Equation (6) exposes the resolution of Eq. (5) with the boundary conditions of infinite temperature and of temperature and time values at the origin.

$$\begin{cases} T_i(t) = T_\infty - (T_\infty - T_b)\exp(-k(t-t_b)) \\ T_f(t) = T_\infty - (T_\infty - T_e)\exp(-k(t-t_e)) \end{cases} \qquad (6)$$

The four parameters T_b, T_e, T_∞ and k are issued from the fitting of the initial and final periods of the experimental curves represented by Eq. (6). Assuming the two parameters T_∞ and k constant during these two periods, general fitting equation from Eq. (6) for the two periods is transformed to:

$$T(t) = T_\infty - [T_\infty - ((1-y)T_b + yT_e)]\exp(-k\tau) \qquad (7)$$

with ($y=0$, $\tau=t-t_b$) for the initial period and ($y=1$, $\tau=t-t_e$) for the final period.

For the determination of δT, an integrated form of Eq. (5) during the main period was used as in the Régnault–Pfaundler procedure [14, 15].

$$\delta T = k \int_{t_b}^{t_e} (T_\infty - T_2(t))dt = k(T_\infty - T_m)(t_e - t_b) \qquad (8)$$

with

$$T_m = \frac{1}{(t_e - t_b)} \int_{t_b}^{t_e} (T_2(t))dt$$

Figure 2 shows the area (dashed zone) of the integration of the main period between t_b and t_e determined by a Matlab® program with the trapezoidal numerical method. The error with this numerical method is larger than with the Simpson method but the influence of the error on the overall uncertainty is null.
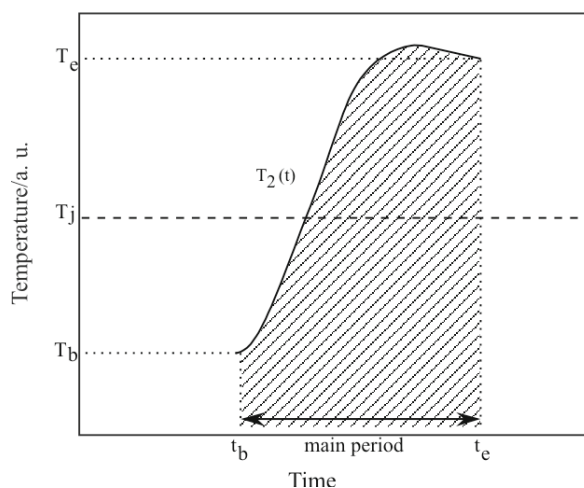

Fig. 2 Area representing the integration method during the main period

Experimental

Figure 3 exposes a schematic of the calorimeter. The combustion takes place in a glass burner in which a given quantity of gas is burned. The gas is initially contained in a pressurized sphere at 24 bars. The container is a 60 mm inner diameter sphere with 0.5 mm thickness and is made of non-magnetic material composed essentially of copper and nickel (ARCAP) in order to minimize disruption of the mass comparator electronics. The flame ignition is produced in the burner by electric spark generated by two platinum electrodes. Times of ignition and extinction of the flame are determined with a Si photodiode located in front of the flame at the external wall of the burner in the water bath. The burned gases circulate in a new and optimised reduced heat exchanger (Fig. 3) and are heading for analysers of unburned hydrocarbons and CO, CO_2 and NO_x components. Before gas analysis, the exhausted gases are drying in two absorption tubes filled with anhydrous magnesium perchlorate.

The calorimeter vessel is thermally uncoupled from outside by the means of an isothermal jacket (glycol stirred bath) maintained at constant temperature T_j of 25°C that characterizes the isoperibolic aspect. This traduces equal exchanges with the calorimetric water bath from 23.5 to 26.5°C. This temperature
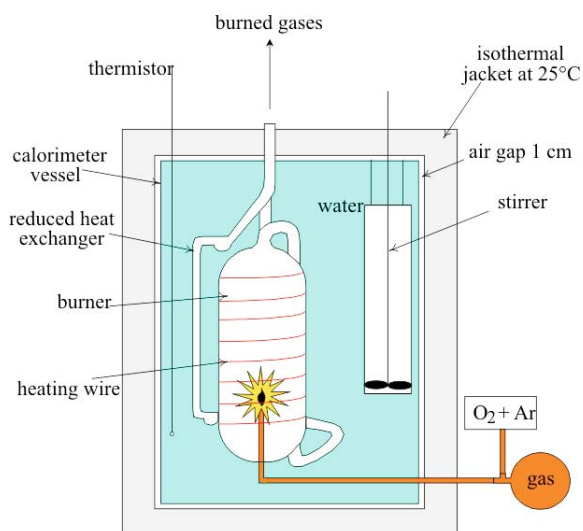
Fig. 3 Schematic of the LNE reference combustion calorimeter

Fig. 4 Geometric model of the calorimeter

level is chosen to respect the combustion reference conditions at which the fuel is notionally burned [1], set at 25°C and atmospheric pressure. This means that all the combustion products and the reactants are theoretically brought back to this temperature, including the produced water.

The thermal insulation of the calorimeter is performed by:

• a 1 cm air gap between the calorimeter vessel and the isothermal jacket (Fig. 3) to reduce heat transfer by convection
• the use of electropolishing stainless steel walls to reduce the radiative heat transfer between the calorimeter vessel and the isothermal jacket.

Thermistor of 10 kΩ resistance was chosen to measure the bath temperature for its high sensitivity (430 Ω °C^{-1}), small geometry (1 mm diameter of the bead) and fast time response (1.5 s in an oil bath) [16]. Thermistor is calibrated in situ by comparison with a 25 Ω standard platinum resistance thermometer.

Concerning the electrical calibration to determine the heat capacity of the whole apparatus, the Joule effect dissipation which the power reaches approximately ~46 W, occurs during 20 min and reproduces the same heat release than during combustion.

Optimisation of the calorimetric design according to simulation results

A detailed transient 3D numerical simulations of the flow and heat transfer in the calorimeter water bath was performed by GDF-Suez in order to define at best the geometry of the calorimeter vessels. The target is to optimise the thermal homogeneity and to maximize heat transfer from heating sources to the water bath. The modelled volume corresponds to the water bath
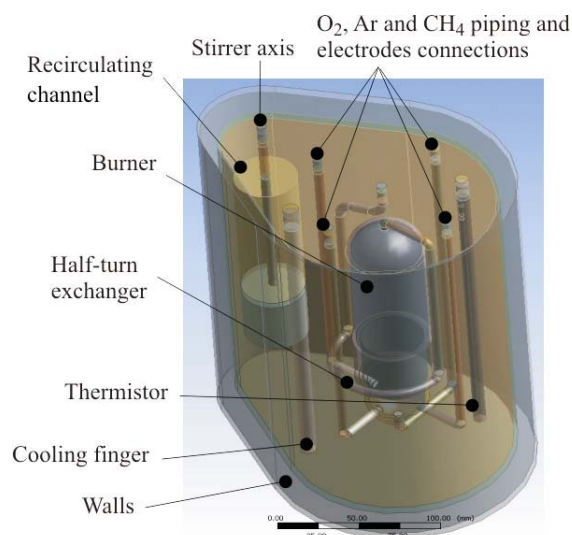
stirred in the calorimeter including the burner thickness, the reduced heat exchanger, the walls of the calorimeter vessels and all the accessories as the volume of the four pipes, the cooling finger, the stirrer axis and the temperature sensors. Figure 4 exposes the calorimetric model realized by GDF-Suez R&D division. Total water volume is approximately 4.2 l.

The results of this modelling are presented in details in [11]. The main conclusions that are summarized hereafter validate technical choices and give proposals of improvements:

• Validation of the calorimetric vessels design: approximately 90% of the total energy is absorbed by the water bath and 10% by the calorimetric walls
• Proposition to reduce the heat exchanger from helicoidally form around the burner to one half-turn made in glass, and addition of water traps to collect liquid water produced by the combustion (liquid water has to remain in the burner in the calorimeter for the determination of the gross calorific value)
• Validation of the temperature sensor's position standing between the burner and the vessel wall at the opposite side of the stirrer (this optimised site allows to measure a good representation of the water bath mean temperature)
• Confirmation of the jacket temperature fixed at 25°C

These numerical simulation results validated some important technical choices for the LNE calorimeter compared to existing reference calorimeters [7–9, 12] as the heat exchanger geometry, the location of the sensor or the temperature of the jacket.

Results and discussion

Experiments were performed using a prototype version of the calorimeter with pure methane (99.9995% CH_4). The flow rate of methane during combustion is 70 mL min^{-1} and the voltage applied during calibration to the heating wire is about 41 V to achieve a dissipation power of 46 W.

The general feature of the thermal behaviour of the water bath is identical for the two cases. The initial and final periods have opposite sign slopes due to heat transfers with the isothermal jacket bath maintained at 25°C. Stirring action takes place during all the experiment and causes a light contribution of heat transferred to the water.

Even if the temperature rise for the calibration is different than in combustion, it is not disturbing the heat capacity calculation of the whole system. Considering the procedure calculation for the temperature rise in an ideal case detailed in the previous section and the mass of gas to be burned, the gross calorific value is reached.

The correction factor K of Eq. (1) has not been determined for the prototype version but it will be done in near future with the final version of the calorimeter. A repeatability study was performed on calorific values of methane. The mean value on six experiments is 55839 J g^{-1} and the standard deviation is 0.077%. The relative deviation to the standard calorific value of methane issued from ISO 6976 is 0.58%. This deviation is mainly due to two phenomena existing during the combustion and concerning the methane mass measurement:

- Methane remaining in the pipes
- Unburned methane

Methane analysis

A small quantity of methane is always remaining in the pipes and especially in the methane mass flowmeter between two experiments. This amount of methane, which is not taking into account in the methane mass measurement, increases the calculated calorific value.

Moreover, a correction has to be applied to the methane mass measurement (carried out by the double weighing method) because methane is not completely burned in the burner and a small part is passing through the calorimeter. Experimental combustions were performed using a FID hydrocarbons analyser that allows uninterrupted measurements of hydrocarbon concentrations in the burned gases.

The CH_4 concentration measurement is based on the principle of ionisation flame detection (FID): the sample is burned in a furnace inside the analyser. Under the heat effect, the C–H bonds of the molecules
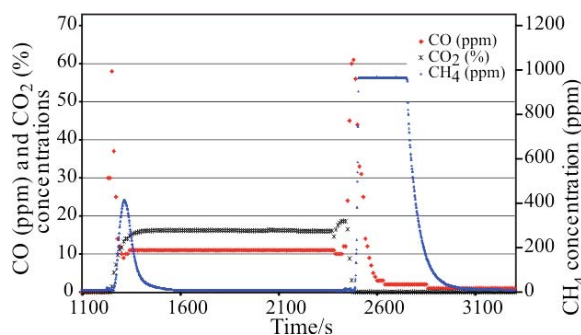

Fig. 5 CO, CO_2 and CH_4 concentrations during combustion

are breaking by forming radicals $CH^{\bullet}$, $CH_2^{\bullet}$ and $CH_3^{\bullet}$. These radicals, in contact with oxygen, release electrons and the generated current is proportional to the number of carbon atoms in the molecules of the sample.

The analyser is implemented in series with an IR analyser detecting CO and CO_2 concentrations. The FID analyser uses very weak sampling flow rate. Figure 5 gives the CO_2 (%), CO (ppm) and CH_4 (ppm) concentrations in the outflowing gases during combustion. The first observations are raising a few drawbacks as the detection limit of the analyser that is around 1000 ppm (0.1% concentration) or its long time delay (approximately 40 s) for a lecture of the methane concentration. A new FID analyser has been installed to increase the detection limit to 30 000 ppm (3%) with a lower time delay (around 2 s). This new apparatus avoids the previous disadvantages. In general, the FID method has advantage to prevent dilution of the gas sample when concentrations are too large because of its high detection limit. Figure 5 exposes that:

- Except the ignition and the extinction periods of the flame, combustion is quasi-complete (no CH_4 and CO concentration measured at 11 ppm between 1600 and 2400 s).
- The CH_4 peaks have a 50 s delay compared to the CO peaks; this is due to the time delay of the FID analyser (see above) and to the time needed for the exhausted gases to run the distance between the two analysers.
- Maximum CO concentration is about 60 ppm both at ignition and extinction of the flame that traduces a bad combustion (unstable premixed flow) at these two moments.
- The CH_4 concentration peak is lower at ignition (~400 ppm) than at extinction of the flame (>1000 ppm) that means that the reactants are correctly premixed at the beginning of the main period and that the mixture is too lean (under the lower flammability limit) to burn at the end of this period.

To correct these problems, it is planned to improve the experimental procedure of combustion with the new FID analyser in order to remove the remaining

methane before the beginning of a new combustion and to optimise the combustion chemical process.

Conclusions

This paper yields an exhaustive description of the French reference calorimeter for natural gas gross calorific value measurements. A repeatability study on measurements performed with the prototype version is exposed and first results of tests for reducing the non-burned methane that is dragged with the burned gases (mainly CO_2 and water vapour) during an experiment are here described. However, it is clearly a duty to evaluate quantitatively the minimized unburned methane to correct properly the calorific values. The calculation method for GCV measurement and especially the temperature rise for an ideal case are explained. First GCV of methane are given as well as the work-in-progress technical evolutions.

Acknowledgements

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