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Measurement of gas calorific value using electric substitution method

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Abstract The calorific value is defined as the amount of heat which would be released by the complete combustion in air, in such a way that the pressure remains constant, all the combustion products except water are gaseous states and all the products returned to the temperature of the reactants. Recently, the mixed fuel like LPG, LNG, hythane, etc., become more popular. But the composition of these fuels changes with time and place where it was produced, which give direct impacts on the calorific value and performance of the heating apparatus. Therefore, the accurate measurements of the calorific value become an issue in the refinery industries and the national standardization fields. So, flame calorimeter was manufactured and characterized to measure calorific value of the gaseous fuel in the flow situations. Electric substitution method initiated by Alexandrov was adopted. Peltier elements were used to emit the heat supplied by a heater and a flame to the cooling water. Freon-11 was used as a heat carrier. To get the accurate calorific value by the experiments conducting in the normal laboratory conditions, correction methods were proposed to count variations in the experimental conditions such as temperatures, electric powers, etc. It was found out that the corrected calorific value of pure methane had 0.36% relative deviation to the standard value.

Keywords Flame calorimeter · Electric substitution method · Calorific value · Methane

Introduction

Shortage of energy resources led to the development of new gas fields in various places around the world. The composition of the natural gas (NG), as a mixed gas fuel, depends on where and when it was produced. Table 1 shows the variations of the NG compositions from difference sources [1]. Calorific value depends on the composition of the natural gas. Variations in the calorific value of the natural gas had an influence on the performance of the combustion devices such as boiler, automobiles, power plants, etc. So, the exact measurement and standardization of the calorific value of NG are one of the fundamental features to calculate effective energy consumption and to estimate fuel quality.

The calorific value of gas was defined in ISO 6976 [2] as "the amount of heat which would be released by the complete combustion in air of a specific quantity of gas, in such a way the pressure p_1 at which the reaction takes place remains constant, and all of these products being in the gaseous state except for water formed by combustion, which is condensed to the liquid state at t_1." These specifications imply that the gas calorimeter should be designed so as to satisfy the definition.

Bomb calorimeter [3, 4] is one of the classical device to measure the calorific value. For gases, flow type calorimeter has been developed [5]. Since gas has low energy density compared with solid or liquid fuels, relatively large amount of gas must be burned to get precise value for the bomb calorimeter or batch type one. Electric substitution method was proposed by Alexandrov [6] of Mendeleev

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Table 1 Natural gas composition with geographic variations [1]

Source	Methane	Ethane	Propane	Buthane	Nitrogen
Alaska (Kenai)	99.72	0.06	0.005	0.005	0.20
Algeria (Arzew)	86.98	9.35	2.33	0.63	0.71
Baltimore Gas & Electric	93.32	4.65	0.84	0.18	1.01
San Diego Gas & Electric	92.00	6.00	1.00	0.00	1.00
Venezuelan	87.30	10.10	2.10	0.20	0.30

Institute of Metrology (IMM), to get accurate calorific value. He used flow type calorimeter. It was designed to use Peltier elements to pump out the heat from the flame and/or heater. Freon-11 was used to carry heat from heater to the Peltier elements. The calorific value was obtained by the measurements of electric powers at the steady flow conditions.

Recently, Haloua et al. [7] of Laboratoire National de Metrologie et d'Essais (LNE) introduced developing isoperibolic French reference gas calorimeter. It burned a given quantity of gas in isobaric process in a combustion chamber which was totally immersed in a coolant fluid. Their relative deviation to the standard calorific value of methane was 0.58%.

Since one of the aim of this study was to get accurate calorific value even in the field conditions, experiments were conducted in the normal laboratory environment not within precisely controlled constant temperature and humidity chamber as in Ref. [6] and correction methods was proposed to account for the variations in the temperatures and electric powers.

It was found out that the measured calorific value of methane (99.95% purity) deviated 0.36% from the theoretical value. The design technique and the experimental data used here could be applied to measure the calorific value of NG directly and establish the national standard of gas calorific value.c

Operational principle

Main body of the gas calorimeter consists of combustion chamber, heater, a heat exchanging device and working fluid as shown in Fig. 1. The heater was installed around the combustion chamber to compensate the amount of the energy which would be generated by the fuel if flame was lit in the system. The heat exchanging pipe (copper) was welded at the upper part of the combustion chamber, through which the exhaust gas flows down to the bottom of the combustion chamber. Freon-11 was used as working fluids to transfer heat at the constant temperature during phase change. Peltier elements were used to pump out the heat from the working fluids.

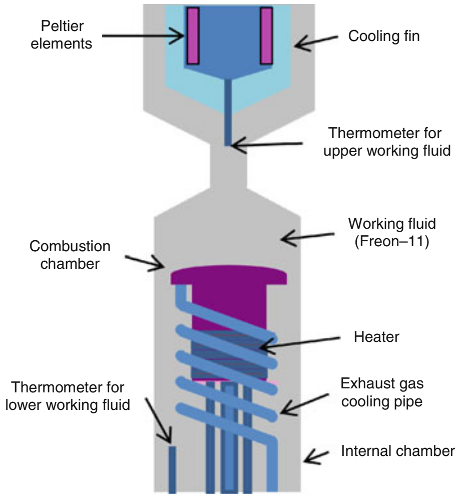

Fig. 1 Schematic diagram of the flame calorimeter main body

The heat generated by the flame and/or the heater was transferred to the working fluid, which made phase change in the working fluid. The evaporated working fluid rose to cooling fins and condensed. Cooling fins were cooled by the Peltier elements which, in turn, cooled by the cooling water. Thus, generated heat was transferred to the Peltier elements via the working fluid, and then it was pumped out to the cooling water.

Figure 2 shows the energy balance diagram for the experiment. When the system is in the steady flow conditions, the input power must equal to the output. Energies were supplied to system by the Peltier element, electric heater, and fuel, which would be denoted as P_{Peltier}, P_{heater}, and P_{fuel}, respectively. Energies left the system by the cooling water and heat loss to the surroundings, which would be designated as P_{water} and P_{loss}.

If the flame is turned on in the system, it is called case A. If not, called case B. For case A, the input power of P_{heater}, P_{Peltier}, and P_{flame} should be equal to the output power of the P_{water} and P_{loss}.

The energy balance could be expressed as,

Case A (with flame),

$$P'_{\text{heater}} + P'_{\text{Peltier}} + P'_{\text{fuel}} = P'_{\text{water}} + P'_{\text{loss}} \tag{1}$$

here the superscript $'$ represents terms in case A.

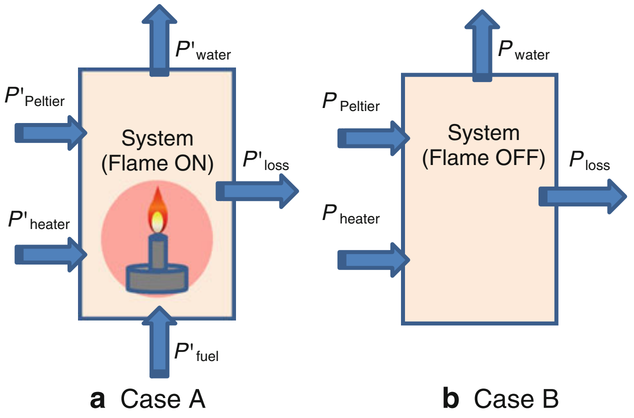

Fig. 2 Energy balance in the experiments **a** case A when flame exists, **b** case B without flame

For case B, P_{heater} and P_{Peltier} should be balanced with P_{water} and P_{loss}, which could be expressed as,

$$\text{Case B (without flame)}, \quad P_{\text{heater}} + P_{\text{Peltier}} = P_{\text{water}} + P_{\text{loss}} \tag{2}$$

Thus, power supplied by the flame could be calculated by these two equations as,

$$\begin{aligned} P'_{\text{fuel}} = {} & (P_{\text{heater}} - P'_{\text{heater}}) + (P_{\text{Peltier}} - P'_{\text{Peltier}}) \\ & - (P_{\text{water}} - P'_{\text{water}}) - (P_{\text{loss}} - P'_{\text{loss}}) \end{aligned} \tag{3}$$

This equation means that the power supplied by the fuel, which is convertible to the calorific value, could be obtained by the measurement of the power differences in two cases. The last three terms in the right hand side are power differences in Peltier, cooling water and environments between case B and A, which occurred out of the flame calorimeter. If the system could be sustained exactly the same situations at the Peltier elements, cooling water and the environment between two experiments, the energy supplied by the fuel would be the heater power changes in case B and A, that is, if surface temperature of the cooling fin, power to the Peltier elements, flowrates and inlet temperature of the cooling water and environment conditions were simultaneously kept unchanged during two experiments. But it is not possible to match all these conditions in the normal laboratory or industrial situations, these terms should be considered to get an accurate calorific value.

Flame calorimeter

The calorimeter system was made of main body as in Fig. 1, the cooling device, the insulator, the flow control systems, and the electric power suppliers.

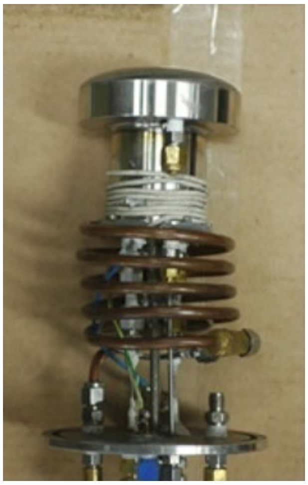

Fig. 3 Combustion chamber

Figure 3 shows the mushroom shaped combustion chamber, the heater and the heat exchanging pipe. Head and the column of combustion chamber were made of stainless pipe, and their diameters were 105 and 61 mm, respectively. For case A, burnt gas flew down through heat exchanging pipe made of spiral copper pipe. Its length was 110 cm to make thermal equilibrium between exhaust gas and working fluid at the exit of the chamber. The fuel and the primary oxygen were supplied through 1.6 mm pipe and the secondary oxygen was fed into the combustion chamber through coaxial 6.4 mm pipe. The igniter was installed in the combustion chamber and the line was insulated with ceramic beads.

Figure 4 shows inside of the combustion chamber. Flame was ignited by the electric spark. To check whether the flame was on or not, thermocouple was inserted in the chamber. Lower part of the combustion chamber was wrapped with nichrome wire heater of 0.6 mm diameter,

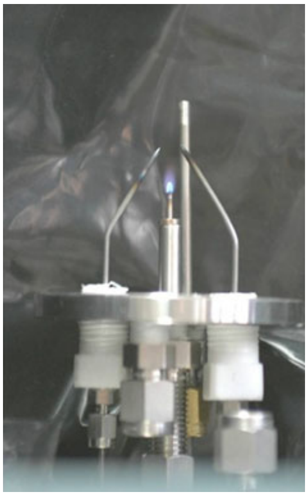

Fig. 4 Interior of the combustion chamber

Fig. 5 Internal chamber

1.6 m length and with a capacity of about 10 Ω. The combustion chamber and the heater were installed in a dumbbell shaped internal chamber as shown in Fig. 5. Up to the middle of the combustion chamber in the internal chamber was filled with the working fluid.

Two Peltier elements, maximum power of 110 W, were placed outside of the cooling fin to take off the heat. The high temperature side of the Peltier element was cooled by cooling water. Thus, the heat generated by the flame and the heater transferred to the working fluid, then to the Peltier elements and after that flowed out via the cooling water. The internal chamber was set within the external one. Ceramic fiber insulator was packed between the two chambers. To make relatively uniform external conditions, another cooling water was flown through the out shell of the external chamber.

To get the calorific value of the fuel, or equivalently P'_{fuel}, via Eq. 3, electric power to the heater and Peltier elements were measured and energy transfer rate to the cooling water was obtained and power loss to the environment was evaluated. P_{water} was obtained by the measurements of the flowrate and temperature increase in the cooling water.

Platinum resistance thermometers (PRT) were used to get the temperatures of the fuel, oxygen, coolant, working fluid and exhaust gas as in Fig. 6. Also thermocouples were used to get the temperature of relatively less important points like room and inside of the combustor. The temperatures of the lower working fluid and the exhaust gas were used to check whether the system was in the steady state. Also lower working fluid temperature was used to control electric power input to the Peltier elements and/or heater. The temperature of the external chamber and the room were used for the heat loss calculation.

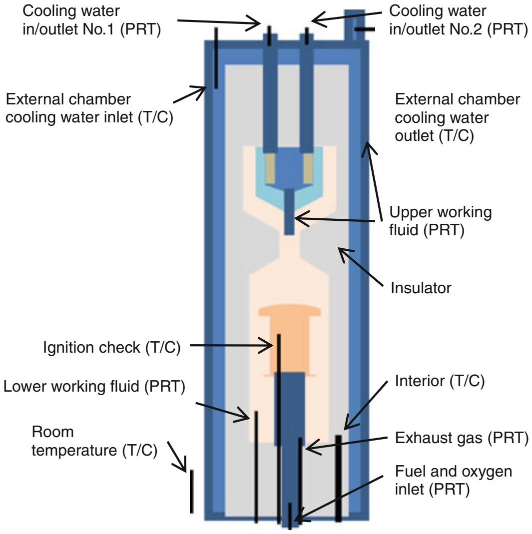

Fig. 6 Location of the temperature measuring points

The flowrate of the fuel could directly influence to the calorific value. Since water has large thermal capacity, flowrate of the Peltier cooling water could significantly affect to the results. Thus, these were carefully controlled and stabilized. The flowrates of the fluids were well controlled except secondary oxygen as shown in Table 2.

To verify the complete combustion in case A, the exhaust gas was collected and methane concentration was measured with gas chromatograph. It was 1.5 ppm, which was less than that in the natural state of 1.8 ppm, which means that it was complete combustion.

Results and discussion

Experiments for the cases of with flame (case A) and without flame (case B) were conducted and compared each other to get the calorific value of methane.

For case A, the power input to the heater was varied to stabilize exhaust gas temperature around 25 °C at a constant Peltier power. When the exhaust gas temperature was remained 0.03 °C variations for 20 min, the system was considered as steady flow state. For case B, Peltier power was set the value of case A and the heater power was changed to make the same lower working fluid temperature, $T_{\text{L.W.F.}}$, of case A. When differences in $T_{\text{L.W.F.}}$ between case A and B tests was less than 0.03 °C and continued more than 15 min, then it was assumed that the system was sustained steady flow conditions and used to evaluate calorific value. If every situation is ideal, the heater power difference between two tests would be the calorific value.

Table 2 Average and standard deviation of flowrates of supplied reactants and cooling water

	Case A						Case B	
	Ar	CH_4	Pri. O_2	Sec. O_2	Water 1	Water 2	Water 1	Water 2
Average	40.18	40.36	26.28	156.64	425.97	299.85	423.90	301.17
Stand. Dev.	0.38	0.36	0.14	4.82	0.74	0.44	0.60	0.75

Units: cc/min for chemical species, g/min for water

Figure 7 shows the temperature of the exhaust gas and the lower working fluid in the steady state for case A. The power for Peltier elements was fixed as 55.912 W. It shows that the exhaust gas temperature was stabilized at 24.945 °C. The fluctuations would be occurred by water drop which passing by the temperature sensor. The average $T_{\mathrm{L.W.F.}}$ was used to control the system in case B.

Figures 8 and 9 show the power supplied to the Peltier elements and the heater. As fluctuations were relatively small, it was considered that the electric powers were also stabilized. Figure 10 shows very little temporal temperature changes in the Peltier cooling water during the experiments.

Temperature differences in two water outlets seems to be caused by uneven the water flowrate through the Peltier cooling elements.

For case B test, the electric power for the Peltier elements was fixed at the same value as in case A and only heater power was changed to keep the temperature of the lower working fluid around 25.15 °C, as in the case A test. Figure 11 shows the lower working fluid temperature stays around 25.16 °C for 2000 s, which indicates that the conditions within main body of the calorimeter in case B test were sufficiently adjusted to those in case A. Figures 12 and 13 show the power supply to the Peltier element and the heater. Even though the settings for the Peltier elements were fixed to the values of the case A, Peltier power changes slightly due to the temporal variations in the power supplier and the power source. The heater power increase around 650 s in Fig. 13 was resulted from the power control to match $T_{\mathrm{L.W.F.}}$ as in case A. Though it was fixed at a certain value after that, it drifts slightly due to the same reason for the Peltier power changes. Values after 800 s in Fig. 13 were used to calculate the calorific value. The temperature of the cooling water for the Peltier elements also kept constant, as shown in Fig. 14.

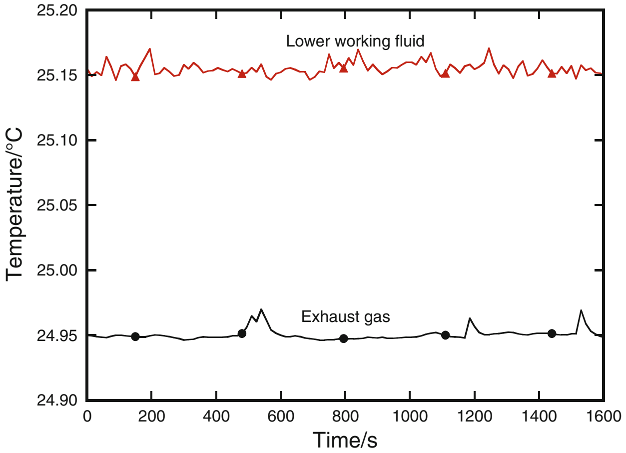

Fig. 7 The temperature of the lower working fluid and the exhaust gas as a function of time (case A)

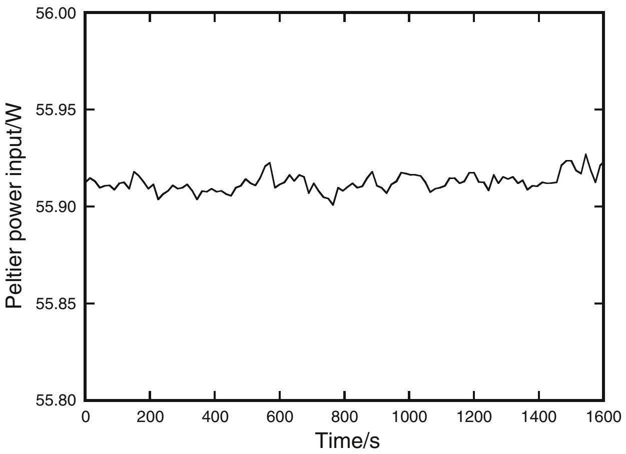

Fig. 8 Variation of the power supply to the Peltier element (case A)

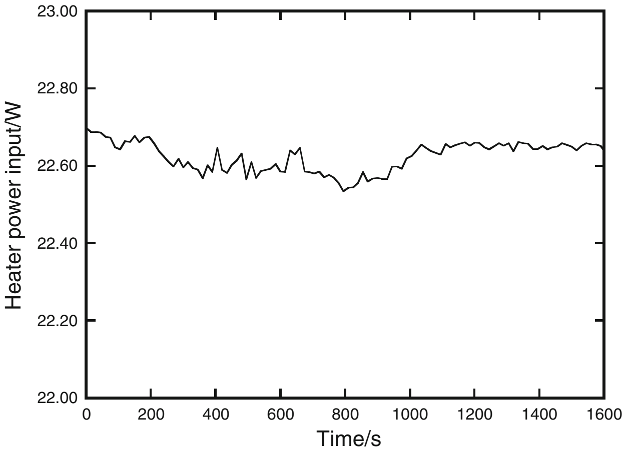

Fig. 9 Variation of the power supply to the electric heater (case A)

Table 3 shows the measured temperatures and the powers during steady flow conditions. It represents that the

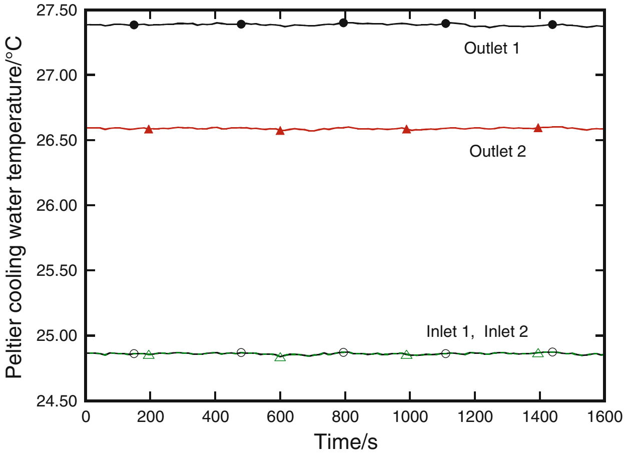

Fig. 10 Variation of Peltier cooling water temperature (case A)

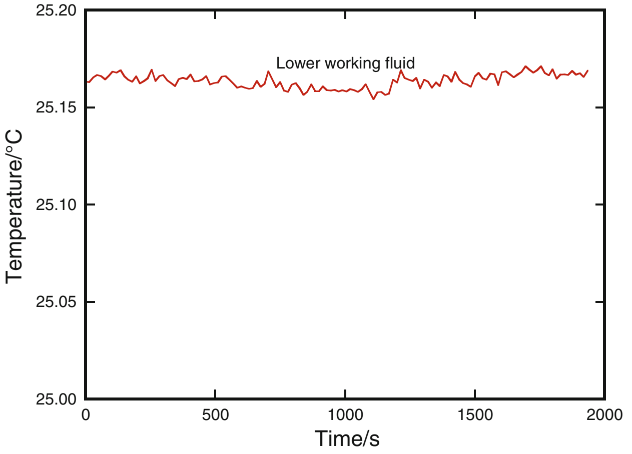

Fig. 11 Variation of the lower working fluid the temperature (case B)

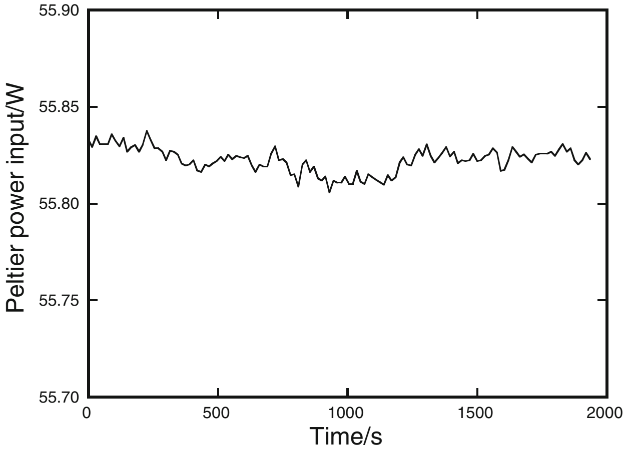

Fig. 12 Variation of the power supply to Peltier element (case B)

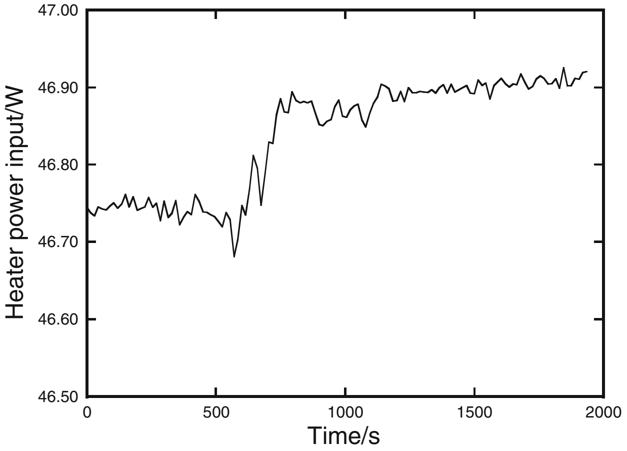

Fig. 13 Variation of the power supply to the electric heater (case B)

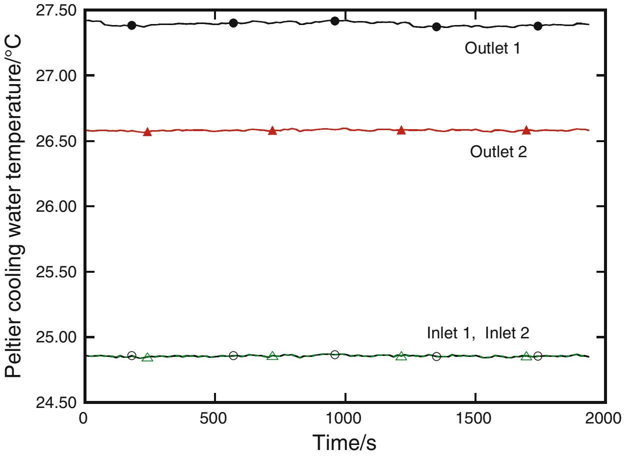

Fig. 14 Variation of Peltier cooling water temperature (case B)

temperatures of the lower working fluid, which was used as the reference values, was located within ±0.01 °C for both tests. However, the temperatures of external chamber, room and cooling water of the Peltier elements have been changed during two experiments. These differences imply that heat losses were not the same value. To get the accurate value of the calorific value, these heat losses and the changes in conditions must be considered, which was not counted in Ref. [6].

To calculate heat losses to the environment and to the cooling water for external chamber, simple one dimensional heat resistance model [8] was used. Heat was transferred to the outer side wall of external chamber of room temperature through the internal chamber, the insulation material, the acrylic tube and the air layer. Heat losses to the upper and lower sides were calculated with the representative temperature of the upper and lower working fluid, respectively.

With simple calculations, it was obtained that the heat loss values are 0.200 W in case A and −0.251 W in case B. Thus, the last term of Eq. 3 is $(P_{\text{loss}} - P'_{\text{loss}}) = -0.451$ W. With the experimental data in Table 3 and Eq. 3, the calorific value of the methane was calculated as 24.475 W.

Table 3 Average and standard deviation of the temperatures and the power inputs

Case		T_{exhaust}/°C	$T_{\mathrm{L.W.F.}}$/°C	$T_{\mathrm{U.W.F}}$/°C	$T_{\mathrm{w1,in}}$/°C	$T_{\mathrm{w1,out}}$/°C	$T_{\mathrm{w2,in}}$/°C	$T_{\mathrm{w2,out}}$/°C
A	Average	24.945	25.154	23.941	24.862	27.386	24.862	26.589
	Stand. Dev.	0.0042	0.0051	0.0158	0.0067	0.0086	0.0067	0.0062
B	Average	–	25.164	23.909	24.856	27.394	24.856	26.582
	Stand. Dev.	–	0.0038	0.0437	0.0060	0.0148	0.0060	0.0052

Case		$T_{\mathrm{Ext.\ chamber}}$/°C	$T_{\mathrm{O_2}}$/°C	T_{room}/°C	Heater power/W	Peltier power/W
A	Average	24.177	24.261	21.537	22.565	55.912
	Stand. Dev.	0.0083	0.0257	0.0363	0.4371	0.0048
B	Average	25.366	24.578	21.355	46.892	55.822
	Stand. Dev.	0.0067	0.0063	0.0313	0.0672	0.0057

Here subscript L.W.F. stands for lower working fluid, U.W.F. for upper working fluid, w for cooling water for the Peltier elements

Since the flowrate of the methane was 4.462×10^{-7} kg/s, as in Table 2, the calorific value for 1 kg methane was 24.275 W/(4.462×10^{-7} kg/s) = 54.852 MJ/kg.

In order to estimate the accuracy of the measurement, it was compared with the theoretical value calculated using the chemical equilibrium code. With the amount of the supplied methane, oxygen, and argon in Table 2, the chemical equilibrium reaction could be expressed as:

$$\mathrm{CH_4} + 4.529\mathrm{O_2} + 0.995\mathrm{Ar} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O} + 2.529\mathrm{O_2} + 0.995\mathrm{Ar}. \tag{4}$$

The absolute enthalpies according to this reaction were calculated using STANJAN code [9] and the results are shown in Table 4.

By the definition of the calorific value, reactants and products must be supplied and left at 25 °C and the phase of H_2O in the products should be liquid. From Table 4, the calorific value of the methane can be calculated as −4666.0 − (−60161.9) = 55.496 MJ/kg which deviated only 0.01% from the Alexandrov's results [6]. That means the results from the STANJAN code could be used as theoretical value.

In this study, the methane was supplied at 21.54 °C instead of 25 °C and the water vapor was contained in the products. Thus, theoretical calorific value for our case could be calculated as −4707.9 − (−59757.8) = 55.050 MJ/kg, which means that the measured and corrected calorific value of the methane has deviated 0.36% from the theoretical one.

This experiment was conducted in the normal laboratory environment, not within precisely controlled constant temperature and humidity chamber as in Ref. [6]. Thus, the major correction was related with the heat loss, which means the insulation would be one of key factors that affect accuracy of the experiment. To get more accurate value, heat loss not only from the internal chamber surface but also through the electric wires and the gas supplying pipes must be considered. Also enhanced insulation and elaborated heat transfer model would be helpful to enhance the accuracy of the calorimeter.

Table 4 Absolute enthalpies of the mixtures in Eq. 4 calculated using STANJAN code

	Water vapor mole fraction in the product	Liquid water mole fraction in the product	Absolute enthalpy/ kJ(kg CH_4)$^{-1}$
Reactants @21.54 °C			−4707.9
Reactants @25 °C			−4666.0
Products @25 °C	0.000	0.307	−60161.9
Products @25 °C	0.022	0.284	−59762.8
Products @24.95 °C	0.000	0.307	−60160.6
Products @24.95 °C	0.023	0.284	−59757.8

Conclusions

To get the accurate calorific value of a gas fuel in steady flow conditions in the industrial or normal laboratory situations, correction methods based on the energy balance equation has been proposed. Flame calorimeter according to the Alexendrov's model has been designed and calorific value was measured. Variations in temperatures and electric powers were considered to correct the measured calorific value. Corrected one was compared with that of the theoretical value which was calculated using the chemical equilibrium code. It was found out that corrected value deviated 0.36% from the theoretical one. As this error was mainly caused by heat loss, the accuracy could be increased by the enhancement of the insulation. The design technique and the heat balance consideration method in this study would be used to establish the national standard for gas calorific value.

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