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Determination of the calorific value of natural gas by different methods

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Abstract

The determination of the calorific value of natural gases is of great economic importance in gas supply. In this paper, different methods for calorific value determination are described.

Besides gas calorimetry using the classical procedure of burning a gas sample, different methods are available: analytical methods which are based on the analysis of the gas sample, correlative methods which allow the calorific value to be calculated as a function of characteristic physical measurands, stoichiometric methods which make use of the almost linear correlation between oxygen required for combustion and calorific value, and state reconstruction which is based on calorific value calculation by offline simulation of the whole gas supply network. The principles of the different methods are described in this paper. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Calorific value; Gas calorimetry; Gas chromatography; Correlations; State reconstruction

1. Introduction

Every year, billions of cubic metres of natural gas are traded world-wide. In Germany alone, the consumption of natural gas in 1999 was 850 billion kWh, i.e. approx. 85 billion m^3 (under reference conditions) [1]. In several countries all over the world, the billing of the amount of gas supplied is based on the calculation of the thermal energy it contains as the product of metered volume under reference conditions and volume-based calorific value.

The definition of the calorific value for the specific purpose in gas supply is given by ISO 6976 [2]: "The amount of heat which would be released by the complete combustion in air of a specified quantity of gas, in such a way that the pressure p_1 at which the reaction takes place remains constant, and all the products of combustion are returned to the same specified temperature t_1 as that of the reactants, 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". Different values are used world-wide as reference temperature and reference pressure, e.g. in Germany 0 °C (volume), 25 °C (combustion) and 101,325 Pa.

The precise determination of the calorific value is of great importance world-wide. During the last 100 years, several methods were developed, that can be roughly subdivided into five categories and whose principles will be described below.

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2. Gas calorimetry

According to the principles of the various calorimetric techniques, the instruments available can be subdivided into three different groups:

1. combustion of a gaseous sample inside a calorimetric bomb (isochoric combustion in an isoperibolic calorimeter);
2. combustion of a gas in an open flame of a gas burner (isobaric combustion in an isoperibolic or isothermal calorimeter);
3. combustion without a flame on a catalyst (isobaric combustion in an isoperibolic or isothermal calorimeter).

These different methods each have specific advantages and disadvantages which will be described below.

2.1. Combustion of a gaseous sample inside a calorimetric bomb

The determination of the calorific value of solid and liquid samples, using bomb calorimetry has been a standard procedure in laboratory practice for decades. The use of a calorimetric bomb to determine the calorific value of gases can be found only in a subset of cases [3]. The reason for this are the conditions of the reaction of the combustion. When solid or liquid samples are burnt, the sample is localised and combustion takes place only at the interface between sample and oxygen. When bomb calorimetry is used for gaseous samples the process taking place is different, because gas and oxygen are uniformly mixed before combustion takes place. The reaction, therefore, starts at the ignition system and the flame front propagates towards the walls of the bomb.

Since the arising heat of reaction furnishes the activation energy of the progressing reaction, solid and liquid samples burn completely. When gaseous samples are burnt, cooling and, thus, quenching takes place close to the walls of the bomb. In this region, the energy necessary to overcome the activation energy cannot be delivered by the heat of reaction. Incomplete combustion is the consequence.

As the calorific value has to be determined in terms of quantity, incomplete combustion has to be corrected for. This includes a complete analysis of the combustion products and of the remaining sample. The application of this method and the great effort involved will be justifiable only if none of the methods described below can be used. Hence calorimetric bombs are used for gaseous samples only in exceptional cases, e.g. fluorochlorohydrocarbons [3].

2.2. Combustion of a gas in an open flame

Calorimetric methods with open flames for the determination of the calorific values of gaseous samples are widely used [3]. The first gas calorimeter, which had been developed exclusively for this purpose, was presented by Hartley in the year 1882 [4]. In the sequel, various instruments were developed, e.g. the Boys calorimeter, the Hyde–Saville calorimeter and the Fairweather calorimeter [5].

In Germany, four different gas calorimeters of this kind have been in use: Junkers calorimeter, Reineke calorimeter, Thomas–Cambridge calorimeter and Cutler–Hammer calorimeter. The basic principle of all the four versions is the same: a specific amount of gas is metered and completely burnt. By a heat exchanger, the heat of combustion released by the burner is transferred to a metered heat absorbing fluid (water or air). As a consequence, the temperature of the fluid increases. The temperature increase is a measure of the calorific value. Calibrations can be carried out using gases of known calorific value, or by calculating the calibration factors from the known volumes of the metered gas and heat absorbing fluid and also the heat capacity of the heat absorbing fluid.

The Thomas–Cambridge and the Cutler–Hammer gas calorimeter are of the continuously working type (cf. Figs. 1 and 2). A mechanical device keeps the ratio of the volume flows of gas and air constant. For the realisation of the volume flows mechanically coupled wet gas meters driven by an electric motor are used. The whole mechanism is located in a big water bath, whose temperature is kept constant. In accordance with the definition of the calorific value in ISO 6976, the gases are fed to the burner at equal and constant reference temperature [2]. The exhaust gases are returned to the same specified temperature as that of the reactants. Most of the water vapour produced by combustion condenses. The increase in temperature of the heat absorbing air is measured by two resistance thermometers and their signal is the input

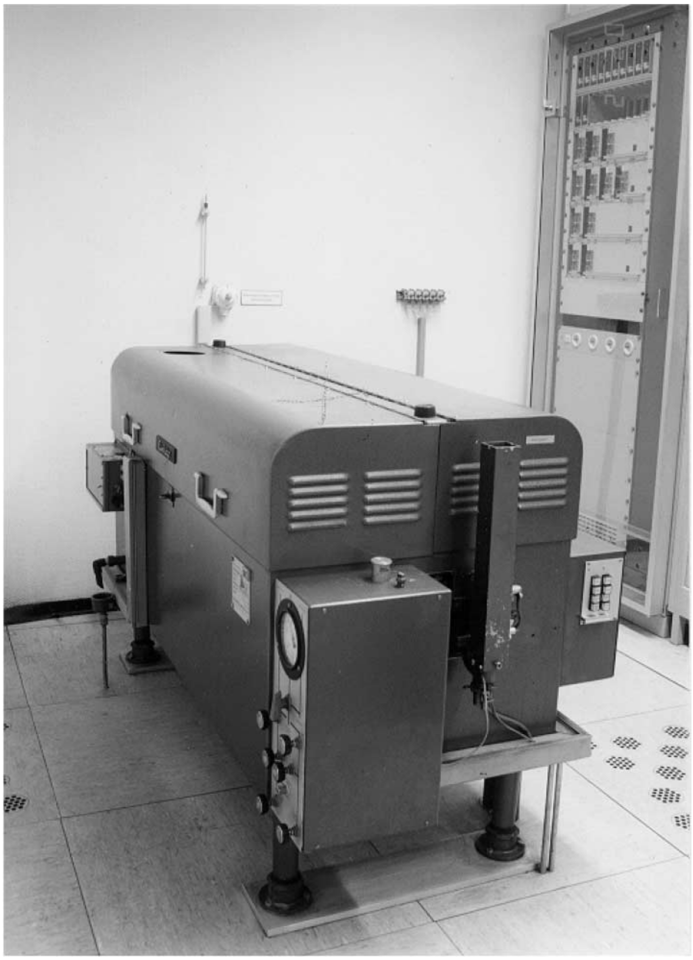

Fig. 1. The Thomas–Cambridge calorimeter.

signal of a measuring transducer giving the temperature difference. The states of the gas and the heat absorbing air are defined by the temperature of the water bath and the ambient pressure. These states are, therefore, the same. Any change of the conditions of state affect both gases equally, the ratio of both being nearly constant. So, the calorific value can be directly indicated.

In contrast to the Thomas–Cambridge and the Cutler–Hammer gas calorimeters, water is used as heat absorbing fluid for the Junkers and Reineke calorimeters. In the case of the Junkers calorimeter a wet gas meter and a water meter measure the amount of gas being burnt and the amount of the heat absorbing fluid [6]. The increase in temperature of the water in the heat exchanger is converted by a thermopile into an electrical voltage and indicated. As the gas is metered under its operating conditions but the calorific value is defined for the reference state, a corrector is inserted between the thermopile and the pen recorder. This corrector takes into account not only changes in ambient pressure but also temperature variations.

The Reineke calorimeter works intermittently. It uses a pair of measuring tubes for the gas and the heat absorbing water [6]. The pair of measuring tubes is periodically filled and emptied using a lifting device (cf. Fig. 3). By pushing out the metered gas towards the burner located inside the heat exchanger the heat absorbing water simultaneously flows through the heat exchanger to the water measuring tube and its

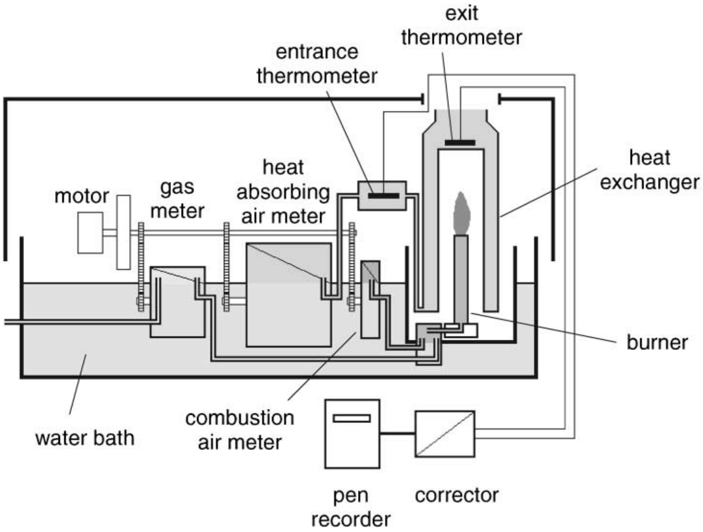

Fig. 2. Principle of the Thomas–Cambridge calorimeter (similar to the Cutler–Hammer calorimeter).

temperature increases. Towards the end of the measuring cycle when the temperatures on the heat exchanger are nearly constant, the signal from the thermopile is measured and displayed until the next measurement takes place. For the transformation of the gas metered in its operational state, a corrector between thermopile and pen recorder is needed.

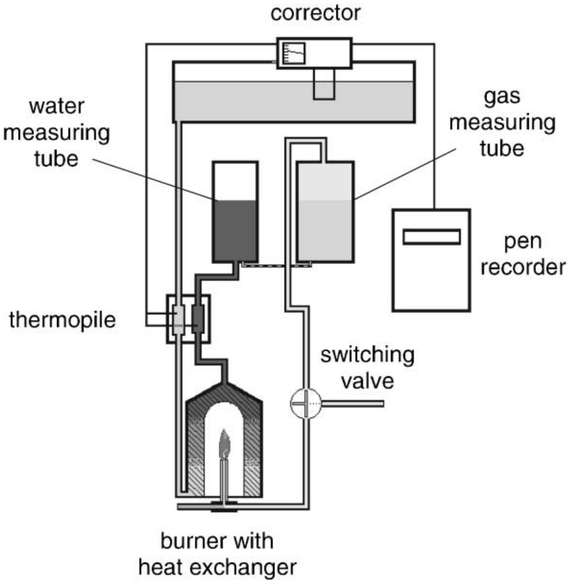

Fig. 3. Principle of the Reineke calorimeter.

These gas calorimeters are commonly used by gas suppliers. Besides that, additional techniques exist making use of an open flame. As early as 1931, Rossini [7] presented a discontinuously working gas calorimeter based on an advanced bomb calorimeter design for solid and liquid samples. It consists of a burner and a heat exchanger for the waste gas. Both are located in a water bath. The heat released through the combustion process leads to an increase in temperature of the water bath.

The water is stored in a metal can which is separated by an air gap from an additional water jacket. As the temperature of this outer water jacket is kept constant, the whole set-up constitutes an isoperibolic calorimeter. This kind of calorimeter needs to be calibrated. This can be realised by the combustion of a gas of known calorific value [8] or by an electrical heater [9]. With this so-called Rossini calorimeter, the most precise measurements of the calorific value of gas can be carried out.

The disadvantage of this equipment is the great experimental effort. That is why it is not used for routine jobs but for special measurements only. Additional information about this instrument can be found elsewhere in this issue [10].

Due to the operational mode of the Rossini calorimeter, the temperature of the water surrounding the burner increases and, as expected, the temperature of the waste gas increases as well, an effect which must be corrected for computationally. However, in accordance with the definition of the calorific value, the waste gas should leave the calorimeter at the temperature of the entrance gases.

A consistent implementation of the definition leads to an isothermal calorimeter. The heat released by the combustion process has to be exchanged with the surroundings at constant temperature. As a result, the waste gas is cooled down to the temperature the entrance gases have. The gas calorimeter of Aleksandrov [11], which is also presented in this issue, almost fulfils these requirements. This calorimeter consists of a gas burner surrounded by a heat exchanger. Both devices are located in a heat pipe.

The heat from the burner and an additional electrical heater at the bottom of the heat pipe is transferred by the working fluid to the upper end. There is a Peltier system ensuring a constant cooling. Due to a closed loop control, an increase in the power of the burner is compensated by a decrease of the power of the electrical heater. In other words, a so-called ‘‘heat balance’’ is realised. Using this principle, the thermal energy of the combustion reaction is traceable to electrical quantities.

2.3. *Oxidation of a gas by catalytic combustion*

In contrast to the combustion of a gas in a burner with an open flame it is also possible to oxidise the gas on a catalyst in terms of the so-called ‘‘cold combustion’’. For this purpose, gas and air are led through a packed bed made of catalyst pellets. During this process, the gas is oxidised and the released heat of combustion leads to an increase in the temperature of the catalyst bed.

To effect a reaction as complete as possible on the catalyst surface, the catalyst bed is thermally equilibrated to approx. 150–400 °C. In one example, the increase in temperature of the catalyst bed can be taken as a measure of the calorific value [12]. In another example, the electrical power necessary to keep the catalyst bed at the selected temperature may be reduced. In this operational mode, a controller keeps the temperature of the catalyst bed constant [13]. With this mode again a compensation principle is realised.

Problems may occur with both principles: the incomplete oxidation of the gas or the poisoning of the catalyst leading to the efficiency being reduced.

3. Calculation of the calorific value using analytical methods

Analytical methods are based on the principle that every constituent of the gas makes a contribution to the calorific value according to its share in the gas. The aim is to determine, e.g. the molar fraction of the constituents by a suitable analysis. The calorific value can be obtained by adding the products of the molar fraction and the corresponding molar calorific value of the pure constituent. With this principle it is possible to calculate the molar calorific value of the gas mixture [2]. The volume-based calorific value of a gas mixture can be calculated considering the real p–V–T behaviour.

Often, a gas sample is taken and analysed using a gas chromatograph (cf. Fig. 4). When the gas mixture passes through one or more separation columns, the individual constituents flow at different rates. This is due to the different interactions between the molecules and the packing material. As a result, the gas mixture is separated in the separation columns into pure constituents which reach detector at different times.

Thermal conductivity detectors are normally used for the gas chromatography of fuel gases. Since pure gases have different thermal conductivities, they give rise to a change in electrical resistance when passing through the detector. This signal can be recorded and constitutes the so-called chromatogram.

Calibration of the instrument can be carried out with one or more calibration gases. As a result, calibration coefficients can be calculated. The molar fractions for each individual constituent may be evaluated using these coefficients. The advantage of this procedure is that additional physical quantities can be calculated. Besides the calorific value, e.g. standard density can be calculated from the composition using an adequate equation of state.

Another analytical method for the determination of the calorific value is based on spectroscopic measurements. Several investigations into this topic have shown that the near infrared can be used [14–17]. Since the calorific value of a given species of molecules depends on the number and character of the chemical bonds of the molecules, the bonds strength of absorption can be taken as a direct measure of the calorific value.

A detailed analysis of the absorption spectrum can be performed to obtain the molar fractions of the

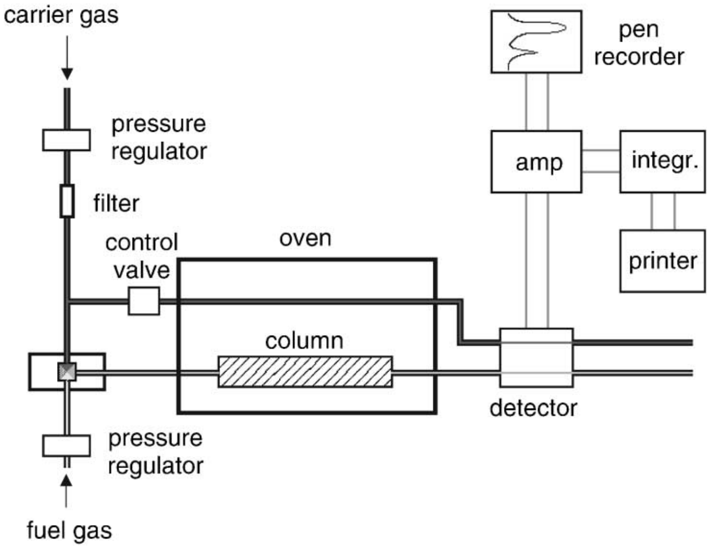

Fig. 4. Principle of a process gas chromatograph.

various constituents of the gas mixture. Using the absorption spectra of several fuel gases of known calorific value, calibration can be performed. The advantage of this measuring method consists in possible online measurements. It is possible even at high pressures to measure the absorption spectra directly on the pipeline.

Nitrogen does not absorb in the near infrared and therefore cannot be detected. Mathematical algorithms were developed to overcome this disadvantage. Using nitrogen-containing calibration gases, direct correlation between absorption spectra and calorific values can be achieved.

4. Determination of calorific values of gases using correlations

Besides the combustion or analysis of fuel gases, it is also possible to correlate and, respectively, calculate the calorific value by measuring the physical properties of the gas mixture. Correlations have to be determined, allowing the calorific value to be reliably calculated as a function of one or several different physical properties. Thus, the relevant physical properties and the calorific values of as many as possible or available different fuel gases have to be measured. Physical properties such as, e.g. the relative permittivity, the thermal conductivity or the speed of sound can be used [18–20].

5. Stoichiometric combustion

Further methods are based on the determination of the stoichiometric oxygen or air consumption. When a natural gas is burnt, there is a linear relationship between air consumption and calorific value (cf. Fig. 5). For determining the stoichiometry, the maximum flame temperature or the residual oxygen content in the waste gas can be measured. To determine the air consumption necessary for stoichiometric combustion, a gas is burnt after mixing with a constant mass flow of air. The constant mass flow of air is realised with the aid of a sonic nozzle. The volume flow of gas is adjusted by a flow regulator in such a way that the highest possible flame temperature for the gas under investigation is reached (cf. Fig. 6). This takes place under stoichiometric conditions. When fuel gas or air is available in excess, the flame temperature decreases as a greater amount of substance is to be heated.

Calibration can be carried out by burning gases of well-known calorific value. Then the stoichiometric air-to-gas ratio can be used as a direct measure of the calorific value [21].

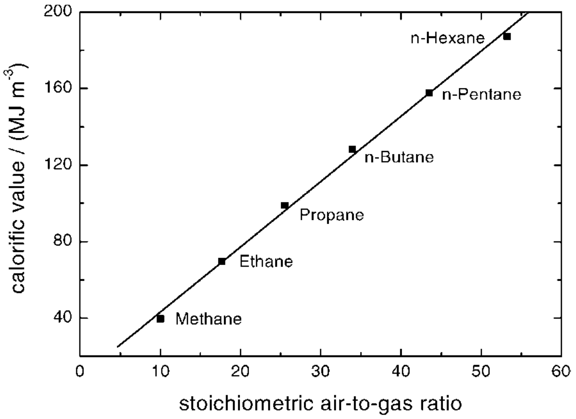

Fig. 5. Relationship between stoichiometry of the combustion reaction and calorific value (data from [2]).

The measurement of the residual oxygen content in the waste gas is based on a similar principle. Natural gas and air are mixed at a constant ratio and then burnt (cf. Fig. 7). Complete combustion will take place because air is always available in excess. The oxygen content in the waste gas is measured using a lambda probe. The minimum necessary amount of air and, thus, the stoichiometric air-to-gas ratio can be calculated.

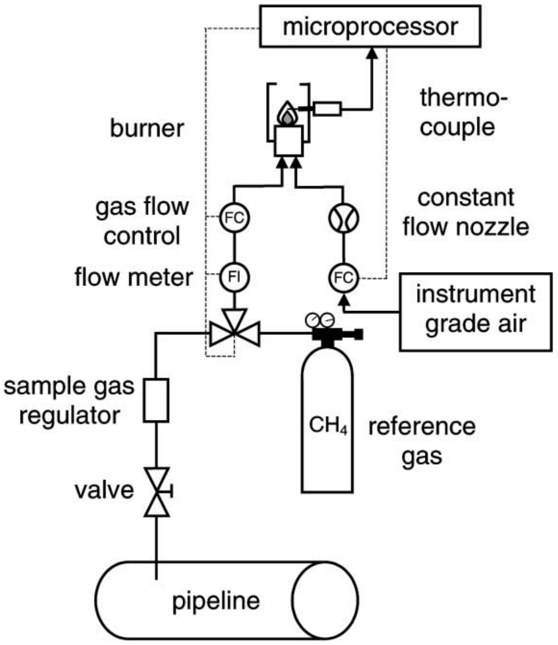

Fig. 6. Principle of stoichiometric combustion.

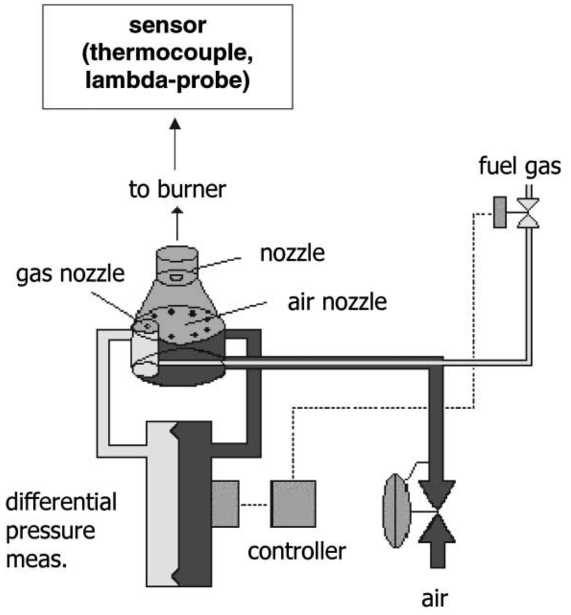

Fig. 7. Principle of excess oxygen measurement.

In comparison with the measurement of the highest possible flame temperature it is the advantage of this method that it is always possible to achieve complete combustion [6].

6. State reconstruction

To avoid confusion, the term “grid simulation” should not be used synonymously with “state reconstruction” [22].

State reconstruction means offline calculation of the set of all relevant pressures and flowrates in a real pipeline or grid on the basis of the complete topology, the checked measured values of the flowrates at all supply and tapping off-take points, and of the pressures and temperatures and possibly additional flow measurements at various points on the pipeline(s) using an appropriate dynamic mathematical model [22]. From this information, the calorific value at any point of the grid can be calculated.

The objective of state reconstruction is to obtain precise information about the real state of flow in a pipeline or grid. The results of a gas quality system

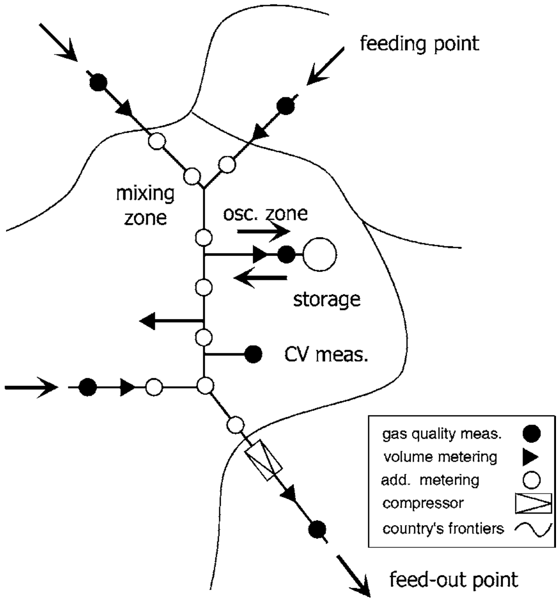

Fig. 8. State reconstruction.

based on state reconstruction, i.e. calorific value, density under reference conditions, etc., may be used for billing purposes. In this case, the operation of such gas quality tracking systems are to be monitored by additional quality measurements at appropriate places on the pipelines (cf. Fig. 8).

In state reconstruction, problems arise for mainly in the so-called oscillating zones. There the gas flow oscillates, due to inflow and outflow, as, e.g. in the supply pipe of a gas store (cf. Fig. 8).

In grid simulation, the calorific values are also calculated for any point on a pipeline or grid, but as the input data (topology, calorific values, flows, pressures and temperatures) are only unchecked online data or even assumed values, the results are not reliable and, therefore, inappropriate to be used for billing purposes.

7. Conclusions

The methods for the determination of the calorific value of gases described differ greatly. Their application depends on the circumstances. The price for the instrument and the operating expenses are the decisive factors. Additional decisive factors for the choice of a calorific value determining device are measurement uncertainty, the measuring range and the requirements for the place of installation, e.g. use in the field. Some instruments, e.g. the Rossini calorimeter, are used for special purposes of scientific research. During the last 50 years in the case of gas calorimetry, new products have scarcely been developed, except for the Aleksandrov calorimeter. In contrast to this, other methods have intensively developed during the last two decades. An end of this favourable trend is not yet in sight.

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