Measuring system for the correlative measurement of combustion gases

By Wilfried Diekmann and Leonard Voßgrag

In Germany, the gas supply is uniformly being converted to type H natural gas as part of the ongoing market conversion [4]. This change is both laborious and costly in the affected regions, as household burners must be converted to suit different gas properties. Optimization of the off-gas values is already required within the narrow limits of type H in some regions [1]. In the industrial sector, the tolerance for fluctuations in properties is often much tighter, e.g. in the production of plate glass.

As a consequence of the Russian war of aggression, Europe has to broaden its scope of supplier countries. Even greater fluctuations with regard to both region and time are to be expected.

As part of the measures for the incremental conversion to renewable energy sources, consumers will have to adapt to mixture components like carbon dioxide from biogas and hydrogen from electrolysis in the coming years.

This diversification poses a problem for measuring technology, however. Many devices are based on the correlation method, which correlates the signals of several cost-effective measurement channels with gas property values such as the combustion value and Wobbe index. The nearly constant substance quantity ratios of the higher alkanes in previous sources is often used here [2]. Should this deviate from 3:1 for the proportions of ethane and propane, indication errors quickly increase. Gas chromatography and calorimetry exhibit a large dynamic range with regard to the measurable mixtures. Handling and the price-to-performance ratio are considerably better with most correlative measuring devices based on non-dispersive infrared spectroscopy (NDIR) and thermal conduction, however. Another advantage over gas chromatography can be seen in the shorter response time, which is required for the regulation of sensitive thermal processes. This device type manages with longer calibration intervals, and regular validation usually occurs automatically. To master the challenges mentioned above, expansion of the acceptance range to suit future gas properties is required.

Measurability of the precision of all gas property parameters

In a comprehensive study, Union Instruments GmbH built a demonstration unit which expands the mixture pallet considerably and is able to measure all gas property parameters with high precision. Multiple NDIR sensors and a thermal conductivity sensor are used as the measurement channels. It could be shown that different mixtures of methane, ethane and propane, as well as higher proportions of hydrogen, nitrogen and carbon dioxide can be correctly indicated with regard to the combustion value, Wobbe index and methane number parameters.

The approach to deriving a measurement value from the individual signals of the measurement channels is based on the correlations yielded empirically from the data for a variety of mixtures. The type of correlations found heavily depends on the selection of wavelengths of the interference filters of the NDIR channels. Two wavelengths lie in the 3.3 to 3.5 μm range here. The alkanes are especially absorbent here, but the overlap of absorption bands is also especially large. For this reason, a focal point of the study was the separation of the influence of ethane and propane on these two measurement channels.

To solve a problem like this, multi-variant calibration methods are worth considering. Linear models from chemometrics are especially suitable for problems of infrared spectroscopy in the case of small concentrations. In the analysis of combustion gas, however, the correlations between the measurement value and substance quantities are heavily non-linear. Another method can be borrowed from the field of deep learning. An artificial neural network can be taught using a large volume of training data so that it can even indicate correct values for mixtures which it has not been taught. ANNs also do well with non-linear input values here.

This method was rejected in favor of a correlative approach, however, as the required volume of training data would have called for an excessive amount of effort in order to calibrate this kind of sensor in production. The current method requires calibration to individual binary and ternary mixtures of the components methane, ethane, propane, nitrogen, hydrogen and carbon dioxide.

NDIR sensors

Using an infrared detector with an upstream narrow-band filter, NDIR sensors measure the change in radiation of a (usually) thermal radiation source when the concentration of an infrared-active substance is changed. The Beer-Lambert law describes this correlation using an exponential function of the product of particle density c and path length l. The latter is usually the length of a cuvette through which the measured gas flows.

A host of influences complicate calculation of the signal. Thermal emitters indicate certain intensity fluctuations and drifting. Changes in temperature affect the particle density, the center wavelength of the narrow-band filter and the signal amplitudes of the detectors. A change in pressure changes the absorption spectrum of the substance. In a mixture, the molecules of different components interact with one another, which—alongside the spectral cross-sensitivity mentioned—also affects the sensitivity of the sensor. The measures for compensating for these influences are well known. A reference wavelength for which no noteworthy absorption by the substances involved is to be expected permits measurement of the emitter output for correction. Pressure and temperature are kept constant. Substance interaction can then only be corrected if the substance quantities of the components of the mixture are known, however. It has been shown that correlations and iterations which result in a sufficient improvement can be used here. The WLD thermal conductivity detector measures the capacity of the gas mixture to transport heat from a source to a sink. The thermal conductivity of different gases can vary widely in some cases. Hydrogen conducts heat approximately 5.5 times better than methane, for example. The thermal conductivity of a mixture can be calculated using known methods if the substance quantities of all components are known. The inverse does not apply, however.

Key indices using standardized calculation rules

Equally, the composition of the mixture cannot be determined from the key indices of the gas properties. If it is possible to determine the substance quantities of all components from the measurement signals, the key indices can be determined using standardized calculation rules. The study conducted by Union Instruments GmbH pursued and achieved this goal, with the result being that the individual substance quantities of the mixture components—in addition to the key gas indices—can be identified.

An initial value for the absorption caused by methane at a wavelength between 7 and 8 µm has to be determined first. The absorption values are modified by this value for filtering in the 3.3 to 3.5 µm range so the influence of the higher alkanes can be separated. For the two measurement channels in this range, correlations are used to determine the combustion value. These correlations were established with mixtures with the concentration ratio of 3 (ethane) to 1 (propane). For such mixtures, the calculated combustion values of both channels are the same. Should the values deviate from one another, this difference gages how far the concentration ratio deviates from the value 3:1. A function which calculates the associated substance volumes for ethane and propane from the two raw values can be formulated from the correlations of the calibration. The error in the methane concentration yielded from the cross-sensitivity to the higher alkanes is compensated for with these substance quantities. The determination of the carbon dioxide quantity is easy to make at a wavelength of 4.2 to 4.4 µm thanks to a lack of cross-sensitivity. All IR-active components are determined at this point. The two remaining non-IR-active substances of nitrogen and
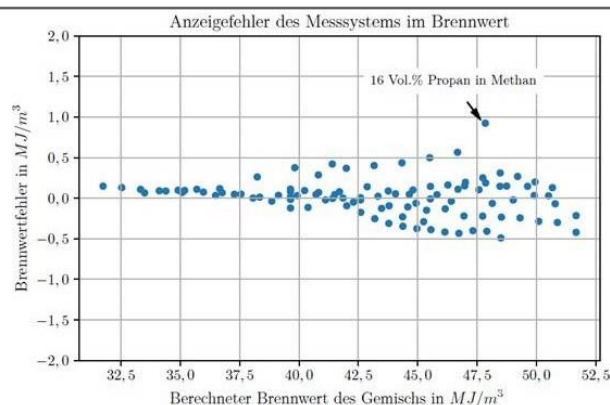

Figure 1: Indication errors of the measuring system in the combustion value plotted against the calculated combustion value of the binary, ternary and quaternary test mixtures comprised of methane, ethane, propane, nitrogen and hydrogen

hydrogen can be assigned using the WLD. A correlation from the calibration data is also used for this.

Figure 1 shows the precision with which the combustion value can be determined. The calculation rule in DIN EN ISO 6976 [3] was used to calculate the precision. It can be seen in the figure that the combustion value can be determined from binary, ternary and quaternary mixtures of methane, ethane, propane and the infrared-active molecules of hydrogen and nitrogen within a error range of approximately ±1 MJ/m^3.

Building upon these results, the measurement method is to be expanded to include the next-highest alkane of butane. A subsequent focal point is optimization of the calibration process so a measurement campaign can be carried out in the field.

Sources

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