

KAZIMIERZ GAJ*, HANNA CYBULSKA*, FRANCISZEK KNOP*

METHOD OF SIMULTANEOUS MEASUREMENT OF TOTAL SULFUR, CHLORINE AND FLUORINE CONTENT IN BIOGAS

The method of determination of total content of sulfur, chlorine and fluorine compounds in biogas has been implemented and verified at real conditions. The laboratory plant and the results of periodical measurements of the composition of biogas have been described. The main effects of the research are: determination of the range of concentrations for the analysed compounds in a typical biogas from sewage sludge digestion and evaluation of average fraction of sulfur from hydrogen sulfide in total sulfur content during multiannual period.

1. INTRODUCTION

New analytic methods for evaluating biogas composition and its properties need to be implemented to respond to intense development of biogas plants expected in the nearest future in Poland [1]. Energy producing combustion, being the basic method of biogas utilization, requires its conditioning so as to eliminate any risk for combustion equipment and environmental hazard as well. This means that apart from evaluating basic process parameters such as: chemical constitution (the content of CH₄, CO₂, N₂, O₂, H₂, H₂O), calorific value, gross calorific value, Wobbe index which can be determined with a sufficient accuracy on the grounds of standards for natural gas, it would be necessary to use specific methods for numerous compounds of sulfur, chlorine and fluorine being present in the biogas. So far, no such methods for biogas were developed. Well known methods applicable to determining the content of sulfur compounds based on combustion [2, 3] which could be adapted to this purpose, have numerous inconveniences. In Wickbolds' method, a sample is burnt out in hydrogen/oxygen flame, hence its inherent drawbacks include risk of explosion (especially during process initiation) and high costs of used gases. The method provides no way of tempera-

*Institute of Environmental Protection Engineering, Wrocław University of Technology, Wyrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland. Corresponding author K. Gaj, e-mail: kazimierz.gaj@pwr.wroc.pl

ture regulation and control within combustion zone which could lead to incomplete combustion. Variable composition of biogas and related fluctuations of calorific value create additional problems with maintaining proper hydrogen/oxygen/gas proportions and stability of combustion processes. In Lingener's method, combustion takes place in air without any additional fuel. Also in this case, no control and regulation of combustion temperature exist. While an analysis is made using this standard, we shall expect lower combustion temperatures than those for natural gas, which can lead to incomplete oxidation of sulfur.

Bearing this in mind, an idea was arisen in the Environmental Protection Institute of Wroclaw University of Technology to develop a method free of the above disadvantages allowing simultaneous measurement of total content of sulfur, chlorine and fluorine in biogas. The method based on flameless combustion of biogas in air followed by spectrophotometric and/or chromatographic analysis of combustion products was proposed. To this purpose, a testing system was built up and also the parameters of combustion processes and sampling procedure were experimentally developed. The system was then used to determine the composition of biogas taken from municipal sewage treatment plant with throughput of ca. 80 000 m³/day [4].

2. HAZARDS PROMPTED BY BIOGAS AND ITS BURNING PRODUCTS

Typical composition of dry biogas generated from sludge digestion is as follows: CH₄ (ca. 65%), CO₂ (ca. 34%), and the rest (ca. 1%), including: N₂, O₂, H₂, H₂S, NH₃, hydrocarbons (C₂–C₇) and trace substances such as compounds of sulfur, chlorine and fluorine. Sulfur can be present in biogas as inorganic compounds (mainly hydrogen sulfide) and also organic compounds (mercaptans, thioethers, thiophene and derivatives, carbon oxysulfide, dimethyl sulfides, and others). A basic source of H₂S is biochemical, anaerobic digestion of sulfur compounds originating from animal organisms, mainly proteins, while sulfur organic compounds are primarily of plant origin. Halogens are generally coming from impurities in sewage. Chlorine compounds may also originate from chemicals used for water purification and sewage treatment. Exemplary compounds of chlorine and fluorine found in biogas are as follows: chloroethane, dichlorofluoromethane, trichlorofluoromethane, chlorotrifluoromethane, trichloromethane, tetrachloroethane, trichloroethane, dichloromethane, dichloroethane, dichloroethene, dichloropropane, carbon tetrachloride, chlorobenzene, dichlorobenzene, tetrachloroethylene, vinyl chloride, etc. [5].

Compounds of S, Cl and F are the most difficult for treatment and cause the highest environmental nuisance among substances found in biogas. Combustion products from these compounds are aggressive for equipment and environment. Also H₂S is distinguished by its corrosive properties. It can also increase fire and explosion hazard as it reacts with iron, leading to generation of self-igniting ferrous sulfide. When bio-

gas containing sulfur compounds and halogens is subject to combustion in gas engines, it causes engine oils life to be shortened and catalyst activity to be reduced.

Table

Admissible concentrations of sulfur and halogen compounds in biogas

| Substance | Admissible limit | Country | Reference |
|------------------------|--|--|-----------|
| Hydrogen sulfide | 5 mg/m ³ | – | [6] |
| | 200 mg/m ^{3b} | – | [9] |
| | 0.15 vol. % | – | [10] |
| | 5 mg/m ³ 20 mg/m ³ 20 mg/m ³ | Germany Hungary Poland | [7] |
| | 6 mg S/m ³ | Denmark, Sweden | [8] |
| Total sulfur | 50 mg/m ³ | – | [6] |
| | 2000 (1150 ^a) mg H ₂ S/10 kWh | – | [9] |
| | 2200 mg/m ³ CH ₄ | – | [10] |
| | 120 mg/m ³ 100 mg/m ³ 40 mg/m ³ | Germany Hungary Poland | [7] |
| | 120 mg/m ³ | Denmark, Sweden | [8] |
| Total halogens | 5 | – | [6] |
| Total Cl +2×total F | 100 (0 ^a) mg/10kWh 100 mg/m ^{3b} | – | [9] |
| | Cl F Cl + F | 100 mg/m ³ CH ₄ 50 mg/m ³ CH ₄ 100 mg/m ³ CH ₄ | – |

^aInstallation with a catalyst.

^bAdmissible limit at the inlet of an adsorber with active coal.

Both the components of escaping biogas and products of its combustion release to atmosphere, causing toxicological and unpleasant smell effects. Some of these compounds, especially chlorinated hydrocarbons, demonstrate carcinogenic action. Chlorine in biogas may cause, when its combustion runs under unfavourable conditions, emission of dioxines and furanes. Due to aforementioned reasons, it is especially important to control both individual selected compounds of S, Cl and F, and also their total content levels. Review of limiting concentrations for S, Cl and F compounds existing in biogas is given in the Table.

3. MATERIALS AND METHODS

Due to the immense number and diversity of S, Cl and F compounds present in biogas, it is impossible in practice to determine their sum based on the concentration

measurements for individual constituents. In the case of measurements of total sulfur compounds, two groups of potentially suitable methods can be distinguished: hydrogenation of sulfur compounds and measurement of generated H_2S , and combustion of sulfur compounds with determination of generated SO_2 . The combustion method can also be successfully applied to determine a total level of chlorine and fluorine compounds. The idea of this method consists in oxidizing S, Cl and F compounds to SO_2 , HCl and HF, respectively, absorbing selectively these compounds and determining them by well-known analytical methods.

Determination of SO_2 was made using the spectrophotometric method [11], selective and neutral with respect to other components of biogas. The method consisted in SO_2 absorption in solution of sodium tetrachloromercurate and spectrophotometric analysis of the obtained complex. To determine HCl and HF, products of combustion of biogas were absorbed in deionised water and the post-sorption solution was analyzed for Cl^- and F^- ions using an ionic chromatograph with a conductometric detector and an anionic column.

A basic element of the research system (Fig. 1) is a furnace for flameless combustion of biogas (Fig. 2) equipped with a quartz tube installed inside a corundum tube around which a heating element (11), in a form of kanthal resistance wire, was wound. The quartz tube was ground on its both ends, the inlet polished section was used to connect glass head of the burner (9), while the outlet one – to connect the glass cooler (12). Two thermoelements, NiCr–Ni (10), installed between the two tubes, were used to monitor and control the combustion temperature. The voltage was adjusted using a laboratory type control transformer (20). Resistance wire was supplied via a contactor (19) controlled by a microprocessor based temperature recorder/controller (14). The recorder received voltage signal from a thermoelement installed close to the point where biogas was introduced into the quartz tube. Additionally, a digital millivoltmeter (15) was used to record temperature measured by another thermoelement located at the furnace outlet. Immediately before and after the measurement, the temperature inside the quartz tube was taken manually using the same type of thermoelements. The furnace was insulated using 150 mm thick thermoinsulating quartz wool with the thermal resistance of 1430 °C and the whole unit was housed in a duralumin sheet.

Combustion air was fed into the furnace via a rotameter (5), a column with acid compound sorbent (7) and a column with active carbon (8). The furnace was fed with biogas from receivers (6) using purity class 5.0 nitrogen supplied from a cylinder (2), via a pressure regulator (3), a flexible Tedlar bag (4) and a rotameter (5). Biogas and nitrogen were introduced into the furnace via a nozzle installed in the inlet head (9) where they contacted with air oxygen within the zone of temperature of 1200 °C. The air was fed so as to ensure turbulent conditions of media mixing while preset volumetric streams of air and biogas and their proportions ensured safe and stable conditions of flameless combustion in the quartz tube and relatively long time of contact exceeding 7 s. Such conditions of combustion gave full oxidation of S, Cl and F compounds.

Combustion products, after cooling down on a glass connecting member (12) to ca. 60 °C, (i.e., 20–30 °C above the flue gas dew point controlled with a thermometer (13)), were directed to a set of aspiration washers (16), and then subject to analysing with a spectrophotometer (21) or an ion chromatograph (22). An automatic aspirator (18) equipped with a silica gel gas dryer (17) was used to ensure flow of media, regulation and recording of the volumetric flow rate.

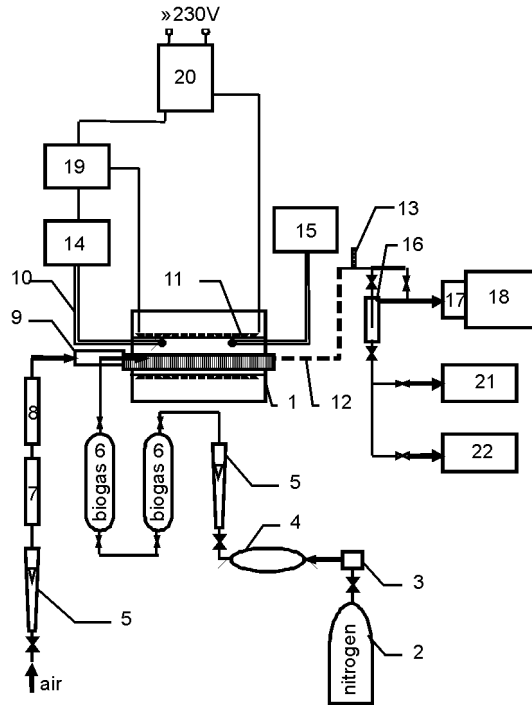


Fig. 1. Schematic diagram of the laboratory plant: 1 – furnace, 2 – cylinder with compressed nitrogen, 3 – pressure regulator, 4 – flexible Tedlar bag, 5 – rotameter, 6 – gas receivers, 7 – column with active carbon, 8 – adsorber of acid compounds, 9 – inlet head, 10 – thermoelement, 11 – heating element, 12 – cooler, 13 – thermometer, 14 – temperature controller and recorder, 15 – millivoltmeter, 16 – gas washers, 17 – gas dryer, 18 – aspirator, 19 – electronic transmitter, 20 – laboratory autotransformer, 21 – spectrophotometer, 22 – ion chromatograph

Prior to measurements, the biogas pressure in receivers was made equal to the atmospheric pressure; receivers, air purifying columns and washer set were connected and the furnace was pre-heated to a specific temperature. Total volume of biogas sample was dependent on hydrogen sulfide concentration, which was measured, along with biogas flow, using spectrophotometric method [12]. When temperature inside the furnace was as required, in order to rinse out the system and to heat up the glass connecting member, the aspirator was turned on (with air inlet being opened, nitrogen and biogas inlet closed

and washer by-pass opened), and then – after temperatures become stable – the by-pass was closed, flow through washers was opened, nitrogen flow was enabled, valves and biogas receivers were made open and streams of media were adjusted so as the air flow rate was 40–50 dm³/h, and nitrogen flow rate about 1 dm³/h. Then, in 20 min periods, the nitrogen flow rate was increased to 2, 6 and 12 dm³/h, respectively. Measurement was terminated when receivers were washed out at least 10 times.

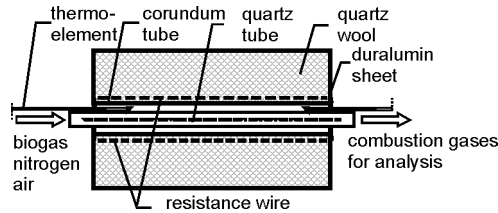


Fig. 2. Schematic diagram of biogas flameless combustion furnace

An exemplary combustion time for biogas sample of 5 dm³ was about 7 h. Post-sorption solutions from washers were analyzed for SO₂, HCl and HF content, and on the grounds of these data the calculations were made for the total content of elements under investigation in the biogas.

4. RESULTS

Fig. 3 shows biogas testing results for the content of total sulfur, chlorine and fluorine get by the aforementioned method, and – for comparison purposes – the results of

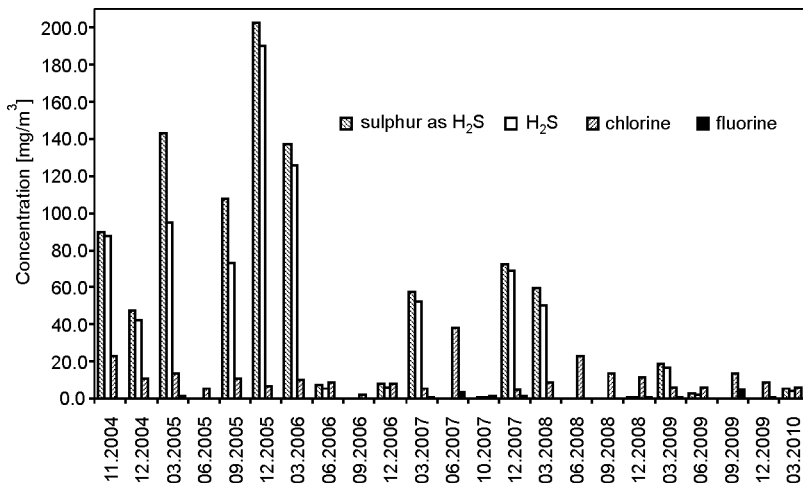


Fig. 3. Concentrations of selected biogas constituents sampled at the inlet of an electric generator gas engine

parallel measurements of H₂S concentrations by the spectrophotometric method. The research was made for biogas, purified by bog ore and active carbon adsorbers, fed into two gas engines of generators with the rated electric power of 601 kW each. The results are averaged values for the two parallel generators, recalculated to standard conditions (273K, 101.3 kPa) and to dry gas.

5. SUMMARY

The proposed method to determine total content of sulfur, chlorine and fluorine compounds in biogas is free of disadvantages of numerous methods being in use. Its most important advantages are as follows: determination of all three elements could be made in a single unit, low cost of system construction, elimination of usage of hydrogen and oxygen, safety of operation, full automatic control over combustion temperature due to application of an electrically heated tube and relevant automation, initiating the combustion process without need to dismount the burner etc. The key matter for the effect of research (i.e. full oxidation of S, Cl and F compounds) was to establish the optimum combustion temperature and reliable temperature of monitoring and automatic control. Examinations allowed one to establish the ratio volumetric flows of air to biogas providing sufficiently long contact time of reagents and combustion conditions eliminating the risk of explosion.

The method was tested and verified in multiple biogas measurements made in 2004–2010 in one of Polish municipal sewage treatment plants. The results of examinations allowed one to determine the range of concentrations for hydrogen sulfide sulfur, total sulfur and total content of chlorine and fluorine compounds in typical biogas generated from sludge digestion and to evaluate average fraction of hydrogen sulfide sulfur in total sulfur. It was proved that this fraction may vary from 66% to 98% with the average value of 83%. Thereby, it was confirmed that periodical determination of total sulfur, apart from determining hydrogen sulfide in biogas which is routinely run in sewage treatment plants, is both justified and necessary.

REFERENCES

- [1] *Polish energy policy until 2030*, Ministry of Economy, Annex to Resolution No. 202 of the Council of Ministers of 10 November 2009 (in Polish).
- [2] *Methods of test for petroleum and its products. Petroleum products and hydrocarbons. Determination of sulfur content. Wickbold combustion method*. PN-EN 24260:2002.
- [3] *Determination of sulfur compounds in natural gas. Part 5. Lingener combustion method*. PN-EN ISO 6326-5:2005.
- [4] GAJ K., CYBULSKA-SZULC H., KNOP F., STEININGER M., *Environ. Prot. Eng.*, 2008, 34 (4), 33.
- [5] GAJ K., CYBULSKA H., KNOP F., MECH J., MENDYKA B., ROBASZKIEWICZ J., *Chem. Inż. Ekol.*, 1999, 6 (4), 337.

-
- [6] WASIAK W., URBANIAK W., *Chem. Inż. Ekol.*, 1997, 4 (4), 631 (in Polish).
- [7] MOLENDĄ J., STECZKO K., *Environmental protection in the gas industry and use of gas*, WNT, Warsaw 2000 (in Polish).
- [8] HAGEN M., POLMAN E., *Adding gas from biomass to the gas grid*, Contract No: XVII / 4.1030/Z/99 – 412, Final Report, Danish Gas Technology Center, Swedish Gas Center, 2001.
- [9] Technical Instr. No. 1000-0300, Jenbacher, 2005.
- [10] HEINZE U., ROCKMANN G., SIGHTING J., *Bauen für die Landwirtschaft*, 2000, 37 (3), 25.
- [11] *Ambient air. Determination of the mass concentration of sulfur dioxide. Tetrachloromercurate (TCM)/pararosaniline method*. PN-ISO 6767:1997.
- [12] *Indoor air. Determination of hydrogen sulphide concentration by spectrophotometry*. PN-Z-04015-13:1996.