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MONITORING OF BIOGAS USED AS A SOURCE OF RENEWABLE ENERGY

MONITORING BIOGAZU JAKO ŹRÓDŁA ENERGII ODNAWIALNEJ

Abstract: Biogas is a mixture of many gasses to which the main contribution of two thirds is brought by methane (CH_4) and one third by carbon dioxide (CO_2), while the other components including steam occur in trace amounts. Effective control of the process of fermentation is based on controlling the following parameters: type and amount of the substrates supplied, temperature of the process, pH value, amount of short-chain fatty acids, the degree of filling of the fermentation tank and the chemical composition of the gas obtained. In this study the measurements of quantitative composition of biogas made by a popular portable biogas analyser GA2000 were verified by gas chromatography determinations. In the analyser the content of methane and carbon dioxide is made by a spectrophotometric method, while the content of oxygen and hydrogen sulphide is electrochemically measured.

Keywords: biogas, gas chromatography, biogas analyser, verification of measurements

Biogas is a product of a complex reaction known as methane fermentation. The organic substances are decomposed by bacteria into simple compounds, mainly methane and carbon dioxide. Besides these compounds, biogas contains many other components that are not inert in the conditions of installation needed for biogas production. Typical composition of biogas and description of their influence on biogas properties and biogas installation performance are given in Table 1.

Not each type of biogas can be used for energy production. The main criterion of biogas for such application is that it must contain at least 40% of methane. For the majority of substrates used, the content of methane is 60÷65% and the content of carbon dioxide is 35÷40%, however, some authors have reported the increase of carbon dioxide content in biogas up to 50÷60% [1]. As far as the contents of nitrogen and oxygen are concerned, these compounds occur at the ratio of 4:1 and get into the biogas produced at very low productiveness of source, eg at the waste dumping grounds, or during technological processes or they are added on purpose in the amount of 3÷5% [1] to ensure the correct course of biological desulphurisation.

Another important component is hydrogen sulphide (H_2S), whose content determines the biogas quality, although it occurs in trace amounts. Its content should not be too high as already in low concentrations it inhibits the process of decomposition and causes corrosion of the biogas production installation, including power-heat units and water boilers. Many producers of biogas generators admit the content of hydrogen sulphide at a level of 0.05% [2]. It should be also mentioned that a product of H_2S combustion is SO_2, so when biogas is subjected only to combustion in a flare the admitted concentration of H_2S is 0.1% [2]. Biogas also contains small amounts of carbon oxide, not exceeding 0.2%. The concentration of another biogas component ammonia is usually kept at a level below <0.1 mg m^{-3}. Its amount is closely related to the type of substrates used and in certain biogas samples the concentration of ammonia reached 150 mg m^{-3} [3]. Other impurities met

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in biogas include chlorine, fluorine and mercaptans, however, their concentration is below 0.1 mg m^{-3} and trace amounts of aromatic hydrocarbons: the concentrations of BTX are below 1 mg m^{-3} and the concentrations of PAH - below 0.01 µg m^{-3} [2]. Important is also the presence of siloxanes getting into the wastewater with cosmetic products, detergents or construction materials. They have deteriorating effect on biogas generators as their combustion in the presence of oxygen leads to formation of silica acting as abrasive material [4]. The above survey of the information on possible impurities of biogas and their effects illustrates the importance of monitoring of the chemical composition of the biogas produced.

Table 1

Typical components of biogas and their effect on biogas and biogas installation performance [2]

Component	Content	Effect
CO_2	25÷60%	- Lowers the calorific value - Causes corrosion if the gas is wet - Increases the methane number and the anti-knock properties of engines
H_2S	0÷0.5%	- Corrosive effect in equipment and piping system - Emits SO_2 on combustion
NH_3	0÷0.05%	- Emits NO_x on combustion - Increase the anti-knock properties of engines
Water vapour	1÷5%	- Causes corrosion of installation - Products of condensation can cause damage to the engine and choke installation
Dust	>5 µm	- Blocks nozzles and fuel cells
N_2	0÷5%	- Lowers the calorific value - Increase the anti-knock properties of engines
Siloxanes	0÷50 mg m^{-3}	- Act as abrasive material causing damage to the engine

Material and methods

Analysis of biogas components was made by a portable analyser GA2000 made by Geotech [5]. For determination of methane and carbon dioxide it uses a double beam of infrared radiation and a reference cell. Determination of oxygen, carbon oxide and hydrogen sulphide is made by electrochemical sensor. The device permits determination of methane to the content of 70%, carbon dioxide to 60%, oxide to 25%, carbon oxide and hydrogen sulphide to 500 ppm.

Fig. 1. Biogas analyser series GA2000

The accuracy of indications declared by the producer for CH_4 and CO_2 at their content above 15% is ±3% and for O_2 in the content up to 5% is ±1%. The accuracy of indications declared for H_2S and CO in the range up to 500 ppm is ±10%. According to the producer's recommendations the analyser was periodically subjected to calibration using a certified mixture containing 30% of methane, 20% of carbon dioxide and 100 ppm of hydrogen sulphide. The calibration for oxygen was performed with reference to its content in the air.

The intake of the biogas sample was continued until getting stabilised indications of the instrument.

The results presented in this paper were made to verify the indications of the above analyser by comparison with those obtained by gas chromatography. The biogas samples for analysis were placed in special bags made of Tedlar® designed for collection of gas samples, produced by SKC, of 1 dm^3 in capacity (Fig. 2) [6].

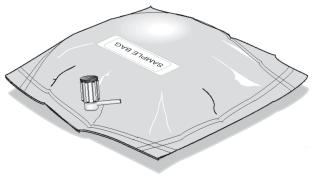

Fig. 2. A bag for collection of gas samples, the version with one valve

Each bag was filled with biogas with the help of a specially constructed kit enabling careful washing of the bag with the sample. Following the recommendations the process of washing the bag with the sample was repeated 10 times before the final filling. The sample collected was analysed on a gas chromatograph HEWLLET-PACKARD model 5890 series II equipped with a *thermal conductivity detector* (TCD).

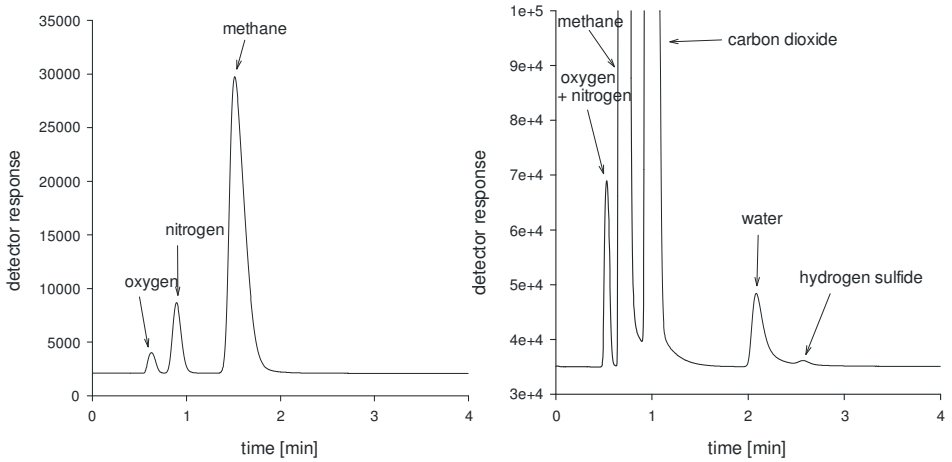

Fig. 3. Exemplary chromatograms revealing the sequence of elution of the components on the columns used. The chromatogram on the left was obtained on the column filled with molecular sieves 5 A, while that on the right on the column filled with HayeSep Q polymer

The sample of 0.3 cm^3 in volume was injected on the column with a gastight syringe. The components analysed were separated on two columns: one of 2.5 m in length and 1/8 inch in diameter filled with HayeSep Q polymer and the other of 1.5 m in length and 1/8 inch in diameter filled with molecular sieves 5A. The first column was used to determine the content of air, methane, carbon dioxide - in the low sensitivity mode and water and hydrogen sulphide - in the high sensitivity mode. The second column was used to determine the content of oxygen and nitrogen - in the high sensitivity mode. The separation was performed in isothermal conditions, at 75ºC for the column filled with molecular sieves and at 80ºC for the column filled with polymer. Exemplary chromatograms of the biogas analysed are presented in Figure 3.

Results and discussion

The monitoring of biogas composition was performed at the Central Wastewater Purification Plant for Poznan, in Kozieglowy (Table 2).

Table 2

Comparison of the biogas composition determined by GA2000 analyser and gas chromatography

Sample labelling (date of collection)	**GA2000**				**GC**				
	Component determined *								
29.03.2010	O_2	CH_4	CO_2	H_2S	O_2	N_2	CH_4	CO_2	H_2O
Bioreactor 18.1	0.0	60.7	38.3	68	0.1	0.4	58.9	39.3	1.3
Bioreactor 18.2	0.0	61.9	36.8	21	0.2	0.8	60.3	37.8	0.9
Bioreactor 18.3	0.0	62.5	37.1	29	0.1	0.4	61.1	37.7	0.7
Bioreactor 18.4	0.0	61.9	37.8	69	1.3	5.9	55.2	36.6	1.0
Bioreactor 18.5	0.0	61.9	37.2	15	0.1	0.7	60.2	38.2	0.8
Bioreactor 18.6	0.0	62.4	38.0	44	0.1	0.4	59.3	39.4	0.8
Before desulphur. chamber	0.0	61.8	37.8	67	0.2	0.5	60.1	38.3	0.9
After desulphur. chamber	0.0	61.8	37.5	45	0.1	0.6	60.5	38.1	0.7
Before power generator	0.0	61.6	38.2	13	0.2	0.8	59.6	38.6	0.8
01.07.2009									
Bioreactor 18.1	0.1	60.8	37.9	162	0.1	0.2	60.5	37.9	1.3
Bioreactor 18.2	0.4	52.0	33.7	122	3.2	12.3	50.7	32.5	1.3
Bioreactor 18.3	0.1	61.9	37.6	12	0.1	0.3	61.1	37.2	1.3
Bioreactor 18.4	0.1	62.1	37.3	117	0.1	0.2	61.7	36.6	1.4
Bioreactor 18.5	0.0	61.3	37.2	0	0.3	1.6	59.9	36.8	1.4
Bioreactor 18.6	0.1	62.7	36.4	190	0.1	0.3	62.4	36.0	1.2
Before desulphur. chamber	0.2	61.3	37.7	163	0.2	0.7	60.6	37.0	1.5
After desulphur. chamber	0.3	61.1	37.7	30	0.3	1.0	60.3	36.8	1.6
Before power generator	0.5	59.9	37.9	0	0.5	1.8	59.4	36.9	1.4
01.07.2008									
Bioreactor 18.1	0.2	58.9	37.8	86	0.1	0.1	60.4	38.8	0.6
Bioreactor 18.2	0.2	58.9	37.7	97	0.1	0.2	60.3	38.8	0.6
Bioreactor 18.3	0.2	58.1	38.5	61	0.1	0.3	60.4	38.6	0.6
Bioreactor 18.4	0.1	59.9	36.9	71	0.1	0.6	61.3	37.3	0.7
Bioreactor 18.5	0.1	59.4	37.1	26	0.1	0.4	61.1	37.9	0.5
Bioreactor 18.6	0.2	58.6	36.5	26	0.2	1.1	61.3	36.8	0.6
Before desulphur. chamber	0.0	59.9	37.6	63	0.1	0.3	60.9	37.9	0.8
After desulphur. chamber	0.0	59.9	37.4	25	0.1	0.3	61.6	37.5	0.5
Before power generator	0.1	59.2	37.8	21	0.2	0.6	60.5	38.1	0.6

* - concentration of all components except H_2S is given in volume %, the content of H_2S is given in ppm

Biogas was collected at a few sites to get the information on its composition in the process of formation and later its use as energy source. The lack of data for water and nitrogen among the determinations by GA2000 is a consequence of impossibility of their determination by the analyser of this type. Similarly it was impossible to determine the content of hydrogen sulphide on the gas chromatograph as the LOD of the analytical system (HayeSep Q filled column and TCD detector) was 300 ppm and in the biogas samples studied hydrogen sulphide occurred at lower contents. Comparison of the results of determinations shows that the difference between the results obtained by the analyser and those obtained by gas chromatography was at a level of 1.0÷1.5% for methane and 0.5÷1.0% for carbon dioxide. These results are much better than 3.0% declared by the producer of the GA2000 analyser. Close agreement between the analyser indications and results of gas chromatography follows from a high quality of the reference standards that were prepared according to PEH (*close manufacturing tolerance*) to maintain the declared composition to the accuracy of 0.1% for methane and carbon dioxide and 1 ppm for hydrogen sulphide.

The use of reference mixtures of the highest quality ensured the close agreement of the results despite the fact that we used reference mixtures from two producers in the period of the study (2008-2010). The use of two mixtures was necessary as the stability of certified material of this type reaches only 2 years. The contents of CH_4 and CO_2 indicated by the analyser were usually slightly overestimated with respect to chromatographic determinations, while the content of O_2 was always a bit lower than indicated by GC. The differences follow from the specific method of sample collection for GC analysis, which makes it impossible to totally remove air from the bags during the filling.

Conclusions

1. The agreement between the GA2000 analyser indications and GC results was at a level of 1.0÷1.5% for methane and 0.5÷1.0% for carbon dioxide, so better than 3.0% declared by the producer.
2. The high quality of the reference mixtures used, prepared according to PEH (close manufacturing tolerance) had important effect on the agreement between the GA2000 analyser and GC chromatography data.

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Abstrakt: Biogaz to mieszanina różnych gazów, wśród których dwie trzecie stanowi metan (CH_4), jedną trzecią ditlenek węgla (CO_2). Pozostałe składniki nieorganiczne, organiczne i para wodna występują w biogazie w ilościach śladowych. W pracy przedstawiono wyniki badań dotyczących oznaczania składu ilościowego za pomocą popularnego przenośnego analizatora biogazu, jakim jest GA2000, w którym odczyt zawartości metanu i ditlenku węgla odbywa się metodą spektrofotometryczną, natomiast poziom tlenu i siarkowodoru elektrochemicznie. Otrzymane wyniki weryfikowano za pomocą chromatografii gazowej.

Słowa kluczowe: biogaz, chromatografia gazowa, analizatory biogazu, weryfikacja pomiarów