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TECHNOLOGICAL AND ENVIRONMENTAL ISSUES OF OF BIOGAS COMBUSTION AT MUNICIPAL SEWAGE TREATMENT PLANT

The composition, physical properties and volume stream of exhaust gases emitted into the atmosphere as a result of biogas combustion in gas-powered energy generator as well as chemical composition of precipitates formed in the exhaust gases/water crossflow heat exchanger are investigated. The content of such basic components of combustion gases as CO₂, O₂, H₂O, N₂, such toxic substances as SO₂, SO₃, NO, NO₂, CO, HCl as well as acid and water dew-points are determined. Precipitate analysis included determining loss on ignition and the content of sulphur compounds, Fe, Mn and Mg. The results of the study allow us to evaluate the noxiousness of exhaust gases in the atmospheric air, to identify the causes of precipitate formation in the heat exchanger and to explore the ways of dealing with the problem of deposit precipitation.

1. INTRODUCTION

Biogas generated during sewage sludge fermentation is widely used as fuel for Combined Heat and Power (CHP) plants. However, modernization of biogas combustion and energy recovery systems is far ahead of the typically used systems for biogas treatment using activated bog ore, inertial dewaterers or standard adsorbers based on activated carbon. Improper treatment of raw biogas prior to its combustion in gaseous engines of energy generators may lead to the limited availability of the installation, mainly due to blockages in ducts and heat exchangers caused by precipitated residue. This may also create environmental hazards to the atmospheric air.

The causes of such negative influence are investigated, based on the research conducted in one of the Polish municipal wastewater treatment plants.

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2. CHARACTERISTICS OF THE SLUDGE-AND-GASEOUS SECTION OF THE SEWAGE TREATMENT PLANT UNDER STUDY

Waste sludge from primary and secondary settlement tanks, after coagulation (using FeCl_3) and thickening, is transported to the closed, heated digestive chambers. Fermentation takes place at the temperature of 309 K. The biogas undergoes initial treatment in defoaming columns, inertial dehydrators and desulphurisers. After final treatment in adsorbers and dust extraction systems, biogas is used as fuel for electric energy and heat production. The system uses desulphurisers filled with desulphurising agent based on bog ore [1]. Adsorbers are filled with extruded activated carbon of N-G II type, in conformity with the Polish PN-90/C-97554 standard. Electric energy is generated using JENBACHER 4-stroke, spark ignition gas combustion engines, paired with AC generators, each of 600 kW_e nominal output. For heat recovery, a horizontal shell-and-tube heat exchanger is used of exhaust/water crossflow type. Combustion gases are treated using an oxidation catalytic converter system, and then discharged into the atmosphere through three independent emitters, each 13 m high and 0.3 m in diameter.

Heat and electric energy produced from biogas are utilised in the plant (e.g. for heating the digestive chambers). Energy surplus is sold to the national energy network.

3. MEASUREMENT RESULTS

3.1. COMPOSITION OF EXHAUST GASES

The measurements were conducted in April 2003 at a nominal load of the generator fed with biogas consisting of CH_4 (65%) and CO_2 (35%). Due to atypical measurement system and potential analytical issues, different measurement methods were used in parallel (table 1). The concentration averaging time was one hour. The concentration values as well as the density and volume stream of exhaust gases were related to the standard conditions of 273 K, 1013 hPa, dry gas (index n). Average concentrations of main air pollutants in the combustion gases are presented in the figure.

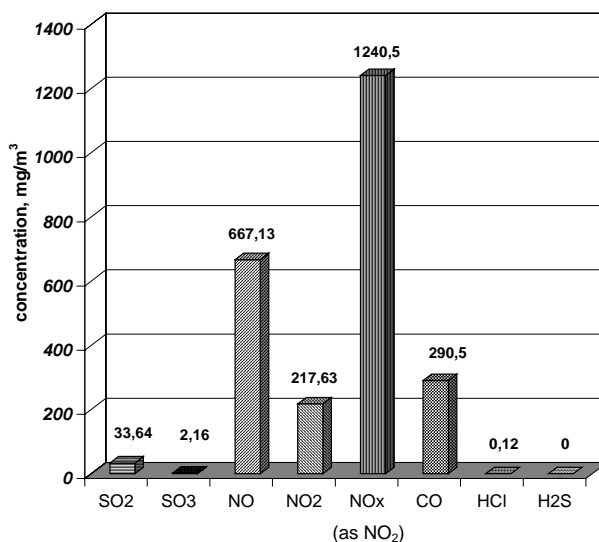
Table 1

Results of measuring the physical and chemical parameters of exhaust gases emitted by gaseous engine of generator fed with biogas

Parameter	Method of measurement	Unit	Measurement results	
			Sample 1	Sample 2
1	2	3	4	5
SO ₂ concentration	electrochemical	mg/m _n ³	37.25	40.75
SO ₂ concentration	iodometric	mg/m _n ³	33.60	30.40
Sso ₄ + Sso ₃ concentration (as SO ₂)	ion chromatography (IC HIC-6 chromatograph by SHIMADZU)	mg/m _n ³	37.88	21.94

1	2	3	4	5
SO ₃ concentration	titration using Toron indicator [2]–[4]	mg/m _n ³	2.35	1.97
NO concentration	electrochemical	mg/m _n ³	665.00	669.25
NO ₂ concentration	electrochemical	mg/m _n ³	212.75	222.50
NO _x concentration as NO ₂	–	mg/m _n ³	1232.25	1248.75
CO concentration	electrochemical	mg/m _n ³	289.00	292.00
HCl concentration	ion chromatography (IC HIC-6 chromatograph by SHIMADZU)	mg/m _n ³	0.09	0.15
H ₂ S concentration	electrochemical	mg/m _n ³	nf.	nf.
H ₂ S concentration	spectrophotometry, PN-Z04015-13	mg/m _n ³	nf.	nf.
O ₂ concentration	electrochemical	%	7.50	7.50
CO ₂ concentration	electrochemical	%	14.30	14.80
N ₂ concentration	from balance	%	78.20	77.70
Exhaust gas temperature	electronic	K	421.0	421.0
Exhaust gas humidity content	psychrometric	g H ₂ O/kg	115	115
Water dew-point of exhaust gases	psychrometric	K	328	
Acid dew-point of exhaust gases	based on SO ₃ /H ₂ SO ₄ density measurement, [2]–[5]	K	388	
Exhaust gas density	–	kg/m _n ³	1.365	1.369
Exhaust gas volume stream	the Prandtl tube	m _n ³ /h	2007.7	1968.2

nf. – not found.



Average concentrations of main air pollutants emitted by gaseous engine of generator fed with biogas

3.2. COMPOSITION OF RESIDUE PRECIPITATED IN HEAT EXCHANGER

One of the key issues that affect the efficiency and disposability of biogas combustion plant is the deposit accumulation in heat exchangers of the generator. In order to identify the causes and to find the ways of avoiding this issue, the samples of such a residue were collected. Chemical analyses were carried out for the samples collected in two temperature zones of the heat exchanger (1 – ca. 373 K and 2 – ca. 773 K, table 2). All determinations (except for loss of ignition) are presented in their corresponding oxide forms.

Loss on ignition (from room temperature up to 1273 K) consists of: unbounded water (humidity), water of crystallization (hydratizing water), constitutional water (chemically bound) and the products of volatile decomposition of chemical compounds (such as CO, SO₃).

Sulphur was found in the form of sulphates(VI), SO₄²⁻, presented as trioxide (SO₃), sulphates(IV), presented as SO₂, and sulphides (S²⁻).

Sulphates(VI) were determined gravimetrically, sulphates(IV) – iodometrically, sulphides – also iodometrically with prior distillation. Metals were determined with flame photometry method (Na, K, Ca) using FLAPHO 4 analyser as well as with AAS method (Fe, Mn, Mg) using AAS 932-AVANTA. Prior to chemical analysis, the samples were finely-ground and mineralized using microwave method with nitric acid or aqua regia. Chemical composition was presented in per cent of residue dry mass, after determining humidity through drying in 378 K.

Phase composition (table 3) was determined based on the results of chemical analysis (table 2) and derivatographic analysis.

Table 2

Chemical composition of deposit (% of dry content)

Component	Sampled in	
	Zone 1	Zone 2
Humidity	2.25	1.40
Loss of ignition at 1273 K incl.:	64.25	62.60
SO ₃ (from SO ₄ ²⁻)	50.88	55.07
SO ₂ (from SO ₃ ²⁻)	0.23	nf.
SiO ₂ together with particles insoluble in HNO ₃ and aqua regia	nf.	nf.
MgO	5.78 · 10 ⁻³	6.18 · 10 ⁻³
Na ₂ O	8.51 · 10 ⁻²	0.11
K ₂ O	4.22 · 10 ⁻²	4.40 · 10 ⁻²
Fe ₂ O ₃	32.92	31.52
CaO	0.56	1.97
S ²⁻	1.85 · 10 ⁻²	2.48 · 10 ⁻²
Cl ⁻	nf.	nf.
Total (excluding humidity):	97.88	96.28

Table 3

Phase composition of deposit based on thermogravimetric analysis
(% of mass content)

Component	Sampled in	
	Zone 1	Zone 2
Total mass loss up to 1000 °C, including humidity	66.5	64.0
CaSO ₄	2.25	1.40
Fe ₂ (SO ₄) ₃	1.35	4.77
Fe ₂ (CO) ₉ · 18H ₂ O	75.80	73.31
MnSO ₄	11.27	9.55
H ₂ SO ₄	0.21	0.30
Total (excluding losses on ignition):	5.10	10.00
	93.73	97.93

4. CONCLUSIONS

In the case of oxygen surplus, sulphur dioxide as a combustion product of biogas sulphur compounds is partially oxidized to sulphur trioxide. The latter, at temperatures below 473 K, reacts with water vapour to produce vapours of sulphuric acid. Apart from oxygen surplus, SO₃ generation may be further accelerated by exhaust system catalyser as well as by the presence of metal oxides (the oxidation of SO₂ to SO₃ is catalyzed, among others, by such compounds as: V₂O₅, Fe₂O₃, CuO, SnO₂, Mn₂O₃, MoO₂, TiO₂).

Low pressure of steam saturated with H₂SO₄ results in the agent condensation when the temperature drops below the acid dew-point. This point changes in the temperature range of 373–423 K for SO₃ concentration of 0.1–100 ppm_v [2], exceeding the water vapour dew-point (table 1).

Variations in the generator rating in the range of 50–100% of nominal output [6], as a result of fluctuations in biogas generation and limited storage possibilities, lead to fluctuations in heat exchanger outlet temperature in the range of 373–423 K. Momentary drops of temperature below acid dew-point are responsible for acid condensation and sulphate formation on the heat exchanger casing. The sulphate residues not only act as crystallization nuclei, but also form porous adsorption structures for sulphur compounds (the precipitate analysis shows the SO₄²⁻ ion content to be higher than the amount that may effectively be bonded by cations, confirming the assumption that sulphuric acid and SO₃ are sorbed by the residue). The sulphur compounds adsorbed may be reintroduced into the exhaust gases with increased temperature (desorption). Moreover, at temperatures above the 773 K (i.e. at the heat exchanger inlet) a partial thermal decomposition of sulphates may also occur.

One of the main causes of precipitate formation in the heat exchanger is the insufficient purification of biogas, especially from the sulphur and volatile metal com-

pounds. Another critical factor is the underload of heat exchanger, resulting in the formation of low-temperature zones. The periodic drops in the efficiency of purification systems are caused by difficulties in providing a proper working environment for desulphurisers and adsorbers, especially in regard to temperature and humidity. The desulphurisers typically operate below optimal temperature range, with no effective control and regulation of the desulphurising mass humidity. In the case of adsorbers, the exact opposite holds true: high temperature of the generator room, together with moisture of the bed, results in reduced efficiency of activated carbon.

As is found in the analysis, the precipitates sampled from the heat exchanger contain mainly iron compounds in the form of iron sulphates and carbonyls. Volatile iron carbonyls form in the presence of carbon monoxide (biogas CO content < 1 ppm_v). Iron content may originate both from sewage sludge and bog ore; in line with [7] it may also originate from steel tanks and piping. Thermal analysis shows the presence of unbounded H₂SO₄ in precipitates, as is proven by the surplus of SO₄²⁻ anions in relation to the cations found. There was no significant influence of temperature upon the qualitative and quantitative composition of precipitates.

In accordance with the Polish Law on Environmental Protection dated 27.04.2001 (Official Gazette No. 62, pos. 627), emission of gas or dust from gas-fuelled energy production systems of total nominal output up to 15 MW_e does not require official permission. Also the Polish standards of emission apply to the sources with the power output of 1 MW and higher. Nonetheless, any construction of biogas combustion and utilization system in Poland is legally bound to be based on report of future environmental impact. For such a report to be reliable, the applicants are required to provide correct evaluation of the types and amounts of toxic substances to be emitted into the atmosphere.

Table 4

Comparison of actual concentrations of exhaust gas pollutants, concentrations warranted by the generator manufacturer, emission concentrations at ground level and atmospheric reference values

Substance emitted	Average concentration in exhaust gas*	Warranted emission value *	Maximum air concentration (S _{mm})**	Reference air value (D ₁)**
	mg/m ³	mg/m ³	µg/m ³	µg/m ³
Sulphur dioxide	42	–	21	350
Nitric oxides (as NO ₂)	1471	500	714	200
Carbon monoxide	344.5	650	166	30000
Hydrogen chloride	0.14	–	0.07	200

* Expressed as dry gas, standard conditions (273 K, 1013 hPa) and O₂ exhaust gas content of 5%.

** Determined in accordance with [8].

As is shown by the results of analysing the pollutants emitted (table 1) and the resulting model approximations of maximum emission concentrations (table 4), of all

the substances analysed under experimental conditions, the emission of nitric oxides, with NO_2 content in total exceeding 25% (in practical applications, often neglected or assumed at 5%), poses the greatest environmental hazard.

REFERENCES

- [1] GAJ K., CYBULSKA H., KNOP F., STEININGER M., *Examination of biogas hydrogen sulphide sorption on a layer of activated bog ore*, Environ. Prot. Eng., 2008, No. 4, 33–41.
- [2] JAWOROWSKI S.J., MACK S.S., *Evaluation of methods for measurement of $\text{SO}_3/\text{H}_2\text{SO}_4$ in flue gas*, JAPCA, 1979, Vol. 29, No. 1, 43–46.
- [3] DOMEK W., SKORUPSKI W. (editors), *Metody manualnych pomiarów zanieczyszczeń atmosfery*, IOŚ, Warszawa, 1990.
- [4] EPA Method 8, *Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources*, CFR40, Part 60, Appendix A, 1999.
- [5] FIEG J., *Temperatura punktu rosy gazów o niskiej zawartości H_2SO_4* , Ochrona Powietrza, 1981, No. 4 (84), 85–89.
- [6] GAJ K. et al., *Badania biogazu pochodzącego z fermentacji osadów ściekowych*. Raporty Inst. Inż. Ochr. Środ. P.Wr., seria SPR, 2002–2008, Nr 18/02, 29/02, 30/02, 6/03, 13/03, 23/03, 36/03, 6/04, 35/04, 43/04, 2/05, 13/05, 16/05, 29/05, 8/06, 13/06, 23/06, 40/06, 8/07, 13/07, 26/07, 34/07, 3/08, 12/08, 19/08, 31/08.
- [7] FELDMANN J., *Determination of $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ in sewage gas by using cryotrapping gas chromatography inductively coupled plasma mass spectrometry*, J. Environ. Monit., 1999, 1, 33–37.
- [8] Ministry of Environment Directive dated December 5, 2002, on reference values of selected substances emitted into the atmosphere – Official Gazette 2003.1.12 dated 8.01.2003.