Biogas composition depending on the type of plant biomass used

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Abstract

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The aim of the work is to determine and analyse concentrations of individual biogas components according to the used raw materials based on plant biomass. The measurement is focused on biogas production depending on input raw materials like maize silage, grass haylage and rye grain. The total amount of plant biomass entering the fermenter during the measurement varies at around 40% w/w, the rest is liquid beef manure. The measured values are statistically evaluated and optimised for the subsequent effective operation of the biogas plant. A biogas plant operating on the principle of wet anaerobic fermentation process is used for the measurement. The biogas production takes place during the wet fermentation process in the mesophile operation at an average temperature of 40°C. The technology of the biogas plant is based on the principle of using two fermenters. It follows from the measured results that maize silage with liquid beef manure in the ratio of 40:60 can produce biogas with a high content of methane; this performance is not stable. At this concentration of input raw material, the formation of undesirable high concentrations of hydrogen sulphide occurs as well. It is shown from the results that the process of biogas production is stabilised by the addition of other components of plant biomass like grass haylage and rye grain and a limitation of the formation of hydrogen sulphide occurs. It follows from the results that the maize silage should form about 80% w/w from the total amount of the plant biomass used.

Keywords: biogas; maize silage; grass haylage; rye grain; wet anaerobic fermentation process

Over the years, the technology and technique of anaerobic treatment has become almost perfect. The fact that the primary purpose of fermentation technology was to stabilise biodegradable waste can be presented as an example. Nowadays, together with the waste stabilisation, the production of biogas and its subsequent use for energy production is more and more in the centre of attention (Malaťák, Vaculík 2008).

At the present level of technological knowledge, energy prices and ecological necessity of substitution of fossil energy sources, many authors recommend to produce biogas using biomass from energy plants and from plant wastes. For biogas production, plant biomass at a harvesting humidity over 45% and with the ratio of C:N within the range of 20–30:1 is especially suitable. More dry plant biomass and biomass with a broader ratio of C:N is more suitable for direct incineration (Pastorek et al. 2004).

For example, during anaerobic treatment in batch fermenters at a temperature of 32°C the grass biomass produced almost the highest amount of biogas

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(compared to animal faeces, abattoir wastes and municipal biowaste). A higher yield was achieved only for sewage sludges. Compared to other substrates, grass biomass shows the highest dynamics of biogas production from the start of fermentation until the 20th day. During this period, 97% of all the production was produced (Malaťák et al. 2006).

In biogas plants for agricultural raw materials, fermentation of plant mass with liquid manure is realised more and more often. Co-fermentation of plant mass with liquid manure enables the stabilised process of biogas production due to the buffering capability of liquid manure in the substrate and it limits dysfunctions caused by higher ammonia contents (Krieg 1995). The addition of plant biomass optimises the ratio of carbon and nitrogen; needed nutrients and microelements necessary for the development of microflora are brought into the substrate by the liquid manure (Kuhn 1994).

The biogas composition depends mostly on the type of decomposed material and subsequent slight differences in chemical compositions could result from that as well. The chemical composition of biogas is as follows: 50–85% CH_4 (methane); 20–35% CO_2; H_2, N_2 and H_2S form the rest (Pastorek et al. 2004).

The chemical composition of dry mass of plant biomass, especially the buffering, C:N ratio, content of proteins, polysaccharides and lignin, degree of polymerisation and cellulose crystallinity of this biomass varies considerably depending on the plant species, soil and climatic conditions, fertilising, time and manner of harvest and means of conservation.

Anaerobic digestion of phytomass, when compared to animal faeces, is more complicated due to the higher content of low-polymer hydrocarbons easily convertible to organic acids and also due to the low buffering capacity of the substrate based on phytomass; both these properties lead to excessive acidification. The buffering capacity measured as the consumption of 1N HCl in ml for the titration to pH 4 for 100 g of the substrate dry matter can be 10–30 times lower for biomass than for the substrate based on animal faeces. The buffering capacity of phytomass differs especially according to the plant species and it decreases with the increasing age of plants and with decreasing nitrogen fertilisation. Re-circulated processing fluid during the stabilised process of phytomass methanogenesis on average shows high buffering. It is recommended to solve the stability of phytomass methanogenesis before excessive acidification using the addition of lye at the dose of 2.5–13 g OH^-/kg of the substrate dry matter. This dysfunction can be also limited by the circulation of processing fluid, multi-level processing or using an appropriate co-fermentation (Váňa 2001).

Biogas showing different concentrations of methane is formed in the biological process of fermentation in the biogas plant. The aim of this work is to determine individual concentrations of biogas components according to the used raw materials based on plant biomass. The measurement is therefore focused on biogas production in dependence on input raw materials. These measured values are statistically evaluated and optimised for the subsequent operation of the biogas plant.

MATERIAL AND METHODS

The biogas plant operating on the principle of a wet anaerobic fermentation process was selected for the determination of the composition of input raw material which is determinative for the final biogas quality. The biogas plant is designed as an accumulation through-flow device. The biogas production takes place during the wet fermentation process in the mesophile operation (average temperature 40°C). The produced biogas is used in a cogeneration unit. The biogas plant operates in automatic mode. In terms of automation, the basic parameters of the biogas plant operation are read.

The technology of the biogas plant is based on the principle of using two fermenters. The substrate is transported to the main fermenter through the dispenser of solid substrate and the income liquid manure basin. A low-speed paddle-wheel agitator with an adjustable interval of agitation is used for homogenisation and for uniform temperature distribution. The main part of the gas production is produced in the main fermenter. The final fermenter which is connected with the main fermenter finishes the anaerobic fermentation process. In the fermenter, the biogas is desulphurised on the basis of the hydrogen sulphide content which is measured by the gas analyser. The maximum allowable amount of incoming air forms 5% from the total biogas production.

For the determination of concentrations of individual biogas components, the stationary biogas analyser BC20 is used. The analyser measures the concentrations of methane, carbon dioxide, oxygen and hydrogen sulphide in biogas. Methane and carbon dioxide are measured using a thermal conductivity sensor, other gases are determined using electrochemical sensors. The measuring range of

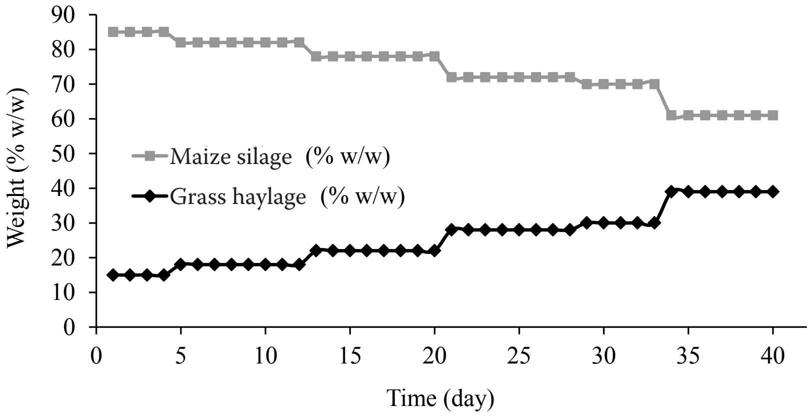

Fig. 1. Proportional composition of 2nd raw material: maize silage and grass haylage

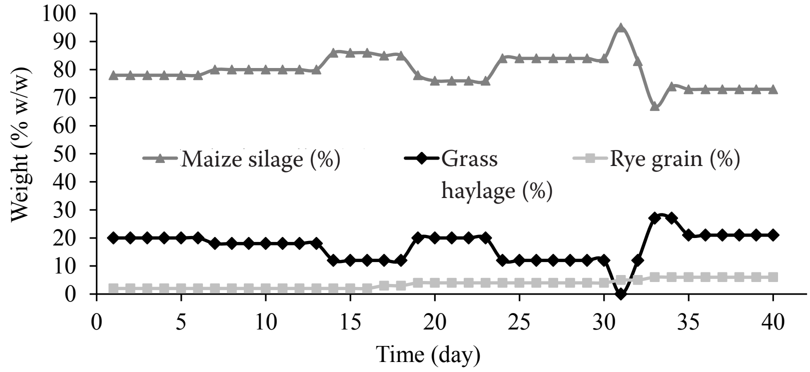

Fig. 2. Proportional composition of 3rd raw material: maize silage, grass haylage and rye grain

sensors for methane is 0% to 100% v/v, carbon dioxide 0% to 100% v/v, oxygen 0% to 20.9% v/v and hydrogen sulphide 0 to 2,000 ppm.

The measurement is divided into three experiments; each measurement takes 40 days. There is an average daily composition of individual components of the resulting biogas assigned to each day. The total average daily amount of raw material is set for 60 t/days. On average, 35.75 t/days from that is formed by liquid beef manure with the dry matter of 10% w/w, the rest is plant material. The plant matter is formed by maize silage with the average dry matter of 30% w/w, grass haylage with the average dry matter of 35% w/w and a small portion of rye grain. Plant biomass is mainly used for the measurement.

The main plant component of input raw material in the biogas plant is maize silage. During the measurement, the percentage of this maize silage varies constantly at around 56% w/w. Other raw materials used during the measurement are grass haylage and, in a smaller extent, also rye grain. These raw materials are entered in the process and individual concentrations of H_2S, O_2, CH_4 and CO_2 are determined. During the measurement, the ration of individual input components of this plant mass gradually changed. The total representation of the plant mass changed once a day for two raw materials:

1st raw material – maize silage 100%,
2nd raw material – maize silage and grass haylage (the proportional composition of the mixture during the measurement is presented in Fig. 1),
3rd raw material – maize silage, grass haylage and rye grain (the proportional composition of the mixture during the measurement is presented in Fig. 2).

RESULTS

During the measurement of individual components of the biogas, the composition of input material of the biogas plant after 24 h is constant. During this period, the average daily concentration of individual biogas components is determined. After the next 24 h, the ratio of individual input raw materials from the plant biomass is changed according to Figs 1 and 2. Graphical representations are plotted from the average daily concentrations of biogas components after 40 days (Figs 3–6).

Hydrogen sulphide (H_2S) is a colourless gas, only slightly heavier than air, with the characteristic foul odour of rotten eggs. Hydrogen sulphide reacts with metals. To prevent the damage of the cogeneration unit by hydrogen sulphide, it is necessary to dose fresh air to desulphurise the biogas. The resulting

Table 1. Testing of resulting biogas parameters (one-sample test)

	H_2S	O_2	CH_4	CO_2
		Raw material 1st		
Average value	289.65	0.375	54.77	41.96
Standard deviation	17.45	0.24	1.42	1.39
	Null hypothesis rejected on the significance level of 0.025	Null hypothesis not rejected on the significance level of 0.025	Null hypothesis rejected on the significance level of 0.025	Null hypothesis rejected on the significance level of 0.025
		Raw material 2nd		
Average value	182.65	0.36	53.97	42.64
Standard deviation	9.62	0.30	0.86	0.76
	Null hypothesis rejected on the significance level of 0.025	Null hypothesis not rejected on the significance level of 0.025	Null hypothesis rejected on the significance level of 0.025	Null hypothesis rejected on the significance level of 0.025
		Raw material 3rd		
Average value	175.47	0.38	54.37	42.49
Standard deviation	9.43	0.23	0.97	0.95
	Null hypothesis rejected on the significance level of 0.025	Null hypothesis not rejected on the significance level of 0.025	Null hypothesis rejected on the significance level of 0.025	Null hypothesis rejected on the significance level of 0.025

concentrations of H_2S are presented in Fig. 3. When maize silage is used, a steep increase of hydrogen sulphide concentration occurs. However, this increase cannot be compensated by desulphurised air, since damage of anaerobic microorganisms can happen. With the addition of other plant components like grass haylage and/or rye grain, the formation of H_2S stabilises (Fig. 3). The average concentrations of hydrogen sulphide are given in Table 1.

Oxygen (O_2) is an undesirable part of biogas, since it binds hydrogen and partly even carbon to produce hydroxides, water and oxides. On the other hand, it has a positive influence on the concentration of hydrogen sulphide in biogas. Increased concentrations in biogas for the mixture of maize silage and grass haylage leads to a decrease of methane production and thus the energy value of biogas (Figs 4 and 5). The average concentrations of oxygen are given in Table 1.

The main and most important component of biogas is methane (CH_4). The biogas heating power depends on the methane concentration in biogas. During the measurement of the methane concentration for maize silage (Fig. 5), high fluctuations occur. With the addition of other plant components like grass haylage and/or rye grain, the concentration of methane stabilises, which is favourable even for its other use. The average concentrations of methane are given in Table 1.

Carbon dioxide (CO_2) is a stable component of the carbon cycle in the environment. Carbon dioxide is a colourless, very heavy (ca 1.5× heavier than air), odourless gas. With its presence in biogas, carbon dioxide decreases the content of other gases, mainly methane, which decreases the heating power of biogas (Fig. 6). The average concentrations of carbon dioxide are given in Table 1.

For the evaluation of resulting biogas components depending on the input raw material, basic one-sample methods of hypothesis testing are used – *F*-test and *t*-test. For the leapfrog test, the significance level is set to 0.025 at *t*-distribution. The resulting test values of the different significance between the sample average and the supposed mean value are presented in Table 1. On the basis of the statistical analysis, the biogas composition during individual measurements is significant, except for the oxygen concentration in biogas, which has no influence on the composition of input raw material.

F-test for comparison of differences between two sample variances is used for the comparison of measured values of the biogas composition between the 1st and 2nd mixture of raw materials and the 1st and 3rd mixture of raw materials. The null hypothesis is therefore defined on the equality of variances of measured biogas components depending on the used input material. The selected significance value for the *F*-distribution is 0.01. On the

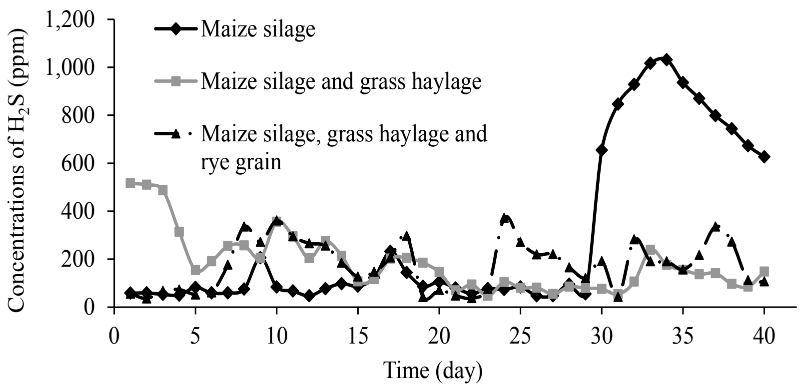

Fig. 3. Concentrations of H_2S

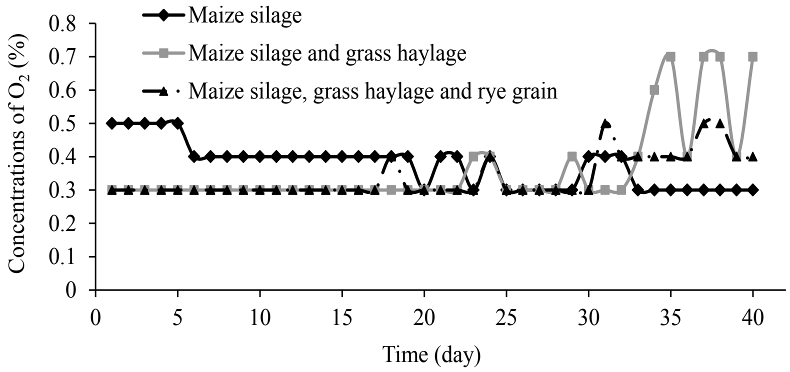

Fig. 4. Concentrations of O_2

basis of the performed *F*-test and non-rejection of the null hypothesis, the *t*-test for the verification of the null hypothesis of equality of variances was performed. The selected significance level was 0.01. The resulting values of the *F*-test and *t*-test are presented in Table 2. The statistical analysis showed high concentrations of H_2S in biogas from maize silage. The significant reduction of H_2S amount by the addition of other mixtures like grass haylage and rye grain is shown from the results.

DISCUSSION AND CONCLUSIONS

With the continually increasing number of biogas plants the demand for appropriate substrates is increasing as well. It follows from the performed analyses of planned biogas plants that maize silage will dominate. It should form 34% of the total amount of used substrates (Kajan et al. 2008). For these reasons, the presented paper solves the use of plant biomass (maize silage, grass haylage and rye grain) for the biogas production on the principle of using two fermenters. The total amount of plant biomass during the measurement varies at around 40% w/w, the rest is liquid beef manure. Mainly individual mass flows of input raw material from the plant biomass are monitored depending on the final composition of the biogas.

It follows from the measurement results that the raw material of maize silage provides the highest production of methane in the optimal course of the

Table 2. Testing of resulting biogas parameters: *F*-test and *t*-test

	Raw material 1st and 2nd	Raw material 1st and 3rd
F-test for H_2S	Null hypothesis H_0: $\sigma_1 = \sigma_2$ Null hypothesis not rejected on the significance level of 0.01	
t-test for H_2S	Null hypothesis H_0: $\upsilon_1 = \upsilon_2$ Null hypothesis rejected on the significance level of 0.01	
F-test for CH_4	Null hypothesis H_0: $\sigma_1 = \sigma_2$ Null hypothesis rejected on the significance level of 0.01	
F-test for CO_2	Null hypothesis H_0: $\sigma_1 = \sigma_2$ Null hypothesis rejected on the significance level of 0.01	

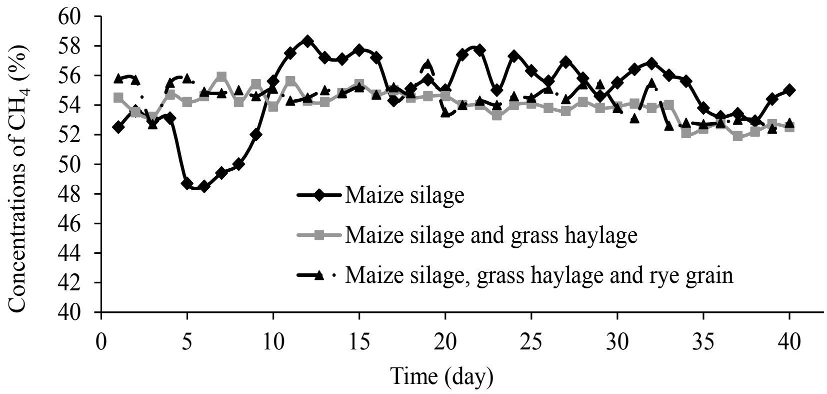

Fig. 5. Concentrations of CH_4

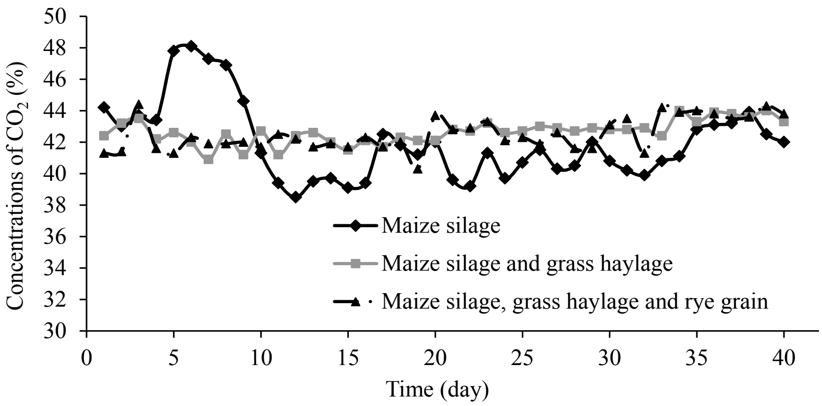

Fig. 6. Concentrations of CO_2

process, but on the other hand, without optimal control of the process there are the highest fluctuations in the methane production to the prejudice of carbon dioxide. With the addition of other raw materials like grass haylage and rye grain, the process of biogas production is stabilised, whereas maize silage should form about 80% from the total plant biomass. When decreasing the ratio of maize silage from the total plant biomass below 70%, the methane production decreases as well.

Similar results were achieved in the project of University of Hamburg (Hamburg, Germany) in the research work of Lehtomaki et al. (2007) who studied the biogas production during co-fermentation of grass haylage, sugar beet top and oat straw with liquid beef manure. The influence of individual components on the course of anaerobic digestion was also studied there (Lehtomaki et al. 2007).

The amount of formed hydrogen sulphide during the process is determinative for the lifetime of equipment for other biogas use. A high amount of hydrogen sulphide was formed with the input raw material composed from liquid beef manure and maize silage in the ratio of 60:40. With the addition of another component like grass haylage, the production of hydrogen sulphide decreases, but on the other hand, the increased ratio of grass haylage and maize silage to the ratio of 40:60 increases the oxygen concentration in the produced biogas as well.

On the basis of the statistical analysis, the daily concentrations of individual biogas components significantly depend on the composition of input raw material, except the oxygen concentration in biogas which varied within 0.3% to 0.7% v/v. Unlike other biogas components, when comparing individual mixtures of input raw materials, the concentration of hydrogen sulphide in biogas is statistically significant.

It follows from the research results that maize silage with liquid beef manure in the ratio of 40:60 can produce biogas with a high content of methane; however, this performance is not stable. It is shown from the results that this process of biogas production is stabilised by the addition of other components like grass haylage and rye grain, whereas maize silage should form about 80% of the total plant biomass.

New studies in waste treatment are focused on the better use of biodegradable wastes. Research studies react to the worldwide requirement for higher exploitation of energy plants and animal manure in biogas plants. The study of Matjaz et al. (2010) was focused on the optimisation of anaerobic digestion of maize and finding the most suitable variety for the high production of biogas and methane, whereas the total methane production in laboratory conditions varied within 50% to 60% in biogas (Matjaz et al. 2010). Another study from Bruni et al. (2010) provides information on the influence of the harvest time and particle size of maize silage on biogas recovery during anaerobic digestion. The highest yields of methane were for the fresh maize from the late harvest and the decrease of particle size of maize silage to the average size of 2 mm led to the increase of methane yields by 10%. All of them are significant factors that have to be taken into account (Bruni et al. 2010). The quality of liquid beef manure influences the methane production as well. The highest yields of methane were from dairy cows with middle milk production with a well-balanced diet (Amon et al. 2007).

One of the latest trends in biogas production is the associated production of biohydrogen. This issue is studied e.g. by Kaparajua et al. (2009) from the Technical University of Denmark (Copenhagen, Denmark), who mentions this possibility as a good supplement before the biogas production itself. In his work, he was concerned with the treatment of waste products from the bioethanol production from maize. He added the anaerobic production of biohydrogen before the fermentation of burnouts producing biogas (Kaparajua et al. 2009).

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