USE OF G-PHASE FOR BIOGAS PRODUCTION

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Received: July 19, 2012

Abstract

HAITL, M., VÍTĚZ, T., KOUTNÝ, T., KUKLA, R., LOŠÁK, T., GADUŠ, J.: Use of G-phase for biogas production. Acta univ. agric. et silvic. Mendel. Brun., 2012, LX, No. 6, pp. 89–96

Biogas is very promising renewable energy resource. The number of biogas plants increase every year. Currently there is a demand for new ways of organic waste treatment from production of different commodities. One of the technologies which produce waste is biodiesel production. One of the wastes from the biodiesel production is G-phase which is mainly consisted from glycerol and methanol. The aim of work was to find the effect of G-phase addition, to fermented material, on biogas resp. methane production. Two lab-scale batch anaerobic fermentation tests (hydraulic retention time 14 and 22 days) under mesophilic temperature conditions 38.5 °C have been performed. The positive effect of G-phase addition to methane production has been found. G-phase was added in three different amounts of inoculums volume 0.5%, 1% and 1.5%. The highest absolute methane production has been achieved by 1.5% addition of G-phase. However it was also found difference in specific methane production due to use of different inoculum consisted of swine or cow manure. The specific methane production in hydraulic retention time of 14 days has been for the same G-phase dose 1.5% higher for swine manure, 0.547 m³·kg⁻¹ of organics solids compare with cow liquid manure 0.474 m³·kg⁻¹ of organics solids.

biogas, biodiesel, waste, G-phase, fermentation

Biogas production by anaerobic fermentation technology strongly increased in last few years. The numbers of treated biogas plants rise every year, most of them are agriculture biogas plants. Agriculture biogas plants use mainly as input material agricultural waste materials like liquid manure and crops like grass or maize silages, planted for energy production. Due to the law requirements it is expected higher biological treatment of organic waste, instead of their deposition on landfills. Unstable prices of agricultural commodities are also one of the important factors, why it is necessary to look for the other way in use of agricultural production. On the other hand if the prices for agricultural commodities are high, the economically advantage of biogas production is lower. There is also another opportunity for using of cheap and easy available waste materials for biogas production. Anaerobic digestion of organic wastes is an alternative way of waste treatment. It has a great number of advantages, low nutrient requirements, energy savings, generation of low quantities of sludge, excellent waste stabilization, biogas production without requiring residue pretreatment (Yadvika *et al.*, 2004; Fryč *et al.*, 2012). Spectrum of organic waste materials which can be used for biogas production is wide. Although a lot of them are effective treated, there are still many waste materials suitable for biogas production.

Renewable energy sources and biofuels including biodiesel, have increasing attention recently as a replacement for fossil fuels. In advances against petroleum diesel fuel are represented by the terms of sulfur content, flash point, content of aromatic substances, and biodegradability (Janaun et al., 2010). With annual production of about 9 million tons, European Union has had leading position in both production and consumption of biodiesel (European Biodiesel Board, 2010). Biodiesel plants are mainly located in Germany, Italy, Austria, France and Sweden (Kolesarova et al., 2011). In Europe, rapeseed oil is predominantly used, while in the world extent, highest quantities of biodiesel are produced from soya. (Demirbaus, 2008). Besides the desired methylesters this reaction provides also few by-products. Isolation of oil from oil seed

plants by pressing and extraction provides oil cakes or oil meal, processing water and G-phase as waste product. In general for every 100 kilograms of biodiesel about 10 kilograms of G-phase is produced (Kolesarova *et al.*, 2011).

Crude glycerol generated by homogeneous basecatalyzed transesterification contains approximately 50-60% of glycerol, 12-16% of alkalis especially in the form of alkali soaps and hydroxides, 15-18% of methyl esters, 8-12% of methanol, 2-3% of water and further components (Thompson et al. 2006; Kocsisova et al., 2006). Crude glycerol contains a variety of elements, such as calcium, magnesium, phosphorus or sulphur, originating from the primary oil and larger quantities of sodium or potassium coming from the catalyst (Kolesarova et al., 2011). Generated glycerol is presently applied, for example, as an ingredient of cosmetics, but a further increase in the production of biodiesel fuels would raise the problem of efficiently treating waste (Vincente et al., 2004; WU et al., 2003).

It is able to use G-phase in the anaerobic fermentation process for biogas production. For biogas production easily degradable and energy rich input organic materials are used.

Several tests with G-phase in mono-fermentation have been done. From achieved results it is clear, that for this energy rich and easily biodegradable material is necessary to find optimal co-fermentation rate with other input material. Otherwise there is a risk of fermentor overloading.

MATERIAL AND METHODS

Tests were conducted in the reference biogas laboratory at Mendel University in Brno. Six batch lab-scale reactors with working volume of $0.12\,\mathrm{m}^3$ and 24 batch lab-scale reactors of working volume $0.003\,\mathrm{m}^3$ have been used. Reactors have been equipped with heating and mixing system, with probes for additive application, substrate and biogas sampling and probe for pH measurement.

Two laboratory tests with G-phase addition have been realized, the first test in small volume (0.003 m³) batch lab-scale reactors and second in big volume (0.12 m³) reactors. In test No. 1 was each variance in three repetitions in test No. 2 in one repetition. The goal of test No. 1 was to find the effect on methane production of different G-phase dose in co-fermentation with liquid manure and maize silage. To reach the goal, G-phase was added to inoculum in three different volumes, concretely 0.5%, 1% and 1.5% of inoculum volume, which was 0.0025 m³. Test No. 2 was performed with addition of 1.5% of G-phase of inoculum volume, which was 0.1 m³. In both tests reference reactor has been fed only with inoculum. Used inoculum originated from an agricultural biogas plants in Nivnice (cattle manure, maize silage) and Čejč (swine manure, maize silage). On the beginning of each test inputs materials were characterized, results are shown in Tab. I and II.

I: Characteristics of G-phase

G-phase characteristics	Test 1	Test 2
Total solids [%]	81.76	81.76
Organic total solids [%]	88.76	88.76
Acid value [mg KOH·g-1]	107.39	107.39
Free Glycerin content [%]	66.7	66.7
Density at 15 °C [kg·m ⁻³]	1 120	1 120
Methanol content [%]	26.56	26.56
pH[-]	12.4	12.4
Fat content [%]	1.5	1.5
Water content [%]	5.2	5.2

II: Characteristics of inoculum

Inoculums characteristics	Test 1	Test 2
Total solids [%]	6.44	4.48
Organic total solids [%]	74.23	77.30

During the tests quantity and quality of developed biogas (CH₄, CO₂ a H₂S) have been measured daily. Biogas production from each reactor was recorded. When evaluating the results the biogas production from the reference reactor was subtracted from the biogas production of the reactor with the addition of G-phase. Quality of generated biogas has been measured with gas analyser Drägger X-am 7000, quantity of generated biogas has been measured with gas flowmeter BG-4 (0.12 m³ reactors) and water-displace gasometer (0.003 m³ reactors). The hydraulic retention time (HRT) was 14 days in test No. 1, and 22 days in test No. 2. Both tests were performed under mesophillic temperature conditions 38.5 °C.

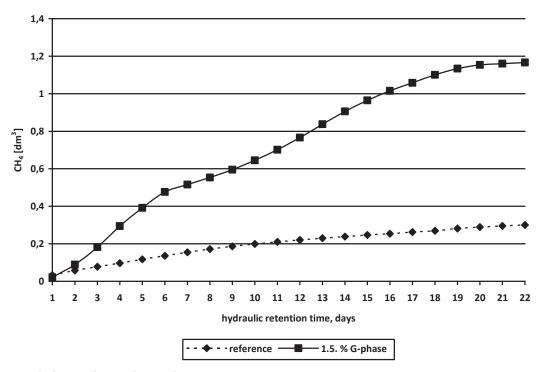
RESULTS AND DISCUSSION

Increase of absolute biogas production in all reactors with G-phase addition has been found. The higher the addition of G-phase, the greater was the absolute biogas, resp. methane production (Fig. 1, Fig. 2).

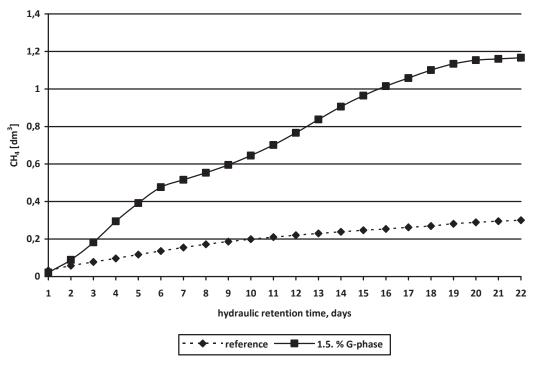
Founded differences in methane dynamics development (Fig. 3, Fig. 4) could be explained due to use of different inoculum. Inoculum in test No. 1 consisted from cattle liquid manure and, in test No. 2 of swine manure.

We focused on confirmation of the hypothesis that swine manure has higher buffer-capacity due to its lower C/N ratio (Fountolakis *et al.*, 2010). The hypothesis was confirmed, because the specific methane production by the same G-phase dose (1.5 % G-phase), in the period of 14 days, was higher for swine manure 0.547 m³·kg⁻¹ oTS, compare to cow liquid manure 0.474 m³·kg⁻¹ oTS Fig. 5 and Fig. 6.

Wohlgemut (2008) found after minimum glycerol addition (0.5% and 1%) the highest methane production, and he recommended this addition as good co-substrates in anaerobic fermentation with swine manure. However Amon *et al.* (2008) found



 $1:\ Absolute\ cumulative\ methane\ production, test\ No.\ 1$

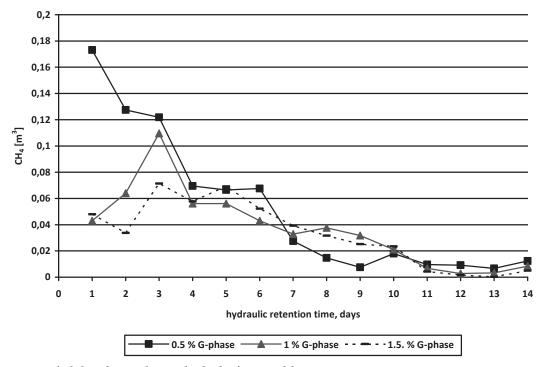


 $2:\ Absolute\ cumulative\ methane\ production, test\ No.\ 2$

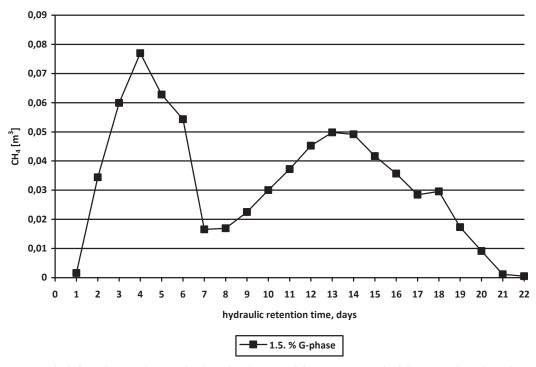
the highest methane production per one kilogram of oTS after G-phase addition in range from 3% to 6% to pig manure, maize silage and rapeseed feed. Concretely he achieved increase in methane production from 0.569 m³·kg⁻¹ oTS to 0.679 m³·kg⁻¹ oTS by addition of 6% of G-phase. In test No. 2

specific methane production 0.710 $\text{m}^3 \cdot \text{kg}^{-1}$ oTS has been achieved Fig. 6.

Developed biogas from the reactors with G-phase addition had high methane content. The methane content in biogas was on the optimal level for its utilization in cogeneration unit (Fig. 7, Fig. 8). In the Fig. 8 we can see that in test No. 2 was the biogas



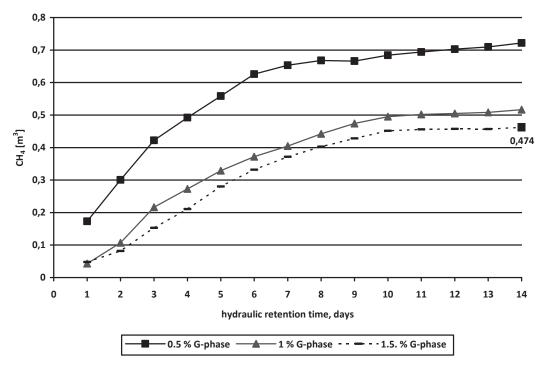
3: Specific daily methane production related on kg of organic solids, test No. 1



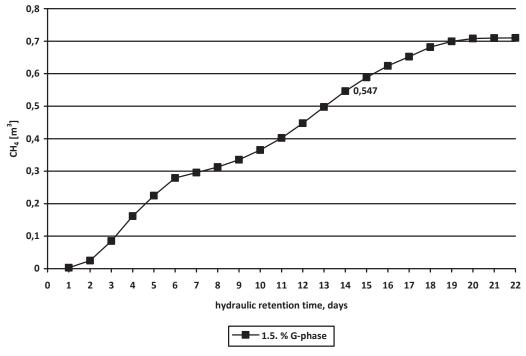
4: Specific daily methane production related on 1 kg of organic solids, test No. 2. Standard deviations of specific methane productions in test No. 1 were by 0.5 % 0.041, 1 % 0.084 and 1.5 % 0.060. Median specific methane productions of tested varieties in test No. 1 were by 0.5 % 0.722 m^3 kg⁻¹ oTS, 1 % 0.517 m^3 kg⁻¹ oTS and 1.5 % 0.504 m^3 kg⁻¹ oTS.

quality more stable and higher compared to test No. 1.

Hydrogen disulfide is minor and undesirable biogas compound and it has corrosive effect on iron technology parts. Higher hydrogen disulfide content in biogas has been found. Hydrogen disulfide content was higher in test No. 2. Current de-sulfurisation technologies are feasible to eliminate achieved hydrogen disulfide volumes.



5: Specific cumulative methane production related on $1\,\mathrm{kg}$ of organic solids, test No. $1\,\mathrm{kg}$

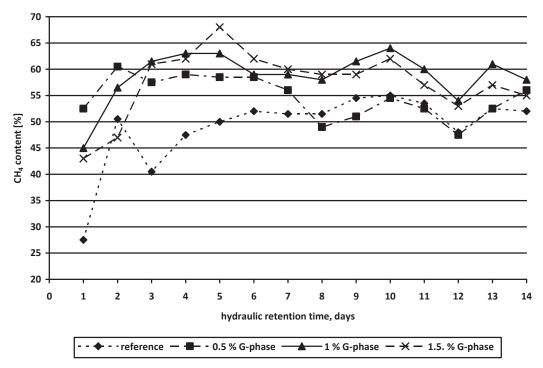


 $6: \ Specific \ cumulative \ methane \ production \ related \ on \ 1 \ kg \ of \ organic \ solids, test \ No. \ 2$

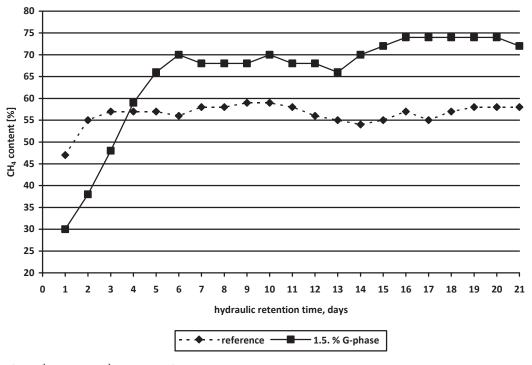
CONCLUSIONS

In lab-scale anaerobic batch fermentation tests high increase of biogas resp. methane production after G-phase addition has been found. G-phase was co-fermented with two different inoculums. The specific methane production was higher by using of swine manure, which was characterized with lower

C/N ratio, in compare with cow liquid manure. For stable methane development is necessary to regulate the feed of G-phase carefully, to avoid overloading of fermentor. G-phase is easy to store and by current high biodiesel production also easy available, thus represent good opportunity for improvement of biogas production on biogas plants.



7: Methane content in biogas, test No. 1



 $8:\ Me than e\, content\, in\, biogas\, test\, No.\, 2$

SUMMARY

The aim of this work was to find the effect of G-phase addition on anaerobic fermentation process. G-phase is energy rich biodiesel waste product consisted mainly of glycerol and methanol. Currently there is problem with its processing. Tested G-phase originated from rapeseeds was characterized by 81.76% TS, 88.76% oTS, glycerol and methanol content of 66.7%, resp. 26.56%. Two lab-scale anaerobic

fermentation tests in six batch lab-scale reactors with working volume of 0.12 m³ and 24 batch lab scale reactors of working volume 0.003 m³ have been provided. Reactors were equipped with heating and mixing systems, with probes for additives application, substrate and biogas sampling and probe for pH measurement. Inoculums originated from agricultural biogas plants consisted in test No. 1 of cattle liquid manure and maize silage (TS 6.44 %), and in test No. 2 of swine liquid manure and maize silage (TS 4.48 %). Tests were conducted under mesophillic temperature conditions and the hydraulic retention time was 14 and 22 days respectively. G-phase was added into the reactors in three different amounts of inoculum volume (0.5%, 1% 1.5 %). The highest absolute methane production has been achieved with 1.5% addition, however highest specific methane production 0.722 m³·kg⁻¹ oTS has been achieved with 0.5 % G-phase addition. It was also found difference in specific methane production due to use of different inoculums consisted of swine and cattle manure. The specific methane production was found higher for swine manure 0.547 m³·kg⁻¹ oTS with dose of 1.5 % G-phase compare to cow liquid manure 0.474 m³·kg⁻¹ oTS, for the hydraulic retention time of 14 days.

Acknowledgement

This study was financed by the Internal Grant Agency of the Faculty of Agronomy MENDELU in Brno No. TP 9/2011, by the Research plan No. MSM6215648905 'Biological and technological aspects of sustainability of controlled ecosystems and their adaptability to climate change', which is finance by the Ministry of Education, Youth and Sports of the Czech Republic and by the Sixth Framework Programme of the European Community for research, technological development and demonstration activities (2007–2017), No. 7AMB12SK076 Production of biogas from non-traditional biodegradable materials.

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