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ANNA KACPRZAK*,**, LILIANA KRZYSTEK*, STANISŁAW LEDAKOWICZ*

ANAEROBIC CO-DIGESTION OF AGRICULTURAL PRODUCTS AND INDUSTRIAL WASTES

The directives from the European Union require member states to increase a renewable energy consumption and to reduce uncontrolled methane emissions. The main objective of the present investigations was to optimize the substrate combinations and the process conditions for maximum productivity of methane-rich biogas.

The paper presents the result of co-fermentation of corn silage and whey together with glycerin fraction, the waste product of transestrification of oils (biodiesel production), in 25-dm^3 bioreactor operating mesophically in semi-continuous mode.

This allowed us to obtain a high productivity of methane-rich biogas, reaching 1.82 dm^3/dm^3/day with methane content being 60–62%, the biogas yield of 2.04 dm^3/g TS removed and 32% COD reduction.

1. INTRODUCTION

Concerns with energy conservation, environmental pollution, and the fact that agricultural organic and industrial wastes are major portion of our waste materials, has created renewed interest in the processing of these wastes for energy recovery. Basically every country in Europe has included bio-energy in its energy and climate policies. For the European Union (EU), targets have been set for bio-energy: in 2010 almost 10% of the energy supply of the EU is to come from biomass (FAAIJ 2006).

Biomass resources that can be used for energy are diverse depending on their availability. They can be either a by-product of other activities or can be specifically cultivated for energy purposes. Of the several available types of energy gaining processes, anaerobic digestion appears to be the most feasible. Anaerobic digestion can stabilize most agricultural wastes while producing biogas.

* Department of Bioprocess Engineering, Faculty of Process and Environmental Engineering, Technical University of Łódź, ul. Wólczańska 213, 90-924 Łódź, Poland.

** Corresponding author: e-mail: annakacprzak81@tlen.pl, phone: *48 042 63136978, fax: *48 042 6313738.

In the last few years, an increasing trend towards anaerobic digestion of energy crops has been observed. European data indicates that almost 16,000 kWh of electricity (plus equal heat) can be produced from corn silage planted on one ha (yield of 45 wet tones) (HOPFNER-SIXT, AMON, 2005).

Recently, it has been realized that the co-digestion treatment (simultaneous digestion of a mixture of two or more substrates) usually improves the biogas yields. It also provides a better nutrient balance, positive synergisms established in the digestion medium and dilution of potential toxic compounds (SOSNOWSKI et al. 2003).

Industrial facilities generate and dispose tons of industrial waste each year. The organic wastes, in solid or liquid form, may form a suitable co-substrate for anaerobic digestion.

During the last decade several full-scale digesters for the treatment of dairy effluents have been taken into operation. Despite all the available information on the anaerobic digestion of dairy factory effluents, very few dairies treat their effluents in this manner. Effluents are either disposed untreated or treated by means of aerobic processes such as activated sludge or biofilter systems (STRYDOM et al. 2001).

Annual world cheese-whey production is increasing and new bioproductions are sought through biotechnology in order to get full use of whey produced (SISO GONZALES 1996).

Anaerobic digestion is again a preferred candidate.

Biodiesel production is another source of waste by-products. Biodiesel has become more and more attractive because of its environmental benefits and the fact that it is made from renewable biological resources such as vegetable oils and animal fat (MA and HANNA 1999). It is known that production of biodiesel is increasing. That is why enormous quantities of glycerol deposit in the market are likely to be generated in the near future (PAPANIKOLAOU et al. 2008). There will be an essential need to treat this kind of waste. It is expected that oil waste – the by-product of transestrification of vegetable oils and animal fat may be the substrate used in co-fermentation with agricultural wastes.

GHALY (1996) digested cheese whey alone obtaining 20% methane and in co-digestion with dairy manure obtaining 60% methane and reported that anaerobic digestion of cheese whey alone without pH control is not feasible. JINGXING MA et al. (2008) co-digested potato processing wastewater with three different types of glycerol. In each case addition of glycerol increased the biogas and methane production.

Although there have been many studies concerning anaerobic digestion of cheese whey (SISO GONZALES 1996, GAVALA et al. 1996, DEMIREL et al. 2005), of agricultural residues (PARAVIRA et al. 2008, SVENSSON et al. 2005) and of glycerol by-product alone (PAPANIKOLAOU et al. 2008), no co-digestion of all these three substrates has been tried until now.

In this study, the optimization of co-digested mixtures of three different substrates: cheese whey, corn silage and glycerine fraction has been investigated in order to obtain maximum productivity of biogas of high methane content.

Highly efficient production of methane-rich biogas would benefit by providing a clean fuel from renewable feedstock.

2. MATERIALS AND METHODS

2.1. EXPERIMENTAL SET-UP

Four experiments were conducted in this study. Experiment 1 consisted in co-fermentation of corn silage and cheese whey and was carried out in the bioreactor with the working volume of 25 dm^3, operated mesophically in semi-continuous mode at a hydraulic retention time (HRT) of 25 days, (figure 1).

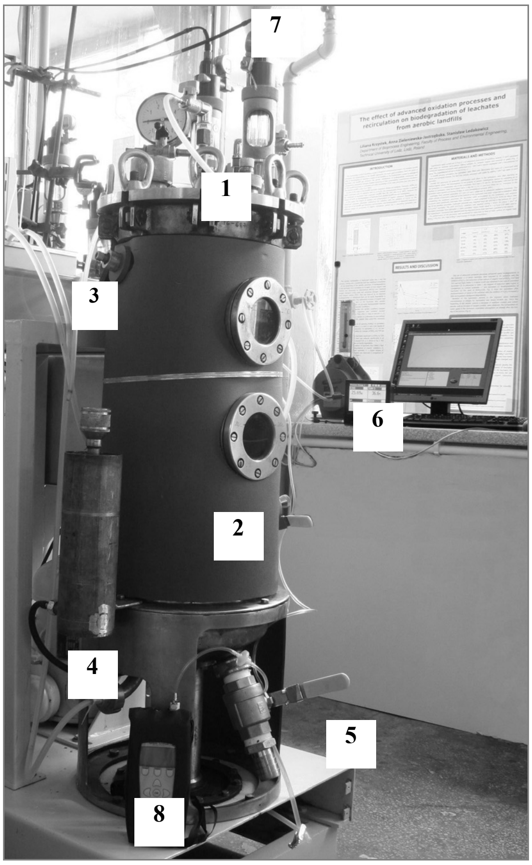

Fig. 1. Bioreactor scheme:
1 – stub pipe for pouring the fermentation broth, 2 – heating jacket, 3 – thermostating system,
4 – stirrer, 5 – valve for fermentation broth withdrawal; 6 – Biogas meter Ritter,
7 – Redox and pH electrodes, 8 – LMS Gas Data methane meter

Temperature was maintained to 37 °C by thermostating system. Inoculum was provided by the methane fermentation stage of Municipal Wastewater Treatment

Plant in Łódź, Poland. Cheese whey came from the biggest Polish diary "Mlekovita".

Feed influent was prepared daily. The mixture of two substrates (corn silage, whey) in specified weight ratio was fed manually to the digester once a day, after withdrawing the same amount of fermentation broth. The content of corn silage in the mixture was in the range of 10–30%. Every three days the ratio was changed in percentages until the highest yield of biogas and methane content as well as steady state were obtained.

At the same time experiment 2 was conducted. It was performed in order to check the effect of glycerin fraction daily feed on pH, gas production rate (GPR) and volatile fatty acids (VFA) concentration. The anaerobic digesters used in experiment 2 were constructed from two glass flasks with the liquid volume of 600 ml. The digesters were sealed with rubber stoppers containing an influent/effluent port to allow injection of feed. Biogas was collected by displacement of water. At the start, each digester was filled with 500 ml of biomass taken as an inoculum from the bioreactor operating in experiment 1. The temperature within digesters was maintained at 37 °C by immersion in water bath. The flasks were continuously shaken with 100 rpm. The digesters were operated with organic loading rate (OLR) of 0.18 and 0.36 g VS /dm^3 d and a hydraulic retention time of 17 and 8 days respectively.

The third experiment consisted in co-fermentation of three substrates (corn silage, whey, glycerin fraction) in the same bioreactor as in experiment 1. Glycerine fraction was provided by the biggest Polish "Trzebinia"Refinery. Now all three substrates were fed daily to the bioreactor. The content of glycerine fraction in the mixture was in the range of 4.5–9%. Every three days the ratio was changed in percentages until the highest yield of biogas and methane content as well as steady state were obtained.

The fourth experiment was also carried out in the bioreactor with the working volume of 25 dm^3, operated mesophically in semi-continuous mode at a hydraulic retention time (HRT) of 25 days. The feeding mode was determined basing on the previous experiments. The first day all three substrates in specified weight ratio were fed to the bioreactor (ORL = 3.02 VS/dm^3d), next two days only glycerin fraction (ORL = 1.43 VS/dm^3 d) was being added. Such three-day feeding cycle was repeated until the highest yield of biogas and methane content as well as steady state were obtained.

2.2. ANALYTICAL METHODS

Mixed samples were daily drawn from the bioreactor and measured to determine: continuously – biogas flow rate (flowmeter Ritter), pH (pH-meter electrode WTW pH 540 GLP), and once a day – biogas content (gas content analyzer LMS GAS DATA), total solids (TS), volatile solids (VS), volatile fatty acids (steam distillation – BÜCHI B-324), elemental content (C, H, N, S) of inoculum and individual experimental feeds, (Elemental Analyzer NA 2500, CE Instruments), chemical oxygen demand (COD) on centrifuged samples (Hach-Lange, method 435).

All analytical procedures were performed in accordance with Standard Methods (APHA–AWWA, 1992).

3. RESULTS AND DISCUSSION

To optimize the co-digested mixtures of three different substrates: corn silage, cheese whey and glycerine fraction in order to obtain maximum productivity of biogas of high methane content the four experiments were performed. Characteristics of these substrates are presented in table 1.

Table 1

Characteristics of substrates used in the experiments

Parameter	Corn silage	Whey	Glycerine fraction
pH	3.7	4.48	7.23
Total solids [%]	27.5	6.1	11
Volatile solids [%]	26.14	5.26	7.2
COD [g O_2/l]	376	66.7	–
Ash [%]	1.36	0.84	3.8
VFA [mg_{CH_3COOH}/dm^3]	1950	2220	1296
C:N ratio	60:1	21:1	25:1

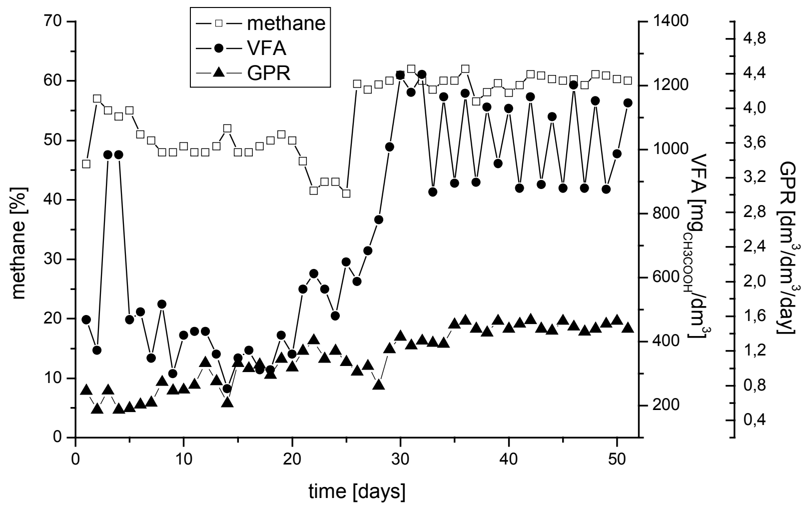

Fig. 2. Gas production rate (GPR), volatile fatty acids (VFA) concentration and methane content in experiment 1

In the first experiment co-digestion of two substrates: corn silage and whey was conducted. In figure 2 the changes of gas production rate (GPR), volatile fatty acids (VFA) concentration and methane content during this experiment are presented. Gas production rate (GPR) was expressed as the so-called space time yield: gas volume/reactor volume/time in dm^3/dm^3 per day. The biogas production rate at the beginning of this experiment was in range 0.5–1.12 dm^3/dm^3/day and methane content was less than 60%. At steady state conditions (measured parameters were not changing more than 10%) from 29th day, the GPR of 1.43 dm^3/dm^3/day and VFA of 1044 mg_{CH_3COOH}/dm^3 were obtained (on average). The methane content of digester biogas varied between 56% and 62%, with an average of 60,1%, figure 2. The main results corresponding to the steady state period are presented in table 2.

Table 2

Operational parameters for all experiments

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
HRT [days]	25	17	25	25
Operation days	1–51	1–6	1–19	1–51
GPR [dm^3/dm^3/day]	1.43*	0.47	1.12	1.82*
Methane content [%] VFA [mg_{CH_3COOH}/dm^3]	52* 1044*	51 1130	50.7 4817	61* 780*

*Mean value at steady state

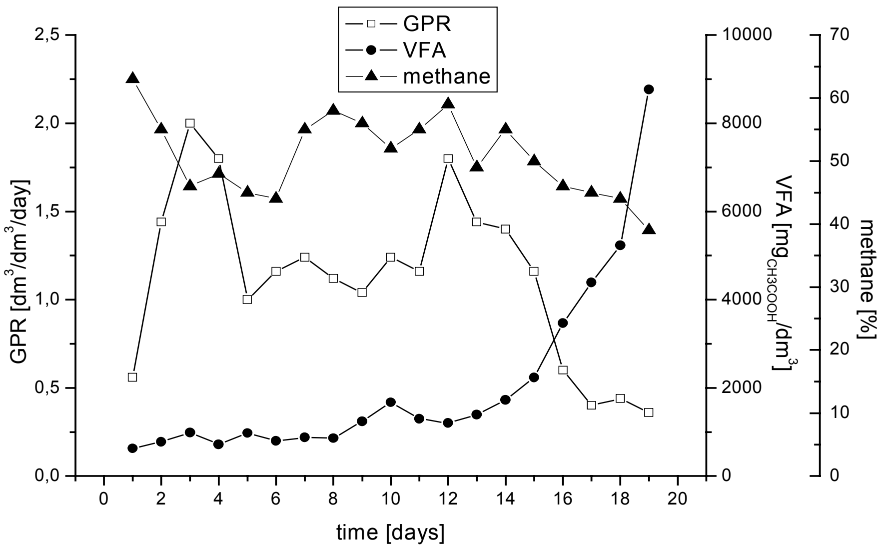

Fig. 3. Gas production rate (GPR), volatile fatty acids (VFA) concentration and methane content in experiment 3

In the third experiment there was the addition of the third substrate which was the glycerin fraction. Now, all three substrates (corn silage, whey and glycerin fraction) in specified weight ratio were fed to the bioreactor every day. The biogas production rate at the beginning of this experiment was in range 0.5–1.64 dm^3/dm^3/day. After 15[th] day the biogas production as well as methane concentration were steadily diminishing. The GPR decreased up to 0.36 dm^3/dm^3/day, while methane content up to 43%, figure 3. The low methane production rates may be contributed to the accumulation of VFA. The concentration of VFA started to increase considerably reaching nearly 9000 mg_{CH_3COOH}/dm^3, Fig. 3. It led to the failure of the digester.

At the same time experiment 2 was conducted in order to check the effect of glycerin fraction daily feed on pH, volatile fatty acids (VFA) concentration, methane content and gas production rate (GPR). The digester operated with organic loading rate (OLR) of 0.36 g VS/dm^3d and a hydraulic retention time of 8 days collapsed after three days as VFA concentration increased rapidly (data not shown). In the second digester operating with OLR of 0.18 g VS/dm^3d and a hydraulic retention time of 17 days VFA concentration increase accompanied by pH decrease was slower. However, the average GPR was 0.47 dm^3/dm^3/day, and methane content 51% (on average), figure 4.

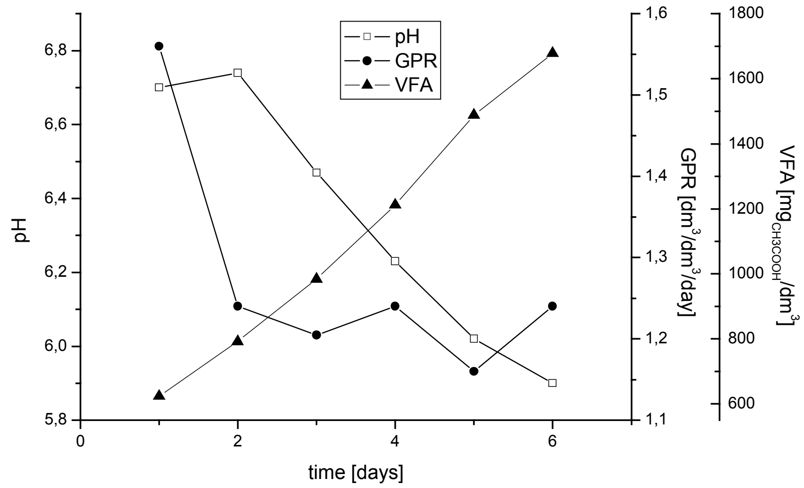

Fig. 4. Volatile fatty acids concentration (VFA), pH and gas production rate (GPR) in experiment 2

Basing on the previous experiments, showing that all three substrates cannot be fed together to the digester daily as the increase in concentration of VFA is considerable and methane content as well as GPR are not satisfactory, new feeding mode was determined.

In experiment 4 all three substrates (cheese whey, corn silage and glycerin fraction) in specified weight ratio started to be fed to the bioreactor (ORL = 3.02 VS/dm^{3}d), next two days only glycerin fraction (ORL = 1.43 VS/dm^{3}d) was being added.

The biogas production rate at the beginning of the experiment 4 was in range 0.98–1.5 dm^3/dm^3/day. During the next days it was steadily increasing reaching 1.56–2.16 dm^3/dm^3 per day, figure 5. Every third day when all three substrates were fed to the digester the GPR is considerably higher in comparison to GPR when only single glycerin fraction was fed.

Comparing the experiments 1 and 4, the addition of the glycerin substrate and the change of experimental mode lowered VFA concentrations from 780–1200 mg$_{CH_3COOH}$/dm^3 to the range of 400–920 mg$_{CH_3COOH}$/dm^3. In experiment 4, concentration of VFA was less than 1000 mg$_{CH_3COOH}$/dm^3, indicating high stability of the bioreactor, which was confirmed by the presence of steady profiles of pH of the reactor, figures 2 and 5.

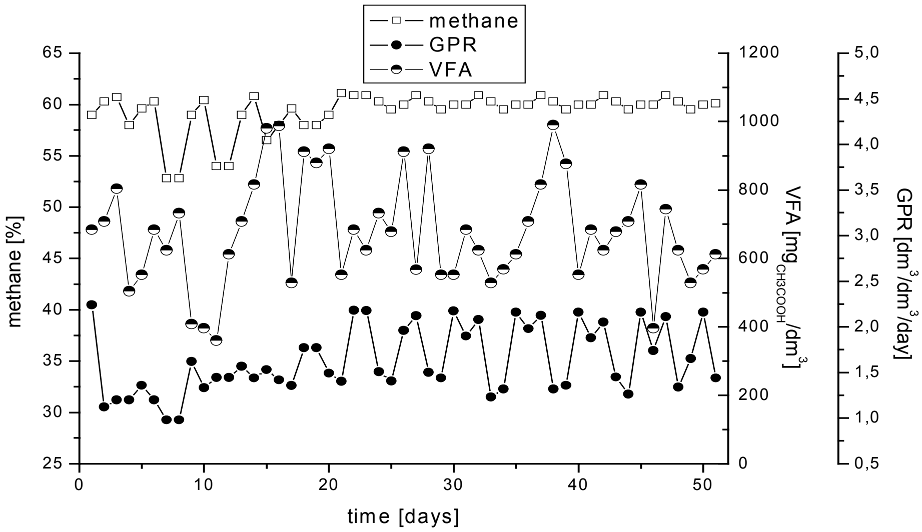

Fig. 5. Gas production rate (GPR), volatile fatty acids (VFA) concentration and methane content in experiment 4

The addition of glycerin fraction changed the biogas yields. This is consistent with literature data of AMON et al. (2006) and JINGXING MA et al. (2008) who found that supplementation of glycerine fraction always resulted in an increase in CH_4 production. Biogas yield with reference to the quantity of removed COD, TS, VS is presented in table 3. COD reduction was doubled from 16% to 32%. Biogas yield increased from 1.64 to 2.04 dm^3/g TS removed as well as from 0.22 to 0.42 dm^3/g COD fed. The steady profile was achieved in the 25th day of the experiment.

Table 3

Biogas yield and COD reduction during experiments

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Biogas yield [dm^3/g COD removed]	1.37	1.2	2.28	1.42
Biogas yield [dm^3/g TS removed]	1.64	–	0.74	2.04
Biogas yield [dm^3/g VS removed]	2.19	–	0.65	1.73
Biogas yield [dm^3/g COD fed]	0.22	0.24	0.27	0.42
Biogas yield [dm^3/g TS fed]	0.06	–	0.04	0.08
Biogas yield [dm^3/g VS fed]	0.08	–	0.08	0.14
COD reduction [%]	16	20	11.8	32

The optimal substrates combination allowed to obtain high productivity of methane-rich biogas reaching 35–55 dm^3/day with methane content being 60–62%.

Previous studies, however reported no optimization of co-digested substrates, they were mainly based on methane potential determination. The methane yields obtained in the present study in the co-digestion of given substrates were of the same order of magnitude as those reported by GHALY (1996) who obtained 0.05–0.25 dm^3/g VS fed.

A semi-continuous co-digestion process using cheese whey, corn silage and glycerin fraction can be expected to result in effective production of methane-rich biogas.

4. CONCLUSIONS

The optimal substrates combination was determined in order to obtain maximum productivity of methane rich biogas. Corn silage, whey and glycerin fraction were co-digested in semi-continuous mode in 25 dm^3 mesophically operated bioreactor.

The experiments proved that anaerobic co-digestion of agricultural and dairy wastes seems to be an attractive method for energy production and the glycerin fraction improves the biogas yields. In the conducted experiments methane content of the biogas was steadily increased and reached the highest concentration of 60–62% when the optimum substrate combination was fed to the bioreactor. The biogas production rate was successfully increased from 1.43 dm^3/dm^3/day in experiment with corn silage and whey to 1.82 dm^3/dm^3/day when three substrates corn silage, whey and glycerin fraction were digested, and, the daily amount of produced biogas from 33 to 55dm^3. For the optimum two-substrate combination and process conditions COD reduction was 16%, which was doubled in co-digestion with the third substrate. Significant increase in biogas yields was also observed.

Due to some new environmental protection acts which promote the recycling of wastes and their utilization for renewable energy formation all obtained results can serve as a base for process biogas production from energy plants and biodegradable wastes by methane fermentation methods on an industrial scale.

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