

Exploitation of anaerobic fermentation of bio-degradable wastes

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Abstract

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The paper deals with assessment of biogas yield from mixtures of *Reynoutria* substrates and livestock manure. The aim was to perform laboratory experiments and suggest suitable fermenter operating conditions (dry matter content, pH, share of substrate components, thermic regime) for metanogenic digestion, then to determine its quality and assess the usability of such produced biogas.

Keywords: biogas; biogas station; renewable energy resources; combined heat and power period

As the existing sources of fossil fuel are exhaustible, it is necessary to replace them as far as possible by renewable and alternative resources of energy, such as biogas (TRNOBRANSKÝ 1998). It can realistically be anticipated that world prices of fossil fuel will increase. It has been stated that whereas the three first crude oil crises were caused by wars taking place near crude oil fields, the last crisis was fully due to excess of demand over supply. People have already used one half of crude oil resources, and at the present (or even increasing) rate of exploitation the supplies will be exhausted within 30 years (VÁŇA 2001).

When dealing with the problem of power-producing exploitation of bio-wastes one has to start from economic aspect: which are determining factors in this case; but also to take into account ecology aspects in order not to impose additional burdens on environment. The energy problem of greenhouse effect that the world population is facing does not merely consist in the question what type of power stations

should be built (whether for fossil fuel or for nuclear fuel) but in the fact that it is impossible to further release any type of energy for power or heat production, transport etc., because heat emissions from human activities have already exceeded tolerable limits in some regions. People will inevitably have to learn to live more economically and to use annually worldwide about 10^{15} to 10^{16} kWh from clean and safe energy sources, and also annually obtain 10^{16} kWh directly from solar energy (CENKA 2001).

Although the exploitation of bio-wastes for power production also has its seamier side, it is impossible not to make use of this possibility to solve the energy problems at least partially, particularly in regions where there have been created corresponding conditions for it. The development of utilisation of bio-wastes for power production fully agrees with “Czech energy policy”. Bio-wastes are processed in fermentation reactors to produce biogas, which also restricts some negative properties of the excrements and thus increases their quality.

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The principle of biogas production has been known since the 19th century and has been sufficiently proved in the 20th century in the area of municipal sewage plants (HAŠ et al. 1985).

One of the first technological devices for sludge stabilisation was put into operation in France in 1881: in principle it consisted in a digestion and sedimentation tank (nowadays called a cesspit). Equipment for purification of municipal sewage water was constructed in England in 1891. This appliance consisted of a tank with horizontal metal grid carrying a layer of pebbles in the middle; the sewage water was introduced into the lower part of the tank, where the sludge sedimented and the water moved up wards and passed through the pebble layer, which operated as a filter. The sludge was periodically removed from the bottom of the tank, and biogas was then released from it spontaneously in a non-controlled process.

A turning point in development came in 1924, when an independent anaerobic purifying tank was constructed in Germany: in this case the sludge was warmed by means of burning the released biogas.

In following years, these technologies undergone a number of improvements and valuable experience was obtained from their operation. Gradually, this technology of biogas production was introduced into the area of processing of excrements of livestock. Nowadays it is intended to utilise anaerobic digestion also for treatment of domestic biodegradable wastes.

Within the context of biogas production and entrapping, biogas began being exploited not only for the process of septicization in itself, but also to be burnt in cogeneration units where electricity and heat are produced. Facilities based on phosphoric acid electrolyte fuel cells (PC25C) pose the most recent innovation.

One of the main reasons for recent emphasizing of the renewable energy sources is the reduction in greenhouse gases (e.g. water vapor, methane, carbon dioxide etc.).

Thermal conversion processes (e.g. combustion, gasification and pyrolysis) prevail during utilization of biomass for energetic purposes, but anaerobic digestion related to the production of biogas and organic fertilizers becomes increasingly applied.

The process of biomass anaerobic digestion shows quite a few of environmental advantages and it is recognised as one of the technologies contributing to the sustainable development of mankind.

Besides animal faeces, biogas stations can also treat scraps from crop and greengrocery production

and processing, waste from slaughterhouse, dairy, fat, tanning and pharmaceutical industries, residues from biodiesel and ethanol fuel production, scraps from greenery maintenance and biodegradable part of separately collected municipal waste. Biogas can be also easily gained from anaerobic sludge stabilization and from compost degassing.

Biogas is a product of anaerobic microbial biodegradation – anaerobic digestion. This process develops either spontaneously in the nature under certain circumstances, unaffected by human factor, or in special-purpose technological processes. Water presence is a precondition of anaerobic digestion and any processed material must contain sufficient amount of biodegradable substances. The engineering solution depends on the input material consistency – it is different for suspensions and dilutions (dry matter content up to 18–20%) and for solid scrapable substances (dry matter content 20–40%).

Biogas is a gas mixture usually comprising 50–75% of methane (CH_4), 30–45% of carbon dioxide and 1 to 3% of minority gases (e.g. nitrogen – N_2 , hydrogen sulfide – H_2S , hydrogen – H_2). Water vapor (H_2O) is a variable component part of biogas. The calorific value of biogas ranges between 18 and 25 MJ/m^3 , whereas if purified to the extent that nearly absolute methane remains (with the calorific value of 35.8 MJ/m^3), biogas can be used as a substitution for natural gas (which usually comprises 99.9% of methane) (JONÁŠ, PETŘÍKOVÁ 1988).

MATERIAL AND METHODS

Production of wastes in starch factories

Starch factories virtually produce three types of wastes: tuber juice (from separation of starch grains), crushing cakes i.e. extracted residues of ground potatoes, and washing waters (white tuber juice).

The tuber juice is composed of soluble components of potato tubers and water (sometimes it is denoted as potato juice or brown tuber water). The extraction technological water from separators of starch grains is called white tuber water. The produced tuber juices are rich in mineral substances and their composition is suitable for fertilising of some farming crops. The density of tuber juice is ca. 1,106 kg/m^3 (the interval is from 1,084 kg/m^3 to 1,134 kg/m^3). From among organic acids, the juice contains citric acid $\text{C}_6\text{H}_8\text{O}_7$ (0.1–0.55%, freshly harvested potatoes up to 1%), oxalic acid $\text{C}_2\text{H}_2\text{O}_4$

(0.017–0.058%), and malic acid. The overall titratable acidity of the juice corresponds to 250–700 ml N-NaOH per 100 g; its pH value varies within the limits of 5.76–6.56 (NORDBERG 1996). At present, the tuber juices are used as fertilizers. The crushing cakes are used as feed for pigs, and with regard to this fact, real starch factory wastes that can be used for biogas production are the two liquid wastes: brown and white tuber juices (waste water from starch separators). Both these liquid wastes were submitted to laboratory tests.

The sludge water produced in the rinsing circuit and a part of technological water from starch production, especially rinsing waters, are led to municipal Waste Water Treatment Plant (WWTP).

If we take into account the chemical composition and mechanical properties of tuber juice for potential exploitation in a biogas station, such application presents no problems and is desirable. This liquid is well pump able and not especially active. Similarly problem less application can be expected in the case of white tuber juice. The sludge waters are problematic due to considerable content of clay and sand. Therefore, before their potential exploitation in biogas station they have to be rid of these components.

Reynoutria species is an invasive plant, whose invasion ability is based, first of all, on easy regeneration from rhizomes and fragments of stalks, the considerable amount of aerial biomass that is produced by this plant, massive root system, and probably also on the observed allelopathia. It particularly colonizes sites affected by man (settlements, communications, disposal sites etc.) and vicinity of larger water-courses. Another problem connected with this plant lies in the fact that it is difficult to liquidate.

At its habitat it gradually creates its monoculture, which results in a biodiversity decrease. It can be especially harmful in protected zones, but it is no less unwelcome in open countryside. The main problem connected with this plant lies in its negative effect upon neighbouring vegetation; that considerably complicates its exploitation for biogas production. For its use in biogas station it has to be pre-crushed.

Procedure of measurements

The aim was to find out the maximum amount of the methane or biogas produced per one mass unit of the material examined $\rightarrow Y_{CH_4,S}, Y_{BP,S}$ (l/g, m³/kg)

($S = CHSK$ [chemical oxygen consumption], or V_L). The mass percentage of dry matter content, from the total content of sample in the case of mixing of substrates, was 5% or 8% of dry matter content in the sample. The laboratory fermenters used were charged with materials containing the dry matter. The resulting biogas production was always related to 1 kg of total dry matter content of the sample.

The measuring vessels were charged with a known amount of inoculum and a defined medium containing buffer, macro- and micro-nutrients (N, P, Fe, Co, Ni etc.). This medium prevents the deficit of nutrients to become a limiting factor in the measurements. The mixture was bubbled through with nitrogen in order to fill with nitrogen the gas volume above the level and was left to stand several hours to stabilise and adjust the required temperature. The last component that was added to this mixture was the substance investigated – the only source of carbon for the anaerobic culture present; before the addition, the temperature of this component was adjusted at the value of cultivation, and the moment of its addition (connected with equilibrating of the pressure in the vessel with atmospheric pressure) was recorded as the start of measurement. The total volume of liquid phase is then $-V_L$.

The experimental conditions adjusted in all the runs were the same. The tested substrates were cultivated in the fermenters at a constant temperature of 42°C (mesophilic region) and the content was discontinuously stirred. For comparison, other fermenters were also kept at the temperatures of 46°C and 55°C (thermophilic region). At definite time intervals, the biogas produced was measured (once per 24 h) by means of a gas analyzer AIR LF, and volume was read at the scale on gas-holder sides. The measurement results always represented an average value from all the fermenters. If necessary, the quality of biogas was checked by chromatographic analysis of gas phase, which is very important, because CO₂ and H₂ are formed in the pre-methanogenesis phase if, of course, the methanogenesis phase is inhibited or blocked.

The measurement was finished when the substrate production of gas was constant – when it stopped increasing with time, i.e. the efficiency of decomposition at the given conditions was at the maximum.

The yield of biogas $-Y_{BP}$ is calculated from the substrate production of biogas $-V_{BP,S}$ (volume difference between total and endogenic production

of biogas), divided by the initial amount of added substrate – S.

$$Y_{BP} = \frac{(V_{BPc} - V_{BPe})}{S} = \frac{V_{BP}S}{S} \quad (\text{l/g, m}^3/\text{kg}) \quad (1)$$

Measuring instruments used

- Gas analyzer AIR LF. The instrument allows determination of CH₄, O₂, CO₂ content, and – as the case may be – also CO and H₂S content in biogas.
- Measuring centre THERM 3280 – 8M. It allows measurement of 10 quantities, temperature, humidity etc. with intensity or voltage input.
- Pressure difference gauge Digima LPU. It allows measurement of pressure differences in the range of 1–5,000 Pa. The instrument was used for pressure measurements in digesting fermenters and gas pipes.
- Polarograph Tribio II – 2. In the course of measurements, it was used for determination of content of trace elements in the substrate.
- Laboratory oven was used for determination of dry matter content of samples and for preparation of samples before further analyses.
- Gas chromatograph Chrom 5 was used for general analyses of samples. The apparatus KJELTEC SYSTEM Tecator is designed for thermo-chemi-

cal mineralization, extraction and distillation for determination of N by physico-chemical measuring methods.

- Spectral colorimeter SPEKOL. The instrument was used for physico-chemical measuring methods determining the P and K content in biomass.

RESULTS AND DISCUSSION

Evaluation of the values measured

Real waste products for biogas production that can be obtained from starch factories are the tuber juice (waste from ground potatoes production) and white tuber water (waste water from starch separators). Both these materials were submitted to laboratory for investigation. Furthermore for comparison, measurements were carried out with *Reynoutria* species, which appears to be a controversial crop: it exhibits an excellent yield of biomass (30–50 t/ha).

During both experiments of biogasification in small fermenters of 3-litres volume, reactor 1f served for control purposes, charged with no additive substance (0%). In biological experiments, control sample outputs serve as a reference, by which means possible negative influences (like undesirable contamination, inconsistent temperature conditions, inferior inoculum etc.) can be estimat-

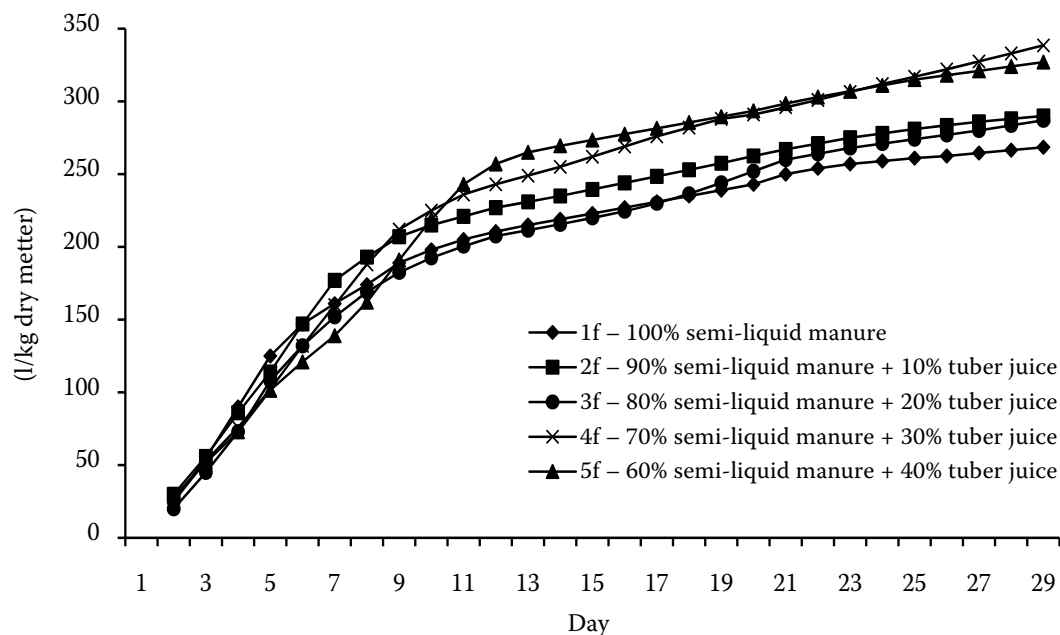


Fig. 1. Cumulative production of biogas (fermenters of 3-litre volume); tuber juice

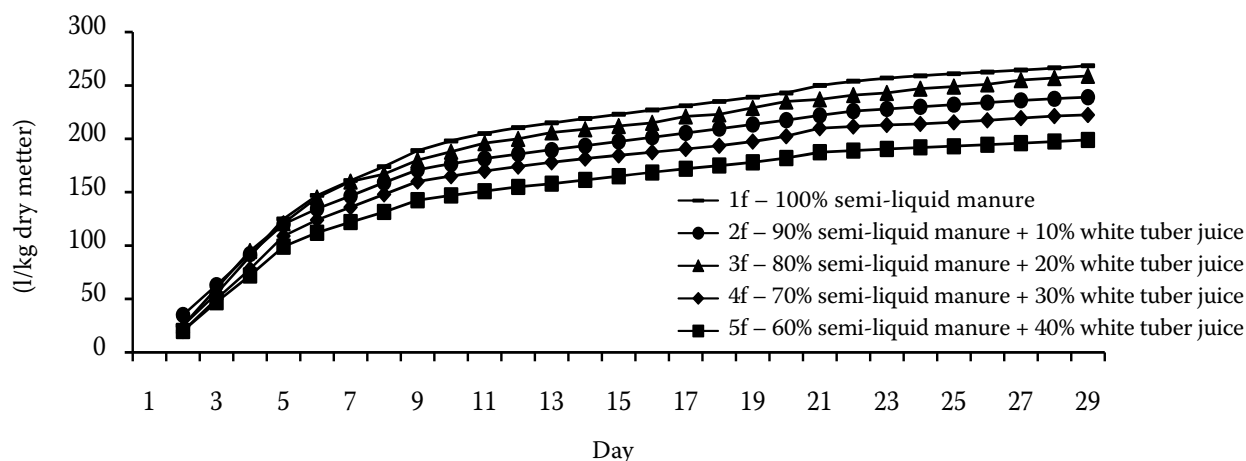


Fig. 2. Cumulative production of biogas (fermenters of 3-litre volume); white tuber water

ed during the course of experiment. Biogas production was measured daily, however cumulative production is shown for each experiment for clear interpretation.

Biogas production in small fermenters was slightly higher with tuber juice (in average 300 l/kg of dry matter, Fig. 1) than with white tuber water (in average 220 l/kg of dry matter, Fig. 2). The course of biogas production is identical for all charges containing 10–40% of additive substance. There were differences in the second stage only (after the 8th day of anaerobic decomposition), characterized by lower cumulative biogas production, when the concentration of individual charges differed by approximately 20 l/kg of dry matter.

In large fermenters, the biogas production from these two sources was comparable, ca. 200 l/kg of

dry matter, Fig. 3 (both the large fermenters operated in mesophilic region at 46°C); exact values of biogas production were 217 l/kg of dry matter from tuber juice and 190 l/kg of dry matter from white tuber water.

In the initial stage of first eight days, the sample charged with white tuber water and placed in a 100-litres fermenter shows higher biogas production than the sample charged with tuber juice. Nevertheless, in the following stage the sample charged with white tuber water already lagged behind the other one in terms of biogas production. The initial stage of anaerobic decomposition is usually characterized by lower volume of methane in the biogas produced.

The energy value of biogas is expressed by the methane content. The volume percentage of meth-

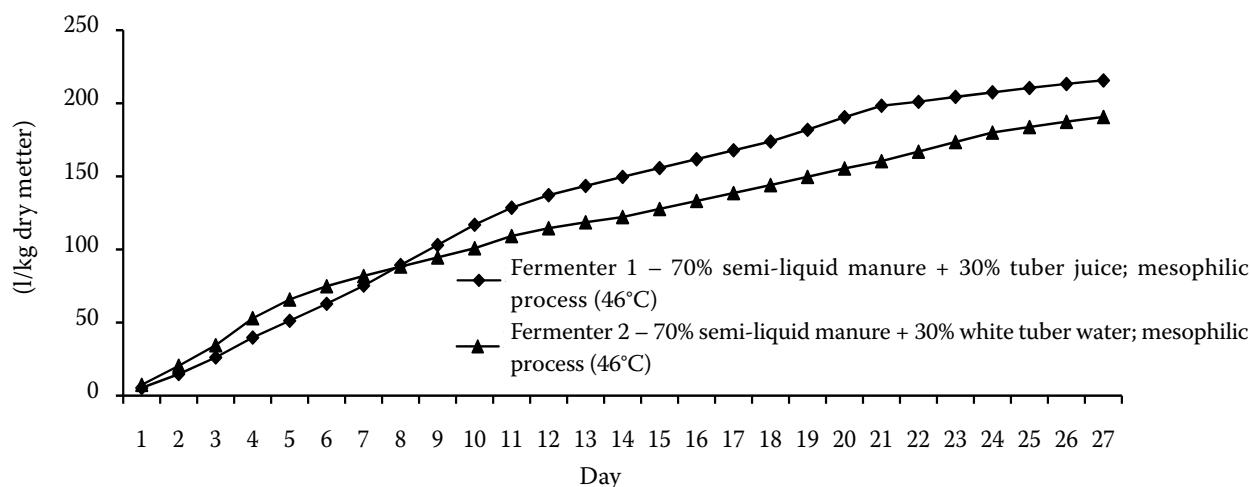


Fig. 3. Cumulative production of biogas (fermenters of 100-litre volume)

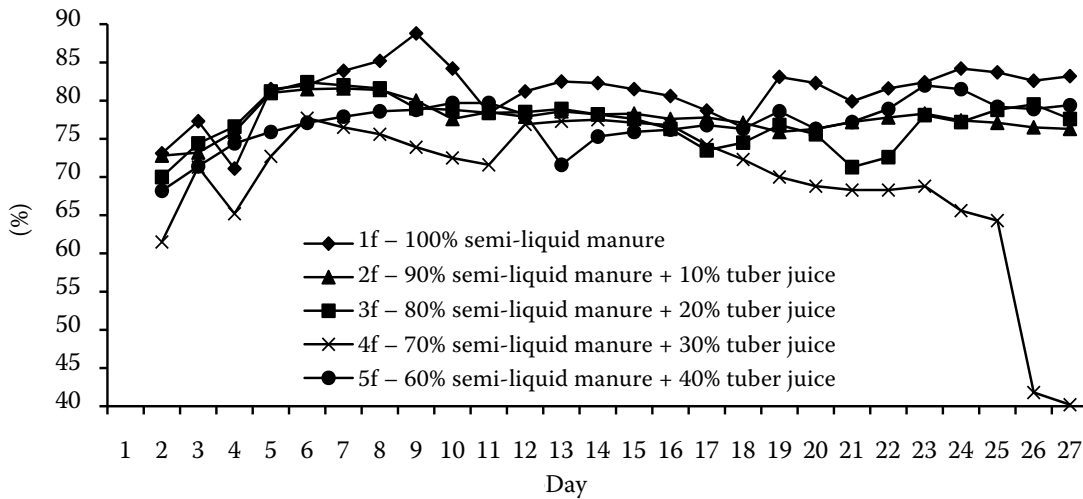


Fig. 4. Amounts of CH₄ in biogas (fermenters of 3-litre volume); tuber juice

ane determines the calorific value of a biogas and it is one of the main criteria for the composition of a charge. The methane part by volume for the experiment with 3-litre fermenters and tuber juice is shown in the Fig. 4, the data for white tuber water experiment are shown in Fig. 5. The rest of percentage is mostly carbon dioxide content, water vapour, oxygen and sulfane can be also present in small amount.

The composition of biogas was very similar with all the samples, for both tuber juice and white tuber water, both small and large fermenters. The meth-

ane content in produced biogas settled down in the 70–80% range with all the samples, the peak values approaching up to the limit of 90%. The production of biogas from starch industry waste was again approximately 30% higher with smaller fermenters used, comparing to the usage of larger fermenters; this can be explained by better temperature stability of small fermenters, for whole filling and during all the retention time. The natural energy was satisfactory for all measured mass portions of starch industry waste. The charge containing 40% of tu-

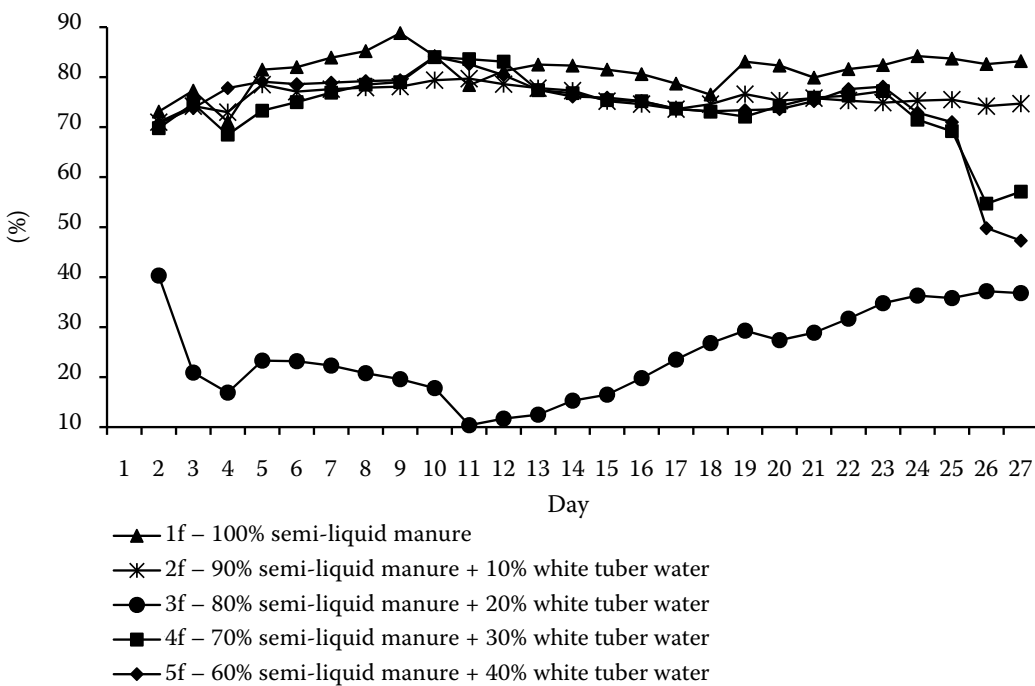


Fig. 5. Amounts of CH₄ in biogas (fermenters of 3-litre volume); white tuber water

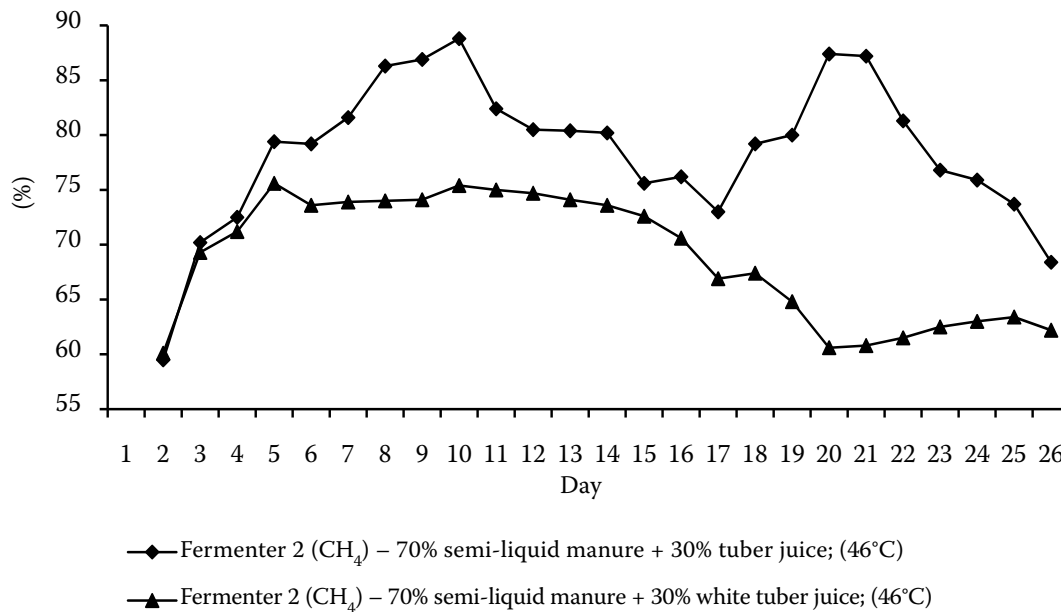


Fig. 6. Amounts of CH₄ in biogas (fermenters of 100-litre volume)

ber juice showed very low concentration of methane in the second stage, which can be explained by anaerobic conditions disturbance in the reactor. The same occurred during the experiment of white tuber water charge (3-litre fermenters); again the charge with 40% white tuber water content showed very low methane concentration in the second stage of experiment. However the anaerobic conditions disturbance occurred no earlier than by the end of so-called impediment period.

According to results of the measurements, the optimum yields were obtained with the ratio of 70% semi-liquid manure + 30% tuber juice (white tuber water). The results gained with such mixtures were satisfactory both in terms of produced biogas volume and rapid production increase in the initial stage. The amount of CH₄ obtained with this ratio was very stable, varying slightly about 80% throughout the measurement period. The result of measurements in small 3-litre fermenters was used

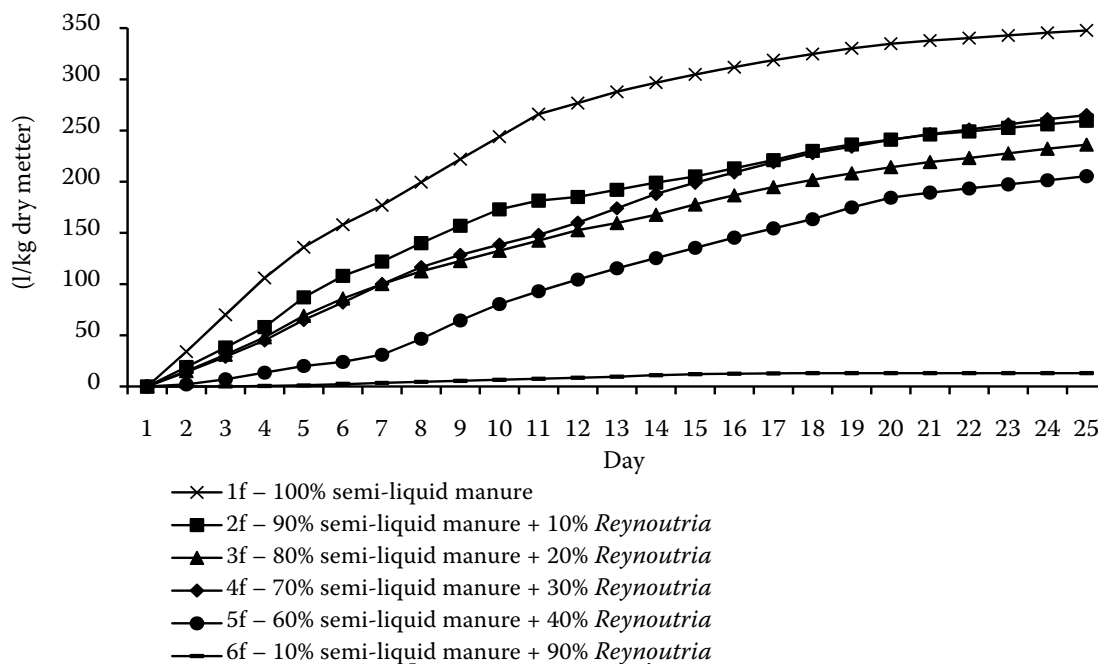


Fig. 7. Cumulative production of biogas (fermenters of 3-litre volume); *Reynoutria*

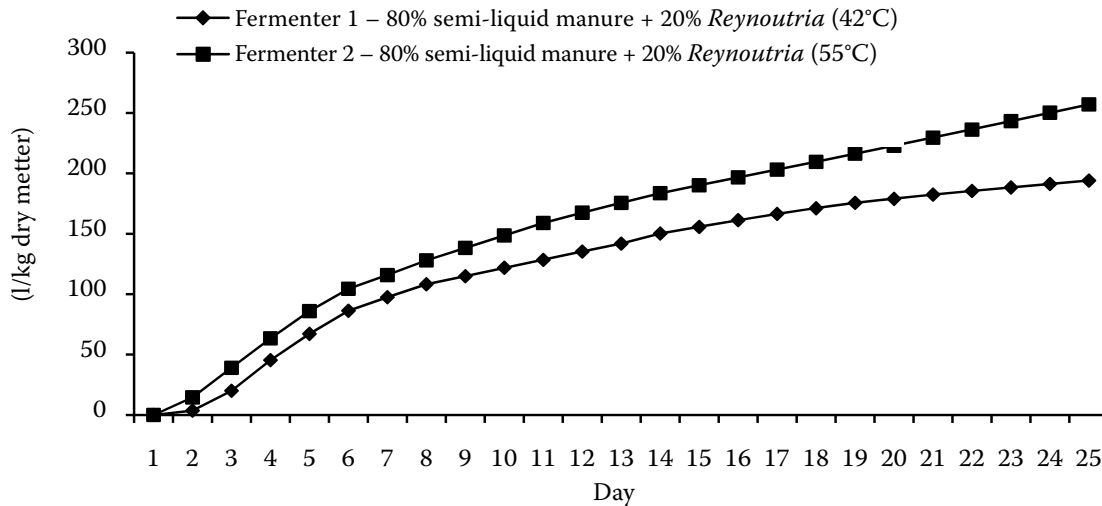


Fig. 8. Cumulative production of biogas (fermenters of 100-litre volume); *Reynoutria*

as the base for further experiment in large 100-litre reactors. The charges containing tuber juice as additive material showed higher methane concentration in biogas and better stability during all the impediment period, even in the experiment with 100-liter fermenters used (Fig. 6).

As evident from the diagram in Fig. 7, the course of biogas production for *Reynoutria* charges with additive material was basically identical. Some small differences were in steepness of the initial stage. Charges with content of 10%, 20% and 30% of *Reynoutria* as an additive material showed faster increase of production than charges with higher *Reynoutria* content. The charge with 90% *Reynoutria* content did not show satisfactory results of biogas production. This

composition cannot be recommended for further applications unless some adjustments of composition or anaerobic digestion conditions are done.

The highest cumulative biogas production was achieved with charge containing 20% of *Reynoutria* (260 l/kg of dry matter). The optimal-appearing *Reynoutria* concentrations from measurements performed in small 3-litre fermenters were used as reference samples for experiments with large 100-litre fermenters (Fig. 8). The large fermenters were run at 42°C (mesophilic range) and 55°C (thermophilic range) for comparison. The charge treated in thermophilic mode of fermentation showed both steeper increase and higher cumulative biogas production, comparing to the charge in mesophilic range.

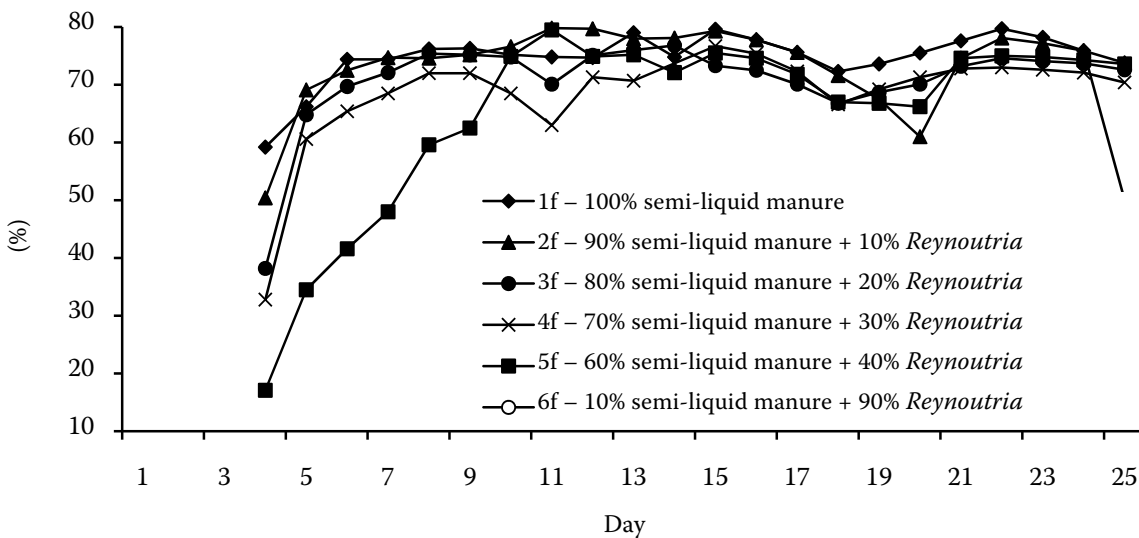


Fig. 9. Amounts of CH₄ in biogas (fermenters of 3-litre volume); *Reynoutria*

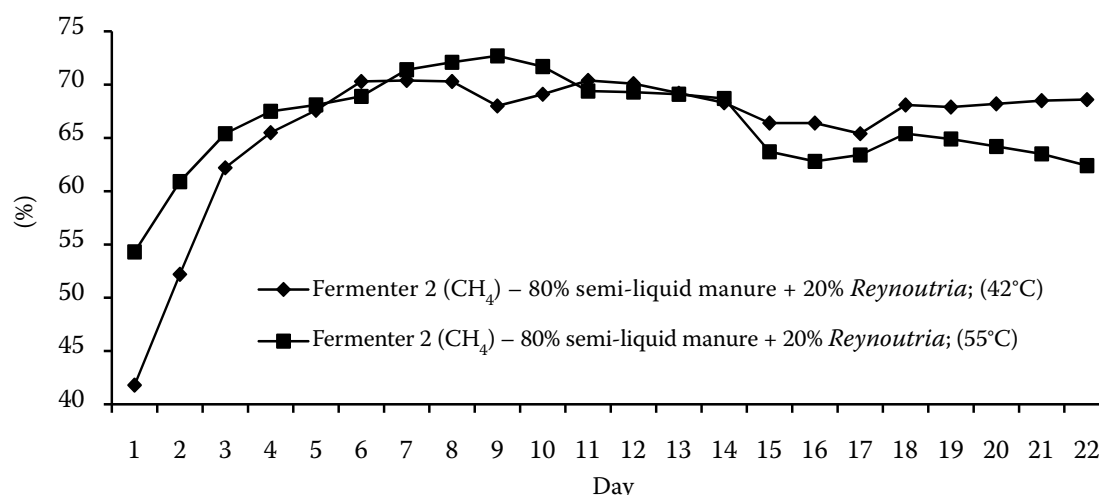


Fig. 10. Amounts of CH₄ in biogas (fermenters of 100-litre volume); *Reynoutria*

After recalculation, the biogas production from 1 kg substrate with added *Reynoutria* is lower than that from semi-liquid manure alone; however, the CH₄ content throughout the stabilised phase of digestion varies around 80% in small fermenters (Fig. 9), and around 70% in large fermenters (Fig. 10). Hence, the methane production is practically the same as that from semi-liquid manure (Fig. 10), which could be interesting from the standpoint of energy production from *Reynoutria*. Only one ratio, i.e. 10% semi-liquid manure + 90% *Reynoutria*, showed virtually no biogas production.

CONCLUSION

The aim of this research was to find out which of the selected ratios of semi-liquid manure and substrates is the optimum for a biogas station and also economically feasible. The procedure in which wastes from animal farming are supplemented with other types of bio-wastes in a certain ratio can lead to the optimum conditions for the course of fermentation process. Our measurements have shown that the optimum ratio for mixing tuber juice or white tuber water with semi-liquid manure from beef cattle is 40% of tuber juice and 60% of the said manure. In the experiments with *Reynoutria* the ratio is 30% *Reynoutria* and 70% semi-liquid manure.

Moreover, it was important to choose the optimum amount of dry matter and to know the suitable pH value of the mixture. For all the measurements carried out the selected dry matter content was 8% with regard to usual standard used both in this country

and abroad. Since it is presumed that the measured mixture will turn slightly sour during the digestion, the adjusted value was pH 8. Last but not least, it was also necessary by measurements to find out what temperature will be suitable for the maximum yield of biogas. Small fermenters were cultivated at a constant temperature of 42°C, the large ones at the temperatures of 46°C and 55°C. The experiments have shown unambiguously that the biogas production is higher in small fermenters operating in mesophilic process. This is certainly an advantage for a biogas station with year-round operation.

Mostly, the optimum retention time is correctly determined only after performing a test run and determination of behaviour of a concrete amount of mixture. Our measurements indicate the retention time of 23–25 days to be the optimum.

Economically, the operation of biogas production is calculated from acquisition costs and the yields, which depend first of all on the production and the ability to utilise the energy. The lifetime of a biogas station is specified as 14–16 years according to the present depreciation rate. Our calculations have shown that, without initial ca. 40% financial support for acquisition costs, biogas stations might not operate with proper profit. All depends upon the ability to economically exploit also side products from biogas production.

In conclusion it can be stated that fermentation processes open quite new possibilities for agriculture or food processing industry, namely by exploitation of biogas as well as by offering services, which is why new sources of income from new forms of organisation are involved.

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