

TESTING OF CO-FERMENTATION OF POULTRY MANURE AND CORN SILAGE

Andrzej JEĐRCZAK¹, Dariusz KRÓLIK^{1,1}, Zofia SADECKA¹,
Sylwia MYSZOGRAJ¹, Monika SUCHOWSKA-KISIELEWICZ¹,
Jacek BOJARSKI²

¹ University of Zielona Gora, Institute of Environmental Engineering, Poland

² University of Zielona Góra, Department of Mathematical Statistics
and Econometrics, Poland

Abstract

The development of the production of poultry meat is connected with an increase in the quantity of the manure. The chemical characteristics predisposes this waste to processing by methane fermentation method. This study investigated the influence of ammonia and volatile fat acids on mesophilic anaerobic digestion of poultry manure. The aim of the studies was: to determine the degree of biodegradation of the poultry manure as well as manure and corn silage mixed in various proportions in the process of mesophilic fermentation, to evaluate the impact of mineral nitrogen and volatile fat acids on the course of fermentation, and to establish optimum proportions of these types of waste. The tests confirmed the positive effect of co-fermentation of poultry manure with corn silage. The most favourable ratio for mixing the substrates is the equal percentage of their dry matter in the mixture. With such waste mixing proportions, the degree of degradation of organic substances contained in the manure amounted to 61.8% and was higher than in the mono-digestion of manure and corn silage.

Keywords: methan, digestion, poultry manure, corn silage, ammonia nitrogen, testing

¹ Corresponding author: University of Zielona Gora, Institute of Environmental Engineering,
Szafrana st 15, 65-516 Zielona Gora, Poland, e-mail: d.królik@iis.uz.zgora.pl, tel.+48683282612

1. INTRODUCTION

The development of the production of poultry meat is connected with an increase in the quantity of the manure produced. The yearly production of poultry droppings in the member states of the EU is estimated at about 113,000,000 tonnes, of which almost 10% is produced in Poland [7].

It is commonly believed that manure is a "natural" side material, which could be used for the purpose of fertilisation. The use of manure for fertilisation can, however, be a great problem for poultry farms with a great concentration of stock. The statutorily permissible nitrogen dose is 170 kg/ha of arable land. Therefore, depending on the nitrogen content in poultry manure, the acreage demand for a farm with a stock of 100 000 laying hens ranges from 350 to 600 ha [24]. Many poultry farms do not have the tillage acreage required by the law, which is connected with the problem of looking for recipients - farmers or companies dealing with manure processing, and forces out the development of alternative management methods [7]. The possible negative effects of unprocessed manure on the quality of underground and surface water (emission of nitrogen and phosphorus), air pollution (emission of odours) and climatic conditions also constitute important problems [5].

The composition of manure depends on such factors as: weight and age of the bird, poultry breeding system, used fodder and quantity of provided water. Table 1 shows literature data of chosen chemical parameters and biogas production of the corn silage and poultry manure [6, 9, 10, 12, 13, 17]. Hens produce from 0.06 to 0.18 kg of manure every day including adult hens - 0.15-0.16 kg of litter and broilers - on average 0.065 kg/day. The share of dry matter in the following types of poultry manure: fresh and humid litter - 12-20%, litter stored for a period of one month - 20-27%, and in the dried litter 27-40%. The artificially dried litter contains 85-95% of dry matter, and litter with bedding - 40-90% of dry matter [6].

The great hydration and high content of biodegradable organic matter, higher than in the droppings of other animals (broilers) [4], predisposes this waste to processing by means of the methane fermentation method.

The application of fermentation for manure processing is beneficial, as it allows both renewable energy and organic fertilizers (biogas and fermentate) to be produced in a way that is safe for humans and the environment, and is also compliant with the "OECD Green Growth Strategy". As part of this strategy, the Danish government has adopted a document in which it sets the processing of 50% of the fertilizers' quantity in the year 2020 as its objective (www.mst.dk). Similar actions have been taken by several other member states including Poland. On July 13th, the Polish government adopted the following

strategy “Directions for the development of agricultural biogas plants in Poland in 2010-2020.” the plan provides for the construction of one biogas plant on average, in each commune where the conditions are appropriate, with a power of 1 MW. In practice, this means the construction of about 2,000 such plants with a total power of 2.000 MW.

Table 1. Characteristics of the corn silage and poultry manure

| Indicator | Units | Corn silage | Poultry litter |
|--------------------------------|---------------------------|-------------|----------------|
| Litter mass from 1 piece/day | kg | - | 0.06-0.18 |
| Litter quantity from 1 DJP/day | kg | - | 25-45.4 |
| Water content | % | 65-80 | 68-90 |
| Content of volatile substances | % d.m. | 85-95 | 57-80 |
| Nitrogen content | % d.m. | 1.1-2.0 | 3.2-7.2 |
| NH ₄ content | % d.m. | 0.15-0.3 | 0.39 |
| Phosphorus content | % d.m. | 0.46-0.69 | 3.2-6.7 |
| Potassium content | % d.m. | 0.16 | 1.4-3.8 |
| C/N quotient | | 10-25 | 3-10 |
| Biogas production | m ³ /Mg | 0.17-0.20 | 70-90 |
| Biogas production | m ³ /kg o.d.m. | 0.45-0.70 | 0.25-0.60 |
| Methane content in gas | % | 50-55 | 60 |

Chicken manure is rich in organic nitrogen [11]. The high content of nitrogen in connection with the high biodegradability of organic matter may cause a decrease in the efficiency of the fermentation process, caused by ammonia accumulation [4, 15].

Webb and Hawkes [26] studied the mesophilic fermentation of poultry droppings suspensions with dry matter content of 1, 2, 4, 6, 7 and 10% for the times of 29.2 and 14.2 of day on the laboratory scale. They obtained the maximum biogas efficiency (0.41-0.44 m³/kg d.m.) for the raw material with the content of 4-6% d.m. With higher concentrations of solids in the input, the efficiency decreased even by about 10% in comparison with the maximum value. The reason for this was an increase in the concentration of ammonia nitrogen up to the level of 4253 mg/dm³ and free ammonia up to 435 mg/dm³. The mean methane concentration in biogas was 58.6%. The high efficiency of fermentation in the laboratory studies of the poultry dropping suspension with the content of 5.0% of d. m. was confirmed by Bujoczek et al. [4]. An increase of up to 10% in the content of solids in the suspended matter triggered

a decrease in the biogas production by about 40%, caused by inhibition. The free ammonia concentration amounted to 250 mg/l.

The inhibitory effect of ammonia during anaerobic digestion of animal wastes has been studied by several authors [18, 22, 23]. The concentrations of ammonium ranging from 1.5 to 3.0 g N/dm³ are regarded as tolerated by the methanogenic bacteria [12]. With the ammonia concentration of about 5 g N/dm³, the maximum speed of growth of the hydrogenotrophic methanogens decreases by almost a half of the value ascertained at the lack of the process inhibition [13, 14]. The free ammonia inhibits the development of the methane bacteria from 55 mg/dm³ [3] to 800 mg/dm³ [2]. The non-methanogens remain active at the concentration of ammonia nitrogen up to 6 g N/dm³ and pH reaction equal to 8 [16].

Acclimation of methanogenic consortia to high ammonia levels has proven a useful strategy for improving the process of anaerobic digestion and production of methane from different kinds of wastes [20]. However, only a few studies have been conducted on CM as a single substrate [19]. Co-digestion of chicken manure with other types of livestock manure was also attempted [8, 25].

The inhibition of methanogenesis by 50% also causes a concentration of about 2,000 mg/dm³ of volatile acids (as expressed by acetic acid) at pH 6.8, and over 3000 mg/dm³ at pH 7.0. With a pH above 7.4, inhibition does not occur. It is thought that the optimum concentration of volatile acids should range from 100 to 500 mg/dm³, with alkalinity not lower than 500 mg CaCO₃/dm³ [16].

The inhibition of methanogenesis by 50% causes the concentration of volatile acids - about 2000 mg/dm³ (in terms of ethanoic acid) at pH 6.8 and over 3000 mg/dm³ at pH 7.0. In case pH is over 7.4, the inhibition does not occur [10, 16, 21]. The optimum concentration of volatile acids should range from 100 to 500 mg/dm³, with the alkalinity not lower than 500 mg CaCO₃/dm³ [9].

The aim of the studies was (1) to determine the degree of biodegradation of the poultry manure as well as manure and corn silage mixed in various proportions of dry matters in the process of mesophilic fermentation of suspensions of this waste with a content of about 6% of d.m., (2) to establish the biogas and methane efficiency in these processes, (3) to evaluate the impact of mineral nitrogen and volatile fat acids (VFA) on the course of transformation and fermentation, and (4) to establish optimum proportions of these types of waste in case of their co-fermentation.

2. MATERIALS AND METHODS

2.1. Characteristics of raw materials

The litter-free poultry manure (O) was obtained from an agricultural farm situated in Niedoradz near Nowa Sól. During the normal operation, the droppings are removed with the use of mobile floor of the Specht company and transported twice or thrice a day, depending on the needs, by means of the belt conveyor system onto the trailers standing on the outside premises of the plant. Total waste test sample was prepared by taking 15 individual samples with a minimum weight of about 4 kg. Waste was collected from the conveyor belt at regular intervals in a random day of operation. Laboratory sample was obtained from the total waste sample by reducing the weight to 10 kg using the quartering method.

The corn silage (K) was obtained from green corn plants stored for a period of about 1.0 - 1.5 year in two windrows covered with foil. The plants were obtained from the corn plantation situated in Niedoradz near Nowa Sól, from the seeds having a commercial name of Pioneer 9000.

Table 2. Physico-chemical properties of waste subjected to the fermentation process

| Indicators | Unit | Manure | Silage | Seeding material |
|--------------------|--------|--------|--------|------------------|
| pH | - | - | - | 8.28 |
| Moisture | % | 66.9 | 65.7 | 96.3 |
| Dry organic matter | % d.m. | 72.7 | 95.3 | 62.3 |
| TOC | % d.m. | 36.2 | 42.0 | 36.1 |
| Total nitrogen | % d.m. | 4.97 | 1.54 | 15.2 |
| C/N quotient | - | 7.3 | 27.0 | 2.4 |

The waste suspensions were vaccinated with fermented sludge from the manure fermentation system manufactured by Biogaz Agri Sp. z o.o. in Niedoradz.

The properties of the studied waste and sewage sludge have been presented in table 2.

All the substrates were supplied to the laboratory in closed plastic containers filled up to the cover, and were used for analysis and preparation of test samples within 4 hours.

2.2. Test stand

The tests were performed in the laboratory scale, in the 12-stand fermenter for periodic fermentation. Each stand consists of three elements: fermentation chamber - a cylinder with a capacity of 1 dm³, a burette for measurement of the

quantity of the produced biogas and a cylinder with the saturated sodium chloride solution for equalisation of pressures.

Upon filling with the raw material, the reactors were connected tightly with burettes and placed in the fermenter bath (thermostat). The metal bath filled with water constituted the thermostat. The bath was equipped with water circulation pumps and two contact thermometers connected with the control device, which controlled the operation of (switched on or switched off) heaters, depending on the indications of the thermometers. The thermostat ensured maintenance of temperature in the reactors at the level of 35 ± 1 °C.

2.3. Preparation of test samples

The shares of components in the tested samples were presented in table 3. The first reactor (P-1) was used to determine the endogenous activity of the seeding material (control sample without waste). The tested waste were put into the other two reactors: P-2 - poultry manure and P-3 - corn silage.

Table 3. Characteristics of test samples

| Specification | | Unit | Sample number | | | | | |
|----------------------------------------------------------|--------|-----------------|---------------|-------|-------|---------------|-------------------|---------------|
| | | | GF | O | K | 26%O +74%K | 51%O + 49%K | 76%O +24%K |
| | | | P-1 | P-2 | P-3 | P-4 | P-5 | P-6 |
| Waste | Manure | g d.m. | - | 60.48 | - | 15.12 | 30.24 | 45.36 |
| | Silage | g d.m. | - | - | 58.38 | 43.79 | 29.19 | 14.60 |
| Seed sludge | | dm ³ | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 |
| | | g d.m. | 18.31 | 18.31 | 18.31 | 18.31 | 18.31 | 18.31 |
| Water | | dm ³ | 0.500 | 0.440 | 0.442 | 0.441 | 0.441 | 0.440 |
| Total dry matter content | | % | 1.83 | 7.88 | 7.67 | 7.72 | 7.77 | 7.83 |
| Quotient of dry organic matter of sludge | | - | - | 3.9 | 4.9 | 4.6 | 4.4 | 4.1 |
| O- poultry manure, K- corn silage, GF - Seeding material | | | | | | | | |

The next three reactors (P-4, P-5, P-6) were provided with manure and silage mixed in quantities corresponding to the share of manure in the mixture, that is, 25.7; 50.9 and 75.7% of d.m. respectively. 0.500 dm³ of the seeding material was added to all the reactors. The contents of the reactors were supplemented with tap water from the municipal water supply system up to the volume of 1.000 dm³. The reactors were closed with a rubber plug, which was locked with

the stirrup bolt. In order to ensure the anaerobic conditions from the space over the surface of the mixture, the air in the reactors was removed by blowing it through with nitrogen. Then, the reactors were connected tightly with burettes and placed in the thermostat. The mesophilic waste fermentation conducted for 58 days, at the temperature of about 35 °C. The tests were repeated twice.

2.4. The scope and control of the process

The process of methane fermentation was controlled by everyday measurements of the volume of produced biogas and periodic measurements of the following contents in biogas: methane, carbon dioxide, oxygen, ammonia and hydrogen sulphide. The composition of gas was determined by means of GA 2000 PLUS apparatus manufactured by Geotechnicals Instruments, after accumulation of gas in the column, in the quantity that enabled the performance of the measurement.

The properties of the fermented material were controlled before and after the fermentation, determining, among other things, pH, dry matter, dry organic matter (ignition losses), TOC (Total Organic Carbon), total alkalinity and total nitrogen in the mixtures, and ammonia nitrogen and volatile fat acids in the sedimentation water. The determinations were performed in accordance with the methodologies specified in the Polish Standard which are in accordance with European Standards [1].

2.5. Calculations

Ammonium (NH_4^+) and free ammonia (NH_3) are the main forms of ammonia nitrogen in the water solution. The concentration of free ammonia in the sample during the last day of tests was calculated on the basis of results of measurements of ammonia nitrogen concentration and pH at 35 °C from the following formula:

$$[\text{NH}_3] = [\text{NH}_4^+] / (1 + 10^{(pK_b - pH)}) \quad (1)$$

where: pK_b - ammonia dissociation constant at 35 °C.

The volatile fat acids may occur in the solution as undissociated particles (H-VFA). Their concentration was calculated on the basis of the total concentration of VFA and pH of the solution from the formula:

$$[H - \text{VFA}] = [\text{VFA}] \cdot (10^{(pK_a - pH)}) / (1 + 10^{(pK_a - pH)}) \quad (2)$$

where: K_a - acid dissociation constant at 35 °C.

3. RESULTS

3.1 The physico-chemical properties of mixtures before and after fermentation

The physico-chemical properties of the samples before and after the mesophilic fermentation have been presented in table 4.

Table 4. Physico-chemical properties of samples before and after mesophilic fermentation

| Specification | Unit | Sample: before (b) after (a) | Sample numbers | | | | | |
|--------------------|----------------------------------------|---------------------------------------|----------------|------------|------------|------------------------|----------------------------|------------------------|
| | | | P-1 (GF) | P-2 (O) | P-3 (K) | P-4 (26%O +74%K) | P-5 (51%O +49% K) | P-6 (76%O +24%K) |
| pH | - | b | 8.00 | 7.53 | 7.41 | 7.47 | 7.47 | 7.53 |
| | | a | 7.65 | 7.64 | 5.55 | 7.59 | 7.61 | 7.63 |
| Total alkalinity | g CaCO ₃ /dm ³ | b | 12.0 | 13.6 | 14.0 | 13.1 | 13.2 | 12.7 |
| | | a | 5.53 | 18.9 | 7.13 | 16.1 | 16.9 | 18.8 |
| Dry matter | g/dm ³ | b | 18.3 | 78.8 | 76.8 | 77.5 | 76.4 | 78.7 |
| | | a | 16.3 | 52.0 | 60.6 | 43.8 | 44.8 | 45.9 |
| Dry organic matter | g/dm ³ | b | 11.3 | 54.9 | 65.9 | 63.6 | 60.5 | 57.1 |
| | | a | 9.45 | 28.6 | 51.0 | 30.8 | 28.3 | 27.4 |
| TOC | g/dm ³ | b | 6.62 | 28.9 | 31.8 | 30.1 | 30.8 | 29.3 |
| | | a | 5.29 | 16.7 | 26.2 | 15.5 | 14.5 | 15.1 |
| TOC | % d.m. | b | 36.1 | 36.7 | 41.4 | 39.7 | 39.4 | 37.2 |
| | | a | 32.4 | 32.2 | 43.3 | 35.4 | 32.4 | 32.9 |
| Total nitrogen | g N/dm ³ | b | 2.80 | 5.75 | 3.68 | 4.20 | 4.75 | 5.25 |
| | | a | 2.80 | 5.70 | 3.65 | 4.15 | 4.70 | 5.20 |
| liquid | | | | | | | | |
| VFA | g CH ₃ COOH/dm ³ | b | 1.75 | 4.10 | 3.21 | 3.69 | 3.97 | 4.10 |
| | | a | 2.04 | 2.50 | 17.9 | 2.18 | 1.73 | 2.26 |
| Ammonia nitrogen | g N/dm ³ | b | 1.68 | 0.42 | 1.05 | 0.91 | 0.74 | 0.84 |
| | | a | 2.73 | 3.22 | 2.52 | 2.92 | 2.87 | 3.08 |

After the fermentation of waste, pH of mixtures ranged from 7.59 (P-4) to 7.65 (P-1), except for sample P-3, for which it amounted to 5.55. The contents of total nitrogen in samples at the time of fermentation did not change in practice, but the ammonia nitrogen concentrations clearly increased and ranged from 2.52 (P-3) to 3.22 g of N/dm³ in sample P-2. The concentrations of VFA in sedimentation water, except for sample P-3, fell to the level of <2.50 g CH₃COOH/dm³. In the sample with corn silage, the concentration of VFA increased up to a very high value - 17.9 g CH₃COOH/dm³.

3.2 Biogas efficiency production

The results of measurements of daily production of biogas and methane from the tested mixtures, in the processes of mesophilic fermentation, have been presented in figure 1.

The maximum daily production of biogas during the fermentation of samples with waste, except for the sample with manure (P-2), occurred during the 1 day of the process and ranged from 2.25 (P-6) to 3.56 dm³ (P-3). It was gas with low content of methane - from 15.2 (P-3) to 18.5% (P-6). For sample P-2, the greatest quantity of biogas was produced during the second day of the experiment (1.93 dm³). The methane content in biogas amounted to about 20%.

The daily production of biogas from sample P-3 started to decrease quickly, and on day 21 of the experiment, it fell to zero. A similarly quick decrease in the daily production was observed for sample P-4. It lasted until the day 6 of the tests. Until day 14, the biogas production was at the low level of about 0.3 dm³/d, then it increased, and in the period from day 18 to day 23, it remained at the level of over 1 dm³/d. In the remaining samples, the daily biogas production decreased slowly, reaching the level of 0.32 dm³/d (P-2 and P-5) and 0.55 dm³/d (P-6) on day 20. For sample P-5, the second maximum value of biogas production occurred on day 28 - 0.79 dm³/d.

The methane content from low values during the first day, increased rapidly during the following days. The share of methane in biogas at the level of $\geq 60\%$ was accomplished for the tested samples on day four - P-2, day six - P-6, day eight - P-3 and P-5 and day fourteen - P-3. The maximum daily methane production was observed on day one - P-3 (0.54 dm³/d), day nine - P-2, P-5 and P6 (1,10, 0.89 and 1.13 dm³/d) and day twenty - P-4 (0.87 dm³/d).

The accumulated net unitary production of biogas and methane from tested samples (production of biogas decreased by the production from the control ample) has been presented in dm³/kg of dry matter in figure 2.

The changes in the curves in regard to the accumulated production of biogas and methane from the tested samples during the measurements clearly show the occurrence of the phenomenon of fermentation process inhibition.

In case of the fermentation of corn silage, a decrease in the production of biogas and methane by about 80% was observed during the third day of the measurements, and on day 7 the process was stopped.

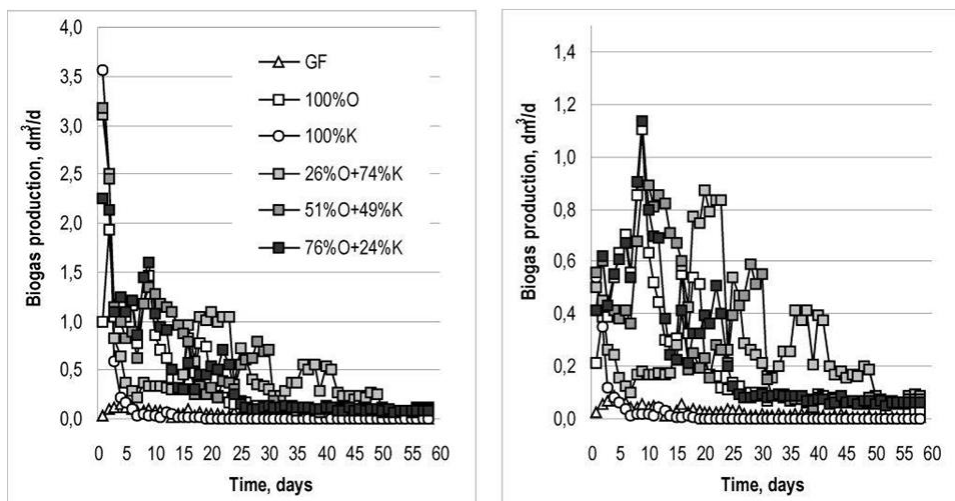


Fig. 1. Daily biogas and methane production

During the fermentation of manure (P-2) and mixtures of manure and corn silage mixed in the dry matter ratio of 1:1 (P-5) and 3:1 (P-6), the inhibition process occurred once.

- Manure (P-2) - on day 10 - the daily production of biogas fell by about 44% to the level of about $6.4 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$, and in case of methane - to about $4.6 \text{ dm}^3/\text{kg d. m. d}$ on day 13, and was kept at the same level for 3 days, and rose stepwise up to about 11 and $7.4 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$ and was kept at this level for 4 days, then it decreased slowly until the end of the experiment.

- Manure + corn silage (P-5) - the inhibition of fermentation occurred on day 16. The daily biogas production fell from 11.6 to $3.5 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$, and in case of methane - from 9.2 to $2.7 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$. During the following 8 days, they were kept at the level of 4.3 and $3.3 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$ respectively, then they rose stepwise, and within 6 days they amounted to 10.5 and $8 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$ respectively. On day 31, again the biogas and methane production fell stepwise to 2.9 and $2.3 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$ and decreased slowly until the end of the experiment.

- Manure + corn silage (P-6) - until day 9 of the tests, the daily production of biogas and methane was high, but unstable (on average about 22 and $10 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$). From day 10 of the fermentation process, just as in case of manure, a decrease in the production of biogas and methane was observed up to 4.7 and $3.7 \text{ dm}^3/\text{kg d. m. d}$ on day 14 of the tests. During the next 5 days, the biogas production was kept at the low level (on average 5.8 and $4.3 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$), and then increased stepwise, and on days 20-23 it amounted on average to about $9 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$ for biogas and about $6.5 \text{ dm}^3/\text{kg d.m.}\cdot\text{d}$ for methane. During the

following days, a slow decrease in the production of biogas and methane, lasting till the end of the experiment, was observed.

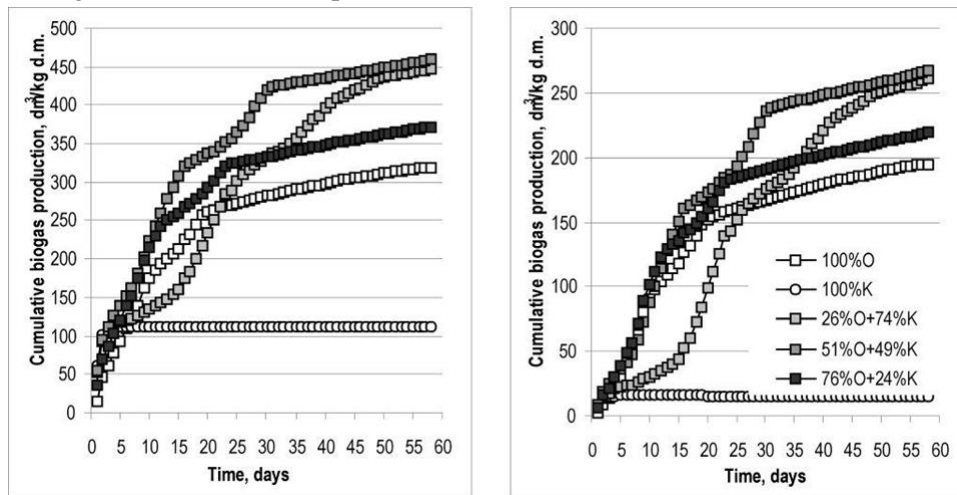


Fig. 2. The accumulated net production of biogas and methane

In case of the fermentation of manure and corn silage mixture, mixed in the dry matter ratio of 1:3 (P-4), two periods with distinct inhibition of the fermentation process occurred.

- The first one occurred already on day 3. The biogas production during the 3 days fell from 41 to about 4.3 dm³/kg d.m.·d, and in case of methane - from 6.7 to 1.6 dm³/kg d. m.·d. After the next 3 days, the biogas and methane production became stable and was at a low level until day 15 (on average: biogas - 4.3 dm³/kg d.m.·d, methane - 2.2 dm³/kg d.m.·d. On day 16, the efficiency of the fermentation process increased stepwise and was on average at the level of 14.0 and 10.5 dm³/kg d.m.·d for 10 days.

- The second period of the inhibition process occurred on day 26 of the tests and lasted 7 days. The biogas and methane production at that time oscillated around the values of 4.9 and 3.5 dm³/kg d.m.·d. On day 34, gas production increased stepwise by about 55% and was kept at this level until day 41, and then fell slowly until the end of the experiment.

The total unitary production of biogas from tested waste and the mean concentrations of methane, ammonia and hydrogen sulphide in biogas have been presented in table 5.

The total production of biogas from poultry manure during the period of 58 days of fermentation amounted to 319 dm³/kg d. m. For waste mixtures, it grew together with an increase in the percentage of corn silage in the input from 372 (P-6) to 460 dm³/kg d.m.·d (P-4). The percentage of methane in biogas decreased from 61.1% for manure to 58.1% (v/v) for the mixture (P-5).

Table 5. Production and chemical composition of biogas

| Specification | Units | P-2 (O) | P-3 (K) | P-4 (26%O +74%K) | P-5 (51%O +49%K) | P-6 (76%O +24%K) |
|------------------------------------------|-------------------------------|------------|------------|------------------------|------------------------|------------------------|
| Biogas production | dm ³ /kg d.m. | 319.0 | 111.0 | 448.0 | 460.0 | 372.0 |
| | dm ³ /kg d.o.m. | 443 | 119 | 507 | 542 | 481 |
| Methane percentage | % (v/v) | 61.1 | 14.1 | 58.2 | 58.1 | 59.0 |
| NH ₃ concentration in biogas | ppm | 249.0 | 0.5 | 22.9 | 151.0 | 205.0 |
| H ₂ S concentration in biogas | ppm | 45.4 | 0.5 | 15.8 | 25.2 | 41.2 |

The concentrations of ammonia and hydrogen sulphide in biogas were low and decreased together with an increase in the percentage of corn silage in the mixture of the tested waste from 249 and 45.4 ppm (P-2, manure) to 22.9 and 15.8 (P-4, mixture 1:3).

4. DISCUSSION

The degree of degradation (DoD) of organic substances, also determined by the effectiveness of fermentation, most frequently signifies a decrease in the value of dry organic matter in the substrate as a consequence of methanogenic processes. In the period of fermentation, its value expresses the quotient of a difference in the content of dry organic matter in the sample before and after the fermentation, and the content of dry organic matter in the input, expressed in percents.

Table 6. presents the degree of degradation of the organic substances expressed as a decrease in the content of dry organic matter and total organic carbon.

The degree of degradation of the organic substances for all the tested waste was very high, which confirms their great biodegradability. The highest degree of degradation of organic matter and TOC was obtained for the mixture of manure and silage mixed in the dry matter ratio of 1:1 (P-5), 61.8 and 60.8% respectively. For the remaining mixtures of manure and silage, it was slightly lower, but much higher than the one established for manure (56 and 49%).

Table 6. The degree of degradation of dry organic matter and TOC during the mesophilic fermentation of samples with tested waste

| Sample number | Sample before fermentation | | Sample after fermentation | | Degree of reduction | |
|---------------|----------------------------|-------------------|---------------------------|-------------------|---------------------|------|
| | d. o. m. | TOC | d. o. m. | TOC | d. o. m. | TOC |
| | g/dm ³ | g/dm ³ | g/dm ³ | g/dm ³ | % | % |
| O | 43.6 | 22.3 | 19.2 | 11.4 | 56.0 | 48.8 |
| K | 54.6 | 25.2 | 41.5 | 20.9 | 23.9 | 16.9 |
| 25%O+75%K | 52.3 | 24.2 | 21.4 | 10.2 | 59.1 | 57.8 |
| 50%O+50%K | 49.2 | 23.5 | 18.8 | 9.2 | 61.8 | 60.8 |
| 75%O+25%K | 45.8 | 22.7 | 18.0 | 9.8 | 60.8 | 56.8 |

The process of corn silage fermentation (P-3) ran in principle for 3 days (fig. 2). During this time, about 95% of the total methane quantity was produced. The unitary biogas production amounted to 119 dm³/kg d.o.m., and in the case of methane 17 dm³/kg d.o.m. Assuming the additiveness of GBP and GMP with regard to the components forming the mixture, the values of these parameters for silage calculated on the basis of results of tests would amount to:

- 25.7%O+74.3%K: GBP - 530 dm³/kg d.o.m., GMP - 304 dm³/kg d.o.m.,
- 25.7%O+74.3%K: GPB - 646 dm³/kg d.o.m., GPM - 361 dm³/kg d.o.m.,
- 25.7%O+74.3%K: GPB - 601 dm³/kg d.o.m., GPM - 324 dm³/kg d.o.m.

Rejecting the values obtained for sample with the high percentage of corn silage, in which fermentation inhibition could take place, the mean values of GBP and GMP for silage would be 623 and 343 dm³/kg of d.o.m. respectively. The mean percentage of methane in biogas would amount to 55%. These are the values which approximate those given in literature [10, 11].

The reason for inhibition of the process of corn silage fermentation was the excessive production of volatile fat acids and their dissociation, causing the withdrawal of carbon acid dissociation with a simultaneous increase in the production of carbon dioxide. The concentration of VFA in sample P-3 increased to 17.9 g. The consequence was a decrease in pH of environment to 5.55. A decrease in pH caused a shift of balance between the dissociated and non-dissociated forms of volatile acids towards the non-dissociated forms. In the sample before fermentation, pH amounted to 7.41, total alkalinity was 14.0 mg CaCO₃/dm³, VFA concentration - 3.2 gCH₃COOH/dm³, including non-dissociated forms - 7.1 mgCH₃COOH/dm³ (Table 7). After the inhibition of the fermentation, pH amounted to 5.55, VFA concentration was 17.9g CH₃COOH/dm³, including non-dissociated forms - 2485 mgCH₃COOH/dm³.

Table 7. Concentrations of toxic products of substrate transformations

| Specification | Unit | Sample: | P-2 (O) | P-3 (K) | P-4 (26%O +74%K) | P-5 (51%O +49%K) | P-6 (76%O +24%K) |
|---------------------|--------------------------------------------|----------------------------|------------|------------|------------------------|------------------------|------------------------|
| | | before (b) after (a) | | | | | |
| pH | - | b | 7.53 | 7.41 | 7.47 | 7.47 | 7.53 |
| | | a | 7.64 | 5.55 | 7.59 | 7.61 | 7.63 |
| VFA | g CH ₃ COOH/dm ³ | b | 4.1 | 3.2 | 2.7 | 4.2 | 4.3 |
| | | a | 2.5 | 17.9 | 2.2 | 1.7 | 2.3 |
| H-VFA | mg CH ₃ COOH/dm ³ | b | 6.9 | 7.1 | 5.2 | 8.1 | 7.2 |
| | | a | 3.3 | 2485 | 3.2 | 2.4 | 3.0 |
| VFA/Z content | - | b | 0.30 | 0.23 | 0.21 | 0.32 | 0.34 |
| | | a | 0.13 | 2.51 | 0.14 | 0.10 | 0.12 |
| Ammonia nitrogen | mg N/dm ³ | b | 420 | 1050 | 910 | 140 | 840 |
| | | a | 3220 | 2520 | 2920 | 2870 | 3080 |
| Ammonia | mg N/dm ³ | b | 15 | 30 | 29 | 4.5 | 31 |
| | | a | 151 | 1.0 | 123 | 126 | 141 |

The high concentrations of VFA occurred also in samples before fermentation - from 2.7 to 4.3 g CH₃COOH/dm³. They were from 5 to 8 times higher than those indicated for the fermentation [12]. However, at the same time, the samples were characterised by very high total alkalinity. The VFA/Z quotient was ≤0.34 and as a consequence of this, pH was higher than 7.4. In these conditions, the inhibition does not occur. In case of this sample, it is necessary to exclude the impact of nitrogen compounds on the course of the process. The ammonium concentration from 1.5 to 3.0 g N/dm³ is considered tolerated by methanogenic bacteria [13].

The observed inhibitions of the fermentation process in the remaining samples, except for P-2, were probably caused by ammonia. The ammonia concentration in sedimentation water from fermented samples of waste mixtures ranged from 123 do 141 g N/dm³. Thus, it was higher than 100 mg/dm³, at which free ammonia inhibits the development of methanogens. The ammonia concentration in the sedimentation water of the sample with manure was even higher than 150 mg/dm³, at which methanogens are killed [9].

5. CONCLUSIONS

The conducted tests confirmed the possibility of fermentation of the poultry manure suspension with the content of 6% of dry matter. The degree of degradation of organic substances included in manure during the mesophilic fermentation process lasting 58 days was very high and amounted to 56%.

They also proved that the corn silage suspension fermentation with such a concentration was inhibited as a result of acidification of the environment by volatile fat acids (degree of degradation 23.9%) which resulted in a very low production of biogas.

Also, the tests confirmed the positive effect of co-fermentation of poultry manure with corn silage. The most favourable ratio for mixing the substrates is the equal percentage of their dry matter in the mixture. With such waste mixing proportions, the degree of degradation of organic substances contained in the manure amounted to 61.8% and was higher than in the mono-digestion of manure and corn silage. The co-fermentation of poultry manure with corn silage were obtained the highest production of biogas. This confirms the improved corn silage fermentation conditions by changing the share of organic carbon and nitrogen in mixtures.

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BADANIA KO-FERMENTACJI OBORNIKA DROBIOWEGO I KISZONKI Z KUKURYDZY

Streszczenie

Rozwój produkcji mięsa drobiowego jest połączony ze wzrostem ilości obornika. Właściwości chemiczne predysponują te odpady do przetwarzania metodą fermentacji metanowej. W artykule przedstawiono wyniki badań wpływu amoniaku i lotnych kwasów tłuszczowych na mezofilową ko-fermentację metanową obornika drobiowego i kiszonki z kukurydzy. Celem badań było ustalenie stopnia biodegradacji obornika drobiowego i kiszonki kukurydzy zmieszanych w różnych proporcjach. Badania potwierdziły pozytywny wpływ ko-fermentacji odchodów kurzych z kiszonką, a najlepszy efekt uzyskano po zmieszaniu badanych substratów w równych porcjach. Stopień rozkładu substancji organicznych zawartych w oborniku wyniósł 61,8% i był wyższy niż w mono-fermentacji obornika i kiszonki z kukurydzy.

Słowa kluczowe: metan, fermentacja metanowa, obornik drobiowy, kiszonka z kukurydzy, amoniak

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