THERMOPHILIC METHANE FERMENTATION OF CHICKEN MANURE IN A WIDE RANGE OF SUBSTRATE MOISTURE CONTENTS

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Abstract. *One of the effective ways of environmental management in poultry waste that allows the increase of energy-saving and reduction of negative environmental impact is methane fermentation. Methane fermentation process is possible in three temperature modes: psychrophilic, mesophilic and thermophilic. Methane fermentation of chicken manure in thermophilic mode is less studied in comparison with mesophilic mode. The article presents the results of the study of methane fermentation of these wastes. The process was carried out in thermophilic conditions at 50 °C. Substrate moisture values varied from 72% to 99%. Biogas production ranged from 10,6 ml / g VS to 382,3 ml / g VS, methane production – from 1,8 ml / g VS to 207,9 ml / g VS. The maximum yield of biogas and methane per unit of mass was reached with the substrate moisture content of 92%. Production of methane from chicken manure in the thermophilic mode with low moisture level of the substrate was also possible despite the high content of ammonia nitrogen and free ammonia. However, with a decrease of the substrate moisture content lower than 80% efficiency of methane fermentation was at the same level and very low.*

Key Words: chicken manure, anaerobic digestion, biogas, ammonia, inhibition

I. Introduction

In market conditions there is a serious struggle for a market niche among producers whose outcome is largely determined by the cost of production. Energetic and environmental factors such as the cost of electricity and fees for environmental pollution impact the cost of production. One of the effective ways of environmental management in poultry waste that allows the increase of energy-saving and reduction of negative environmental impact is methane fermentation.

Methane fermentation process is possible in three temperature modes: psychrophilic, mesophilic and thermophilic. Waste treatment and wastewater treatment in industrial scale is carried out mainly in mesophilic or thermophilic conditions. Most of the works on methane fermentation of chicken manure were carried out in mesophilic mode.

Studies of anaerobic digestion of chicken manure report that high nitrogen content in poultry manure often creates problems of ammonium toxicity for anaerobes. It is believed that concentration of ammonia nitrogen is the limiting factor for the dilution coefficient [11]. In its turn, the increase of influent concentration is economically valuable as it leads to reduction of reactor volume and lowers consumption of water and energy for its heating, the amount of effluent, the cost of transportation and storage.

The periodic process with substrate moisture content ranging from 82 to 94% at 50 °C has been carried out by the authors in their previous work with the aim to investigate high-solid methane fermentation of chicken manure in the thermophilic mode [13].

Since methane fermentation took place in all range of substrate moisture values, the purpose of this study was to investigate the process at lower moisture values to find the value at which it is still possible. The process was also conducted at high dilution of the material in order to establish general regularities of methane fermentation of chicken manure.

II. Materials and methods

The experiments were carried out in thirty three 60 ml syringes three times in a row. Moisture content of the substrate was 72%, 74%, 76%, 78%, 80%, 82%, 84%, 94%, 96%, 98% and 99%. Manure was diluted with tap water to get the desired moisture level. Each syringe contained 20 g of substrate. Mass fraction of anaerobic sludge was 10%. The syringes were placed in a dry-air thermostat TC 80 M2. The process was carried out in the thermophilic mode at 50 °C. The amount of produced biogas was determined by deviation of the syringe piston. The concentration of carbon dioxide was measured by passing the biogas through 2% NaOH solution. The burnability of biogas was also checked. Chicken manure was obtained from Vasilkovska poultry farm where the egg-laying hens were kept in battery cages. Excessive anaerobic active sludge obtained from methane tanks of Bortnychi aeration station (where sludge from the primary clarifiers is processed) was used as inoculum. The sludge was clarified and the obtained liquid was decanted.

Chicken manure and anaerobic active sludge were stored in a refrigerator at 4 °C.

The content of total solids (TS) was measured by drying the sample in a drying oven at 105 °C to constant weight. To determine the volatile solids (VS), dry residue was heated in a muffle furnace at 600 °C. The pH level was measured using a pH meter pH-150 МИ. Electric conductivity was determined using PHYWE cobra4 mobile-link with module «Conductivity». The concentration of ammonia nitrogen and volatile fatty acids (VFA) was determined by distillation.

The content of free ammonia was calculated basing on concentration of ammonia nitrogen by the formula [5]:

$$NH_3(mg\ /\ l) = NH_4^+ - N(1 + 10^{(pK_w - pK_b - pH)})^{-1}$$

where pK_w is a constant of water ionization at 50°C that equals 13.262 [3], pK_b is a constant of ammonium dissociation at 50 °C that equals 4.723 [4].

The content of free VFA was calculated basing on the concentration of VFA by the formula [4]:

$$Free\ VFA(mg\ /\ l) = \frac{VFA \cdot 10^{(pK_a - pH)}}{1 + 10^{(pK_a - pH)}}$$

where pK_a is a constant of dissociation of acetic acid that is 4.787 at 50 ºC.

III. Results and discussion

Chicken manure obtained as a natural output of bird's vital activity has moisture level of 75%. During the first stage of the experiment the moisture content was 72.2% and during the second – 71.4%.

Chicken manure contains a larger proportion of organic matters, capable of biological decomposition, than other animal wastes [6]. The content of VS in the manure during the first stage of the experiment was 70%, and during the second – 69.8%. In the study of Webb and Hawkes (1985) the content of VS varied from 60 to 70.59% [14], in the work of Huang and Shih (1981) – 76% [7], Niu and al. (2013) – 73.84% [9, 10].

The characteristics of substrate with different moisture values (during the first and the second stages of the experiment) before methane digestion are given in Table 1 and after methane digestion – in Table 2.

Table 1. *Characteristics of chicken manure before methane digestion*

Primary moisture, %	General nitrogen, mg / l	N-NH_4^+, mg / l	NH_3, mg / l	VFA, mg / l	Nondissociated VFA, mg / l	pH	Electric conductivity, µS / cm
99	475	143	0,25	145	13,10	5,79	1200
98	950	285	0,60	290	22,60	5,86	2533
96	1900	570	1,34	580	40,63	5,91	3992
94	2652	796	2,05	831	53,44	5,95	4871
92	3536	1061	3,06	1140	65,78	6,00	5811
90	4420	1326	4,09	1449	78,33	6,03	6420
88	5304	1591	5,14	1757	90,93	6,05	8107
86	6188	1856	6,89	2066	93,75	6,11	7887
84	7072	2122	8,63	2374	98,64	6,15	8457
82	7956	2387	11,14	2683	97,62	6,21	8120
80	9500	2850	14,25	2898	98,64	6,24	8257
78	10450	3135	18,82	3188	90,78	6,32	8533
76	11400	3420	21,01	3478	96,84	6,33	8436
74	12350	3705	27,33	3767	87,65	6,41	8771
72	13300	3990	32,24	4057	86,27	6,45	8964

Table 2. *Characteristics of chicken manure after methane digestion*

Primary moisture, %	General nitrogen, mg / l	N-NH_4^+, mg / l	NH_3, mg / l	VFA, mg / l	Nondissociated VFA, mg / l	pH	Electric conductivity, µS / cm
99	451	451	164,97	60	0,02	8,30	3964
98	903	902	379,44	210	0,05	8,40	6990
96	1805	1804	830,5	420	0,09	8,47	11455
94	2522	2522	1978,37	885	0,04	9,10	13244
92	3363	3222	2831,98	3210	0,08	9,40	15807
90	4199	3082	2608,43	7080	0,23	9,28	15160
88	5037	4483	3617,27	6840	0,29	9,16	20380
86	5879	3362	1229,79	8100	2,49	8,30	19840
84	6720	3642	2554,72	7140	0,54	8,91	28180
82	7558	4644	2404,84	14990	2,47	8,57	21480
80	9358	5648	155,17	12230	76,16	6,99	25372
78	10293	6168	8,92	9281	1010,49	5,70	21376
76	11229	6760	4,68	12700	2582,66	5,38	21370
74	12165	7269	4,00	16315	3967,93	5,28	21280
72	13101	7816	4,72	13582	3078,47	5,32	19780

With a decrease in the substrate moisture content from 99% to 92% biogas and methane yield from VS increased, and from 90% to 80% - decreased. In the range from 72% to 82% biogas and methane yield were relatively at the same level. Biogas production ranged from 10.6 ml / g VS to 382.3 ml / g VS and methane production – from 1.8 ml / g VS to 207.9 ml / g VS. The maximum yield of biogas and methane per unit of mass was 382.3 ml / g VS and 207.9 ml / g VS respectively with the substrate moisture content of 92% (Figure 1).

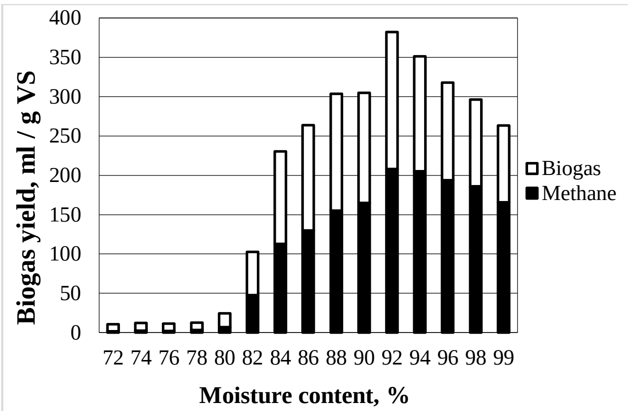

Figure 1. *Gas yield from VS with different moisture values of substrate*

With a decrease in the substrate moisture content from 99% to 84% biogas yield per unit of volume increased, and from 82% to 80% – decreased. In the range from 72% to 80% biogas and methane yield was relatively at the same level. Biogas production ranged from 2.2 ml / ml to 25.8 ml / ml, and methane production – from 0.4 ml / ml to 13 ml / ml. The maximum gas yield was 25.8 ml / ml with the substrate moisture content of 86% and methane yield - 13 ml / ml with the substrate moisture content of 88% (Figure 2).

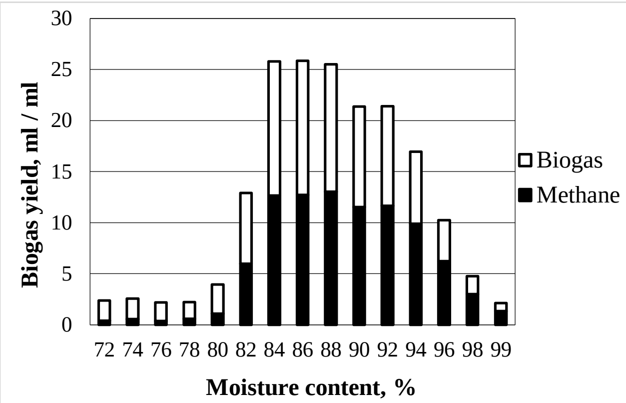

Figure 2. *Gas yield from the volume with different moisture values of substrate*

In the range of moisture values between 84% and 80% biogas and methane yield per unit of mass and unit of volume decreased sharply.

The concentration of methane in the biogas increased with an increase in the substrate moisture content. The content of methane in the produced gas ranged from 16.8% to 62.9%. Substrate moisture content of 80% led to a sharp decrease in the concentration of methane in the produced gas (Figure 3).

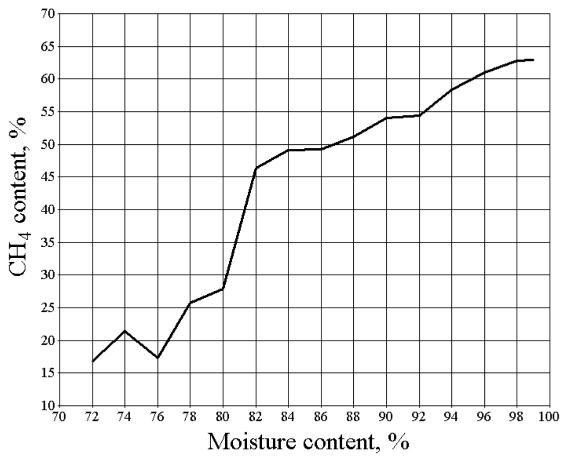

Figure 3. *The proportion methane / biogas with different moisture values of substrate*

Increasing of methane concentration in the biogas from the beginning of the experiment was faster with greater moisture content of the substrate.

The maximum rate of methanogenesis increased with an increase in the substrate moisture content. Its maximum value was 37 ml CH_4 / (g VS • day). The growth was exponential in nature. In the range of the moisture content values from 72% to 78% maximum rate of methanogenesis was relatively at the same level (Figure 4).

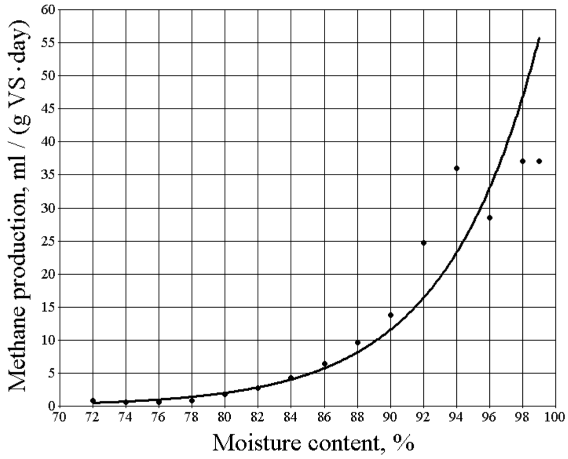

Figure 4. *The maximum rate of methanogenesis with different moisture values of substrate*

Mass of the substrate at the end of the experiment was lower than at the beginning due to its partial transition to the mass of gas.

After the methane fermentation a decrease in substrate viscosity was observed due to the conversion of organic matter of chicken manure into biogas.

The degree of destruction of TS and VS of chicken manure resulting from methane fermentation was proportional to the yield of biogas per unit of mass. In this regard, its values changed with a decrease in the substrate moisture content values similar to values of biogas production per unit of mass. The degree of decomposition of TS ranged from 1.28% to 67.59% and VS – from 1.83% to 96.55%. Maximum decomposition of TS and VS was with substrate moisture content of 92% and amounted to 67.59% and 96.55% respectively (Figure 5). Under different process conditions Webb and Hawkes (1985) obtained the decomposition of VS, ranging from 48.97% to 66.5% [14], Huang and Shih (1981) – 66% [7], Safley (1987) – 53.1% [12].

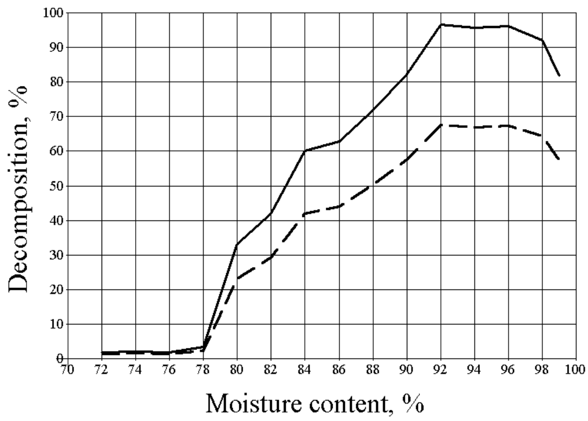

Figure 5. *Decomposition of VS and TS resulting from methane fermentation*

In our study pH of the substrate decreased with an increase in the manure moisture content from 6.45 to 5.79, which corresponds to an increase in ammonia nitrogen content. After the methane fermentation pH increased with a decrease in the substrate moisture content from 99% to 92%, and decreased with the further reduction in the moisture content from 90% to 72%. With the substrate moisture content ranging from 72% to 78% pH value was lower than at the beginning of the process, which can be explained by the accumulation of significant amount of VFA. Safley and al. (1987) noted an increase of pH from 7.2 to 8.05 as a result of anaerobic processing of poultry manure with moisture content of 94% in a continuous process at 35 ºC and 22-day duration [12].

Electrical conductivity of the substrate increased with the decrease in moisture content from 1200 to 8964 μS / cm. As a result of methane fermentation electrical conductivity increased due to mineralization and ranged from 3964 μS / cm to 28180 μS / cm. Safley and al. (1987) noted an increase in the electric conductivity from 22802 μS / cm to 26855 μS / cm [12].

During the second stage of the experiment, the content of ammonia nitrogen in poultry manure was 14.25 mg / g TS, while during the first stage it was 13.26 mg / g TS. Ammonium concentration with a decrease in the substrate moisture content increased from 143 mg / l to 3990 mg / l. As a result of methane fermentation the content of ammonia nitrogen increased and ranged from 451 mg / l to 7816 mg / l. McCarty (1964) indicated that when ammonia nitrogen concentration exceeds 3000 mg / l, the anaerobic digestion processes are inhibited at any pH [8].

The toxic effect of ammonia nitrogen is associated with nondissociated ammonia. It has been shown that it diffuses into the cell membrane and is ionized to form ammonium ions NH_4^+, leading to pH imbalance inside and outside the bacterial cell. It negatively affects both the transport of substances and the enzyme activity [9]. The content of nondissociated ammonia in the substrate ranged from 0.25 mg / l to 32.24 mg / l. After methane fermentation the concentration of ammonia increased due to ammonification and increasing pH. However, with the substrate moisture content ranging from 72% to 78% ammonia content was lower than at the beginning, as pH decreased as a result of methane fermentation. The concentration of ammonia varied from 4 mg / l to 3617 mg / l.

With the decrease in moisture content of the substrate VFA content increased and amounted from 145 mg / l to 4075 mg / l. After the methane fermentation with the substrate moisture content ranging from 96% to 99% VFA concentration was lower than at the beginning of the experiment, and from 72% to 94% – higher. VFA content ranged from 60 mg / l to 16315 mg / l. Safley and al. (1987) reported a decrease of VFA content from 8447 mg/l to 3403 mg/l [12]. Pechan and Knappovfi (1987) reported an increase in the content of VFA up to 4600-9300 mg / l as a result of semicontinuous methane fermentation of chicken manure with moisture content values ranging from 85.9% to 88.7% in case of duration of the process 27-58 days in mesophilic conditions [11].

VFA can exist in solution as unionized molecules. Similarly to free ammonia the unionized form of VFA can also be toxic. Its concentration increases with a decrease of pH solution [5]. Inhibitory levels can be as low as 10 mg / l as acetic acid, however, acclimations in the range of 30-60 mg / l as acetic acid were reported [2]. The concentration of nondissociated VFA at the beginning of the process ranged from 13.1 mg / l to 98.64 mg / l. After the methane fermentation, with the substrate moisture content ranging from 82% to 99%, concentration of free VFA was lower than at the beginning of the experiment, and from 72% to 80% – higher. The content of nondissociated VFA ranged from 0.02 mg / l to 16315 mg / l.

IV. Conclusions

1. The regularities of methane fermentation of poultry manure in batch mode in thermophilic conditions depending on the moisture content of the substrate in a wide range of values have been determined.

2. Production of methane from chicken manure in the thermophilic mode with the low moisture level of the substrate is possible, despite the high content of ammonia nitrogen and ammonia. Moisture content

value of the substrate, ceasing the production of methane, was not detected.

3. With a decrease in the substrate moisture content lower than 80% efficiency of methane fermentation was relatively at the same level and very low.

References

[1] Abouelenien F. Dry mesophilic digestion of chicken manure for production of methane by repeated batch culture / F. Abouelenien, N. Nishio, Y. Nakashimada // J. Biosci. and Bioeng. - 2009. - № 107(3). - pp. 293-295.

[2] Anaerobic treatment process stability / E.J. Kroeker, D.D. Schulte, A.B. Sparling, H.M. Lapp // Journal of Water Pollution Control Federation. – 1979. - № 51(4). – pp. 718-727.

[3] Bandura A.V. The ionization constant of water over wide ranges of temperature and density / A.V. Bandura, S.N. Lvov // J. Phys. Chem. Ref. Data. - 2006. - Vol. 35, № 1. - pp.15-30.

[4] Bates R.G. Acidic Dissociation Constant of Ammonium Ion at 0° to 500 C, and the Base Strength of Ammonia / R.G. Bates, D.P. Gladys // Part of the Journal of Research of the National Bureau of Standards. - 1949. - Vol. 42. - pp. 419-430.

[5] High solid anaerobic digestion of chicken manure / G. Bujoczek, J. Oleszkiewicz, R. Sparling, S. Cenkowaski. // J. Agric. Eng. Res. - 2000. - № 76(1). - pp. 51-60.

[6] Hill D.T. Simplified Monod kinetics of methane digestion of animal wastes / D.T. Hill // Agricultural Wastes. - 1983. - № 5. - pp. 1-16.

[7] Huang J.J.H. The potential of biological methane generation from chicken manure / J.J.H. Huang, J.C.H. Shih // Biotech. and Bioeng. - 1981. - № 23(10). - pp. 2307-2314.

[8] McCarty P.L. Anaerobic waste treatment fundamentals III / P.L. McCarty // Public Works. – 1964. – № 95. – p. 91.

[9] Mesophilic methane digestion of chicken manure at a wide range of ammonia concentration: Stability, inhibition and recovery / Q. Niu, W. Qiao, H. Qiang [et. al.] // Bioresource Technology. - 2013. - № 137. - pp. 358–367.

[10] Microbial community shifts and biogas conversion computation during steady, inhibited and recovered stages of thermophilic methane fermentation on chicken manure with a wide variation of ammonia / Q. Niu, W. Qiao, H. Qiang, Y.-Y. Li // Bioresource Technology. - 2013. - № 146. - pp. 223–233.

[11] Pechan Z. Anaerobic Digestion of Poultry Manure at High Ammonium Nitrogen Concentrations / Z. Pechan, O. Knappovfi // Biological Wastes. - 1987. - №20. - pp. 117-131.

[12] Safley L.M.J. Operating a full-scale poultry manure anaerobic digester / L.M.J. Safley, R.L. Vetter, D. Smith // Biol. Wastes. - 1987. - № 19(2). - pp. 79-90.

[13] Salyuk A. Thermophilic methane digestion of chicken manure / A. Salyuk, S. Zhadan, E. Shapovalov. // Ukrainian Food Journal. - 2014. -Vol. 3(4). – pp. 587–594.

[14] Webb A. R. Laboratory scale anaerobic digestion of poultry litter: Gas yield-loading rate relationship / A.R. Webb, F. R. Hawkes // Agric. Waste. - 1985. - № 13(1). - pp. 31-49.