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THE LIQUID PHASE RECIRCULATION UNDER METHANOGENIC FERMENTATION OF CHICKEN MANURE

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Abstract. The article is devoted to the analysis of the methanogenesis of chicken manure with effluent's liquid phase recycling with and without nitrogen stripping. It was determined that methanogenesis with full recirculation of the liquid phase is possible both with the sorption of ammonia nitrogen and without it. However, it was characterized by an inhibited state. Methane production was 0.51 l/l in a reactor with ammonia stripping and 0.23 l/l in a reactor without ammonia stripping. The ammonia removal efficiency was 12.5 % ammonia nitrogen. Proposed technology stripping of ammonia is characterized by a positive economic effect.

Key words: methanogenesis, liquid phase recirculation, ammonia, sorption, inhibition.

1. Introduction

The problem of poultry waste utilizing is topical. Chicken manure is characterized by high nitrogen level. This factor can have a negative influence on the environment in case of using this waste as a fertilizer or during its dumping. Chicken manure utilizing is possible in several ways. However, each of them is characterized by some disadvantages. One of the most attractive methods of chicken manure utilizing is methane fermentation. However, the excess of the effluent that requires processing or storage is a limiting factor for the use of methanogenesis.

Reducing the amount of waste generated in the process of methane fermentation is possible either by the solid phase fermentation or by the liquid phase recycling. According to our previous results, dry fermentation of waste with high solid content was characterized by worse performance than liquid fermentation, in particular by a less stable process, especially in thermophilic conditions. However, thermophilic conditions are characterized by some advantages which actualize it. Thus, it is topical to provide methanogenic fermentation under liquid recycling.

There was provided very little research on methanogenic fermentation of chicken manure under the liquid phase recycling. The research was conducted with nitrogen removing because it is the main inhibitor of the process [1, 4, 9].

Nie et al. conducted the research on the methanogenic fermentation under the liquid phase recycling with nitrogen removing by sorption at high temperature. The effluent formed in the process of methane fermentation was centrifuged and then purified by sorption of ammonia by phosphoric acid in a special tank with boiling up to 70 °C under low pressure without pH control. The purified effluent was used to dilute chicken manure to 15 % of dry matter content. Dry and liquid fractions of effluent and fresh chicken manure were used to prepare influent in different proportions. The hydraulic retention time of the process was 12–15 days. Methanogenesis was characterized by a stable state under the load rate of 5.3–6 g TS*l-1*day-1[4].

Wu et al. conducted the research on methane fermentation with hydraulic retention time of 25 days. The total length of the research was 100 days. The recycling coefficient was 0.6. The authors investigated the possibility of recirculation of the liquid phase, both with and without ammonia purification. Purification was provided by periodical additions of calcium hydroxide to bring pH to 11 and by air blowing for 4 hours. Methane production was more stable in the research reactor and it was 1.4 l*l-1*day-1[9].

Belostotskiy et al. used the 10 l reactors in mesophilic conditions with the load rate that was proportionally raised up to 3.9 g TS*l-1*day-1. The purification of nitrogen was provided by boiling to 80 °C under the pressure of 600 mbar with sorption by phosphoric or sulfuric acid for 4 hours. This purification was provided after centrifugation of the effluent. After centrifugation, liquid and dry phase were used to obtain the necessary level of ammonia nitrogen [1].

The results of the previous research on chicken manure methane fermentation under liquid phase recycling are presented in Table 1 [1, 4, 9].

Table 1

The results of the previous researches of chicken manure methane fermentation under liquid phase recycling

Author	TS content, %	Temperature, °C	Hydraulic retention time, days	The way of ammonia nitrogen purification	Biogas production, $l*l^{-1}*day^{-1}$
Nie's et al. study [4]	15	40	12-15	Sorption by phosphoric acid under boiling to 70 °C and low pressure	1.08–1.98
Wu's et al. study [9]	10	37	25	Blowing under pH 11	1.4
Belostotskiy's et al. study [1]	12	Methopilic condition	79–160	Sorption by phosphoric acid under boiling to 70 °C and 600 mbar pressure	1.36–2.1

2. Materials and methods

Two reactors were designed for the research. One of them was used as a control reactor without purification of ammonia nitrogen and the other was a research one which involved ammonia nitrogen purification. The research installation is presented in Fig. 1.

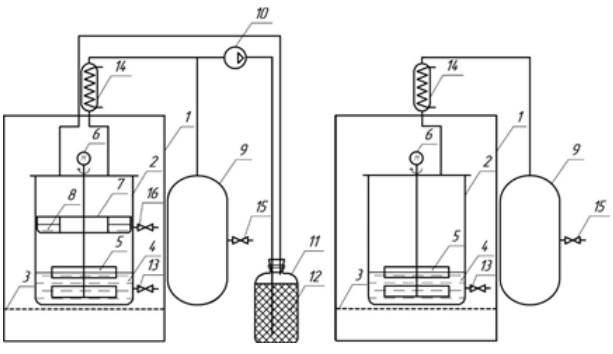

Fig. 1. The research installation: 1 – thermostat; 2 – reactor; 3 – lattice stand; 4 – substrate; 5 – mechanical stirrer; 6 – electric motor; 7 – plastic tank; 8 – optophosporic solution; 9 – gas bags; 10 – compressor; 11 – adsorber; 12 – iron(III) oxide; 13 – output connection ; 14 – humanity separator; 15 – test gas outlet; 16 – output connection

Useful volume of stainless steel reactors 2 was 2 l. The humidity of substrate 4 was 92 %. Methane fermentation of chicken manure was conducted in semi-continuous mode with hydraulic retention time of 5 days [6]. The reactors were located in thermostats 1 on the lattice stands 3 for boiling to 50 °C. Mixing of the substrate was provided by mechanical stirrer 5 with upper blades placed in such a way as to prevent the formation of the crust.

Mechanical stirrer was connected with electric motor 6. The stirrer provided mixing of the substrate for 15 min. every hour with a rotational speed of 38.8 rpm. The research reactor was fitted with a plastic tank 7 for ammonia sorption. The phosphoric acid 8 with a concentration of 4 M was loaded into the ammonia sorption tank. The acid volume was 0.4 l. The contact surface area of the sorbent with the gas phase was 0.025 m^2, and the substrate with the gas phase was 0.035 m^2. Produced biogas was stored in gas bags 9 connected with the reactors by silicone hose. Copper tube was used to test biogas quality. A manual piston pump with measure marks was used to measure the biogas quantity.

Effluent after methane fermentation was centrifuged. Suspenate was used fully to dilute the substrate to necessary humidity.

In both reactors, gas was purified from moisture in separators, and in the experimental reactor, it was additionally purified from hydrogen sulfide in an adsorber 11, filled with ferrum (III) oxide 12.

Biogas was pushed to the adsorber by compressor with volumetric speed of 0.005 l/s and then recycled back to the reactor.

The produced biogas volume, methane concentration, pH and conductivity of influent and effluent were measured daily except weekends. The content of ammonia and hydrogen sulfide in the biogas was measured at least once per 10 days, starting from the 10 th day of the process. Total solids (TS) content and volatile solids (VS) content were measured at the start as well as at the end of the process. Volatile fatty acids content was measured at the end of the process.

Ammonia nitrogen content is characterized by a linear dependence in relation to the electrical conductivity of the solution. To calculate the content of ammonia nitrogen, the formula developed by MidWest Plan Service [2] was modified:

$$NH4+=0.0897 \cdot Cond+451, \text{ mg/l},$$

where Cond is conductivity of the researched solution.

3. Results and discussion

Both reactors were characterized by unstable state, which indicates the unfavorable conditions for the process.

The research reactor was characterized by better condition than the control one. Thus, biogas production varied from 0.044 to 0.83 l/l, and in the research reactor – from 0.11 to 1.1 l/l. During the 6th and 7th retention of the reactors, the average value of biogas production in the research and control reactors was 0.63 and 0.36 l/l, respectively, and methane – 0.51 and 0.23 l/l, respectively. The production of biogas and methane in the control and research reactors is presented in Fig. 2.

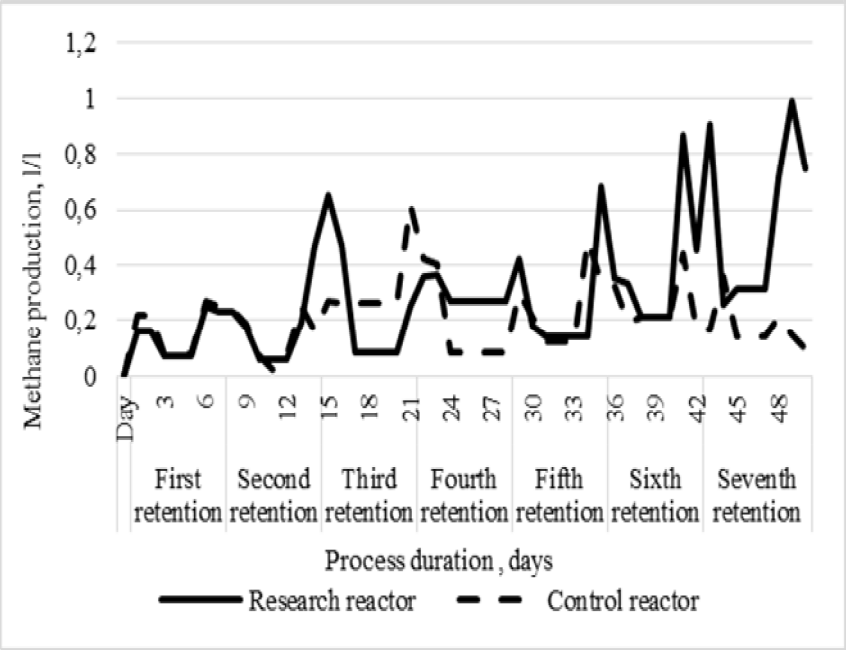

Fig. 2. Biogas and methane production in the control and research reactors

The Mann-Whitney U-criterion was used to compare the quantitative indicators. The production of biogas was characterized by a lack of statistically significant difference, since the difference in median values in the thermophilic and mesophilic conditions was not high (P = 0.235). However, methane production was significantly higher in the research reactor and was characterized by a statistically significant difference (P = 0.009).

Production of methane under the conditions of liquid phase recirculation varied from 1.4 l/l * day (Wu et al.) to 2.15 l/l* day (Ni et al.), and methane from 0.7 (Belostotskiy et al.) to 1.29 l/l * Day (Nie et al.) [1, 4, 9]. Thus, the production of methane in this

study is lower than in the previous studies, which may be associated with a larger load on the reactor. In addition, our previous studies without liquid phase recirculation were also characterized by better results than this study [5, 8].

The content of methane in the biogas of the research reactor was higher. Thus, in the research reactor it varied from 45 to 90 %, and in the control reactor – from 48 to 80 %. The share of methane in the research reactor was 73.64 %, while in the control one it was 63 %. It is worth pointing out that after the fourth reactor turnover, the concentration of methane in the research reactor was significantly higher than in the control one. Thus, the content of methane in biogas varied from 70 to 90 % in the research reactor, and in the control one – from 50 to 85 %. The difference in the median values of methane content in the control and research reactors was greater than that which could be obtained by accident; and, consequently, there was a statistically significant difference ($P < 0.001$). The content of methane in the biogas of the research and control reactors during the experiment is presented in Fig. 3.

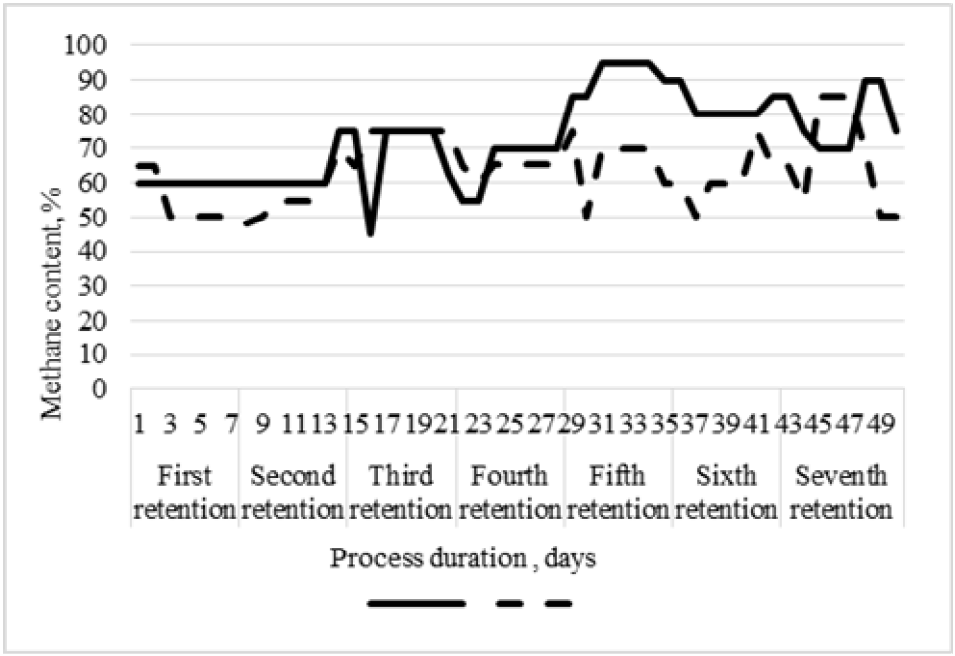

Fig. 3. The content of methane in the biogas of the research and control reactors during the experiment

In the study, Nie's et al. the share of methane was 60 %, while in the Wu's et al. study it was 50 % [4, 9]. Thus, the content of methane in this study is greater than in the previous studies.

After the fourth turnover, the pH was in the range of 7.77–8.2 in the research reactor and 8.05–8.58 in the control reactor. In the Nie's et al. study, the pH was close to the value of 8.1, in the Wu's et al. study – 7.7 in the ammonia nitrogen removal reactor and 8.1 without its removal. The pH level was within the range of 7.9–8.0 in the Belostotskiy's et al. research [1, 4, 9]. The median difference in pH values in the control and research reactors is greater than that which could be obtained by accident, and, therefore, there is a statistically significant difference ($P < 0.001$). Thus, a decrease in pH may be due to the removal of ammonia nitrogen [5, 8]. The pH of the effluent of the research and control reactors during the experiment is presented in Fig. 4.

The electrical conductivity after the fourth turnover of the reactor was lower in the research reactor and ranged from 36000 to 57000, while in the control one it varied from 37200 to 66000 μSm/cm. The conductivity of the effluent of the research and control reactors during the experiment is presented in Fig. 5.

The ammonia nitrogen content at the end of the process was 5.15 g NH4-N/l in the control reactor and 4.58 g NH4-N/l in the research reactor. Such indicators are significantly higher than the optimal ones. According to McCarthy's et al. studies, the methanogenesis at the concentration of ammonia nitrogen above 3 g NH4-N/l is inhibited at any pH value [3]. Thus, the process was characterized by the inhibited state of the methanogenic consortium both the control and research reactors. Consequently, it is impossible to recycle 100 % of the liquid phase under such conditions without inhibition. However, the proposed technology of ammonia nitrogen removal allows to provide significantly better performance of

the process. It is possible to avoid the inhibition of the process by reducing the reactor's load rate, increasing the hydraulic retention time of the reactor, changing the shape of the reactor and increasing the contact are of the phases between the ammonia and the sorbent.

The content of ammonia nitrogen in the control and research reactors during the process is presented in Fig. 6.

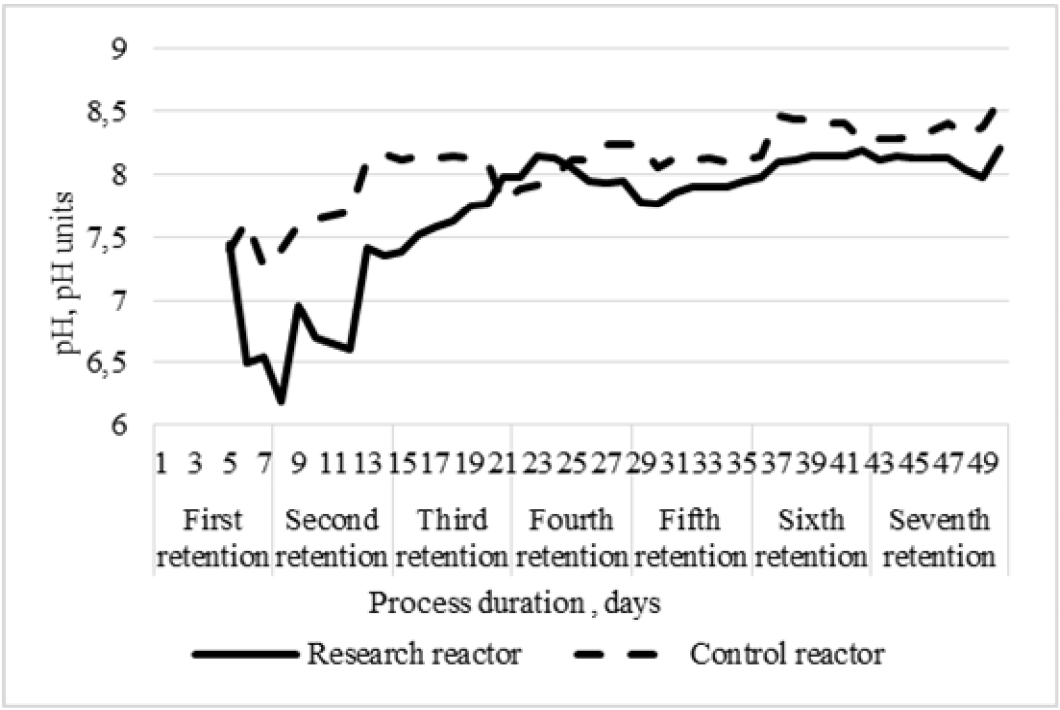

Fig. 4. pH of the effluent of the research and control reactors during the experiment

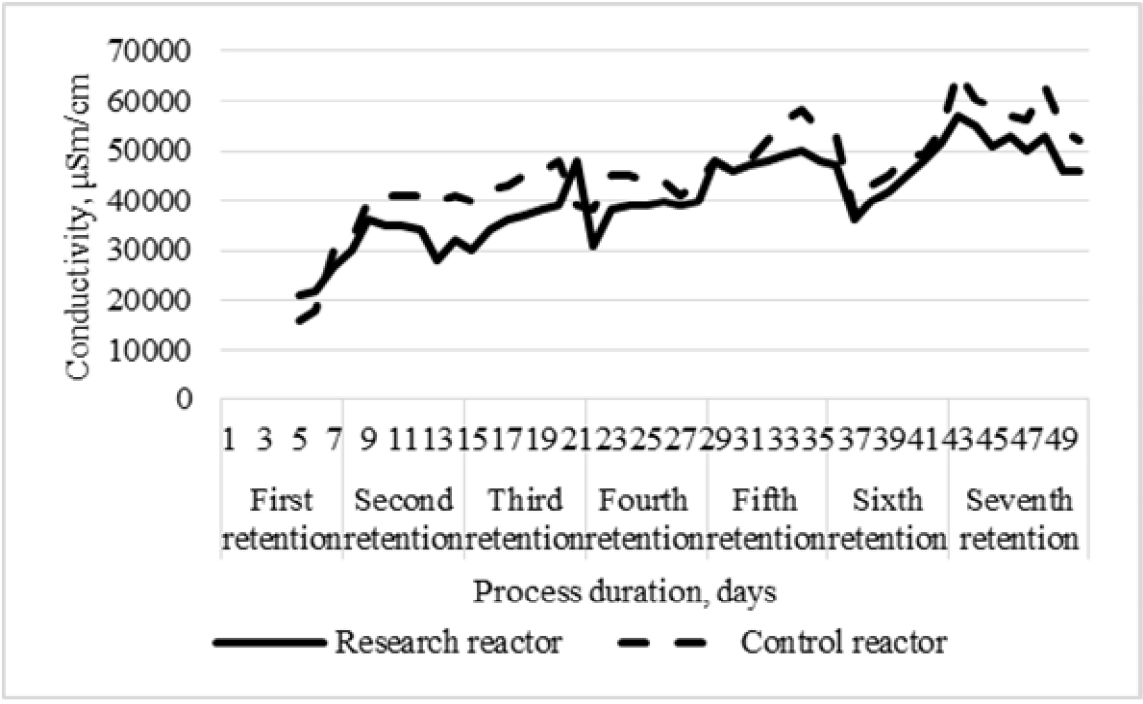

Fig. 5. Electrical conductivity of the effluent of the research and control reactors during the experiment

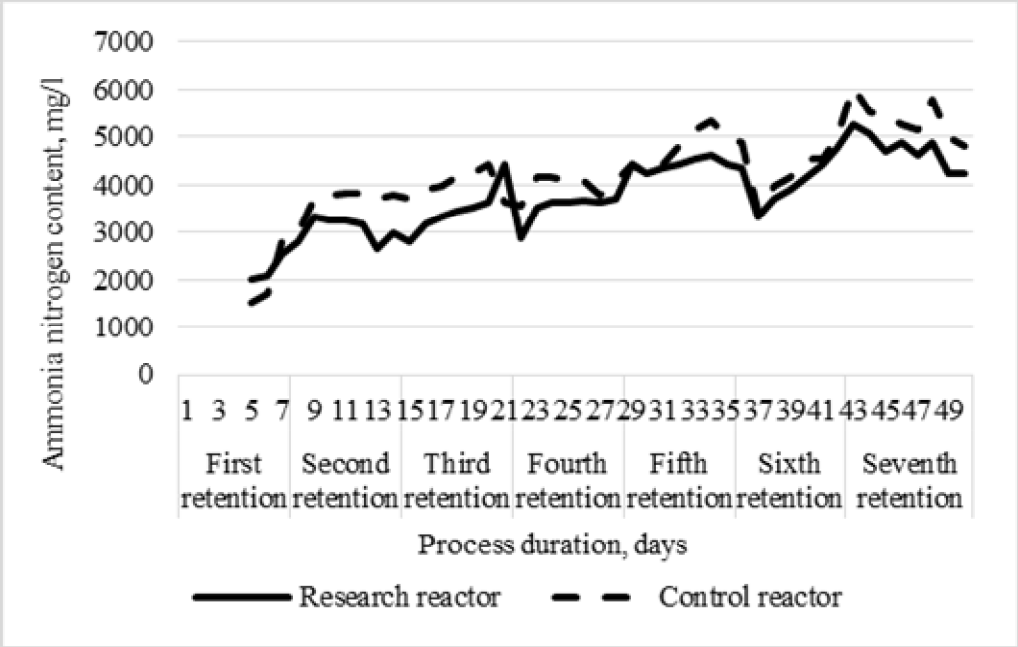

Fig. 6. The content of ammonia nitrogen in the control and research reactor during the process

In the study without liquid phase recirculation, the content of ammonia nitrogen in the control reactor was 3 g/l, and in the research one it was 2 g/l with the same ammonia stripping as in this research [5, 8].

The highest content of ammonia nitrogen was observed in Nie's et al study. Thus, it ranged from 5.6 to 6.96 g/l [4]. The lower content of ammonia nitrogen was found in Wu's et al. (5 g/l for case of liquid phase recycling and 3 g/l in case of liquid phase recycling and ammonia nitrogen removal) and in Belostotskiy's et al. (1.4 g/l) studies [1, 9].

In this study, the efficiency of ammonia nitrogen removal was 12.5 %. Significantly higher removal rate of ammonia nitrogen was observed in Wu's et al. study and accounted for 43 % [9]. It is worth pointing out that the economic efficiency of the technologies proposed is dubious. However, the technology proposed by us is characterized by a positive economic effect.

At the end of the process, the ammonia content in the gas phase of the control reactor was 25 mg/m^3 and of the control one it was 2 mg/m^3. The content of ammonia in the gas phase of the control and research reactors during the experiment is presented in Fig. 7.

The content of VFA at the end of the process was 2.85 g/l in the research reactor and 2.43 g/l in the control reactor. In the Nie's et al. study, the content of VFA was 3.5–6.5 g/l and in the Wu's et al. study, with the removal of inhibitors it was close to 6 g/l. Thus, VFA content in this research is lower than in the previous ones [4, 9].

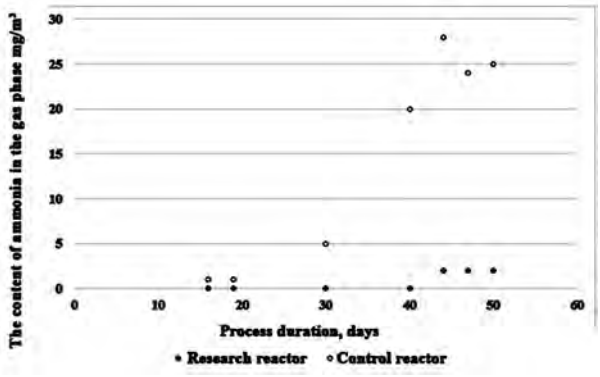

Fig. 7. Ammonia content in the gas phase of the control and research reactor during the experiment

Conclusions

1. Methane fermentation under the condition of complete liquid phase recirculation is possible with the removal of ammonia nitrogen and without it.

2. The content of ammonia nitrogen was 4.58 g/l in the control reactor and 5.15 g/l in the research reactor, indicating the inhibited state of both reactors in case of methane fermentation of chicken manure with humidity of 92 % under liquid phase of effluent recycle and reactor hydraulic retention time of 5 days.

3. The research reactor was characterized by a higher level of methane production, high proportion of methane, lower level of pH and electrical conductivity, which indicates positive effect of the proposed technology on the methane fermentation of chicken manure under the liquid phase of effluent recycling.

4. The indicators of the process efficiency were low, which indicates the necessity of technology optimization, including mathematical modeling.

5. The efficiency of ammonia nitrogen removal was 12.5 %.

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