ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

UDC [628.4.032+631.862].002.84:[661.152.4+662.767.2]

A.V. Ivanchenko, PhD, Assoc.Prof.
Dniprodzerzhynsk State Technical University, 2 Dniprobudivska Str., 51918 Dniprodzerzhynsk, Ukraine; e-mail: ivanche.anna@yandex.ru

INVESTIGATION OF TECHNOLOGIES FOR PRODUCING ORGANIC-MINERAL FERTILIZERS AND BIOGAS FROM WASTE PRODUCTS

А.В. Іванченко. **Дослідження технології отримання органо-мінеральних добрив і біогазу з відходів.** Сучасне сільське господарство вимагає особливої уваги до збереження родючості ґрунту, розробки систем удобрення культур, виробництва нових форм органо-мінеральних добрив, коефіцієнт засвоєння поживних речовин яких був би максимальним. Внесення штучних мінеральних добрив негативно впливає на ґрунти. ***Мета:*** Метою дослідження є виявлення наукових закономірностей технології отримання органо-мінеральних добрив і біогазу з побутових відходів і гною великої рогатої худоби із додаванням ферментативної добавки. ***Матеріали і методи:*** Доступною органічною сировиною для виробництва органо-мінеральних добрив є гній великої рогатої худоби. Екологічною технологією знешкодження й утилізації гною є його анаеробна біоконверсія у зброджене добриво і біогаз. Під час конверсії гною у біогаз відбувається знешкодження відходів, розклад складних полімерів до простих сполук, більш відновлених і доступних для рослин. Експериментальні дослідження проведено для трьох видів завантажень у модельний реактор анаеробного зброджування об'ємом 1 дм^3 на суху речовину. В дослідах використовувався мезофільний (при температурі 33 °С) режим зброджування. ***Результати:*** Вперше встановлено, що додавання сироватки до вхідної сировини у співвідношенні 1:30 прискорює процес анаеробного зброджування і виділення біогазу в 1,3…2,1 разу. Проведено аналіз складу органо-мінерального добрива на основі гною великої рогатої худоби. Розроблено технологічну схему отримання органо-мінеральних добрив і біогазу з відходів. ***Висновки:*** Впровадження результатів досліджень на фермерських господарствах і міських спорудах переробки відходів приведе до підвищення енергетичного потенціалу нашої держави і розширення асортименту якісних органо-мінеральних добрив, які добре засвоюються рослинами.
Ключові слова: органо-мінеральні добрива, біогаз, анаеробне зброджування, відходи

A.V. Ivanchenko. **Investigation of technologies for producing organic-mineral fertilizers and biogas from waste products.** Modern agriculture requires special attention to a preservation of soil fertility; development of cultures fertilization; producing of new forms of organic-mineral fertilizers which nutrient absorption coefficient would be maximum. Application of artificial fertilizers has negative influence on soils. ***Aim:*** The aim of the study is to identify the scientific regularities of organic-mineral fertilizers and biogas technologies from waste products and cattle manure with the addition of fermentation additive. ***Materials and Methods:*** The affordable organic raw material for production of organic-mineral fertilizers is the cattle manure. Environmental technology of the decontamination and utilization of manure is its anaerobic bioconversion to fermented fertilizer and biogas. The waste decontamination and the degradation of complex polymers into simple renewable and plant-available compounds take place during the conversion of manner to biogas. Experimental research carried out for the three types of loads to the model reactor of anaerobic fermentation with 1 dm^3 volume for dry matter. The mesophilic fermentation mode used in the experiments (at 33 °C). ***Results:*** It has been shown that the addition of whey to the input raw materials in a ratio of 1:30 accelerates the process of anaerobic digestion and biogas generation in 1,3...2,1 times. An analysis of organic-mineral fertilizers from cattle manure was conducted. Technological schemes of organic-mineral fertilizers and biogas technologies from waste products were developed. ***Conclusions:*** Implementation of research results to farms and urban waste treatment facilities lead to increased energy potential of our country and expansion of high-quality organic-mineral fertilizers variety, which are well absorbed by plants.
Keywords: organic-mineral fertilizers, biogas, anaerobic fermentation, waste products.

Introduction. Modern agriculture requires special attention to a preservation of soil fertility; development of cultures fertilization; producing of new forms of organic-mineral fertilizers which nutrient absorption coefficient would be maximum. Plants poorly absorb artificial fertilizers; their application negatively affects the soils. All this leads to the development and use of other types of fertilizers, primarily — organic fertilizers that have been pre-digested. Timeliness of the work is in the fact that currently in Ukraine there is a large number of accumulated sediment of organic-mineral origin: municipal waste, animals waste, wastewater sludge. These wastes are valuable because of its composition contains the nutrients components for plants. Simultaneously, the current energy crisis in Ukraine stimulates the scientists to search for new energy sources. Today the country pays much more attention to the issues of saving materials and energy resources, environmental protection. World experience of utilizing the anaerobic technology for processing of sludge and other organic waste to produce biogas and fertilizers, indicates the profitability and prospects of its industrial scale implementation.

DOI 10.15276/opu.3.47.2015.18

However, one of the outstanding issues of such technologies implementation in Ukraine is to reduce the run time of the units implementing those technologies. For example, the average run time of the anaerobic fermentation reactor ranges between 30 ... 55 days, which complicates the possibility of mass application in Ukraine.

The organic-mineral fertilizers — humic compounds consisting of chemically bound or adsorption-organic and mineral substances [1].

Mandryko et al [2] presents organic-mineral fertilizers containing peat, sapropel, manure, seston, charcoal, brown coal, bone meal and organosilicon compounds. Ivanchenko and Voloshin [3] proposed the technology for producing organic-mineral fertilizers from products obtained as a result of phosphates removal from urban waste water. New types of organic-mineral fertilizers are offered to be created based on solid waste [4], which contains a large amount of substances of organic origin: food waste, residues of paper, fabric and wood. Belianskaya et al [5] recommends utilizing the dispersion process to intensify the anaerobic fermentation process.

Biogas technology is not widely applied in Ukraine compared to many other countries despite a large amount of agricultural and municipal waste accumulated. Basically, installations for recycling municipal and livestock waste are in operation; there are only 22 such installations in our country (Fig. 1).

Fig. 1. Interactive map of biogas plants operating in Ukraine

However, biogas production in the European Union is developing intensively. Conclusions of the studies performed by "Öko-Instituts" and "Institut für Energetik" (Leipzig, Germany), refer to the possibility of biogas production only in Germany by 2020, that exceeds the currently imported natural gas volumes from Russia to the EU [6]. Biogas is produced in the EU either from livestock farms' manure runoffs, or from a variety of organic wastes of plant and animal origin.

The main problems that arise with regard to biogas plants implementation in Ukraine, in addition to their extra large run time, are climate features (sharply continental climate with cold nights and frosts in winter below –29 °C), are the absence of scientific and technical basis, lack of qualified specialists in this field [7].

Cattle manure is an affordable organic raw material for producing organic-mineral fertilizers. Anaerobic bioconversion into fermented fertilizer and biogas is the environmentally friendly techno-

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

logy of disposal and recycling of manure. Waste disposal, breakdown of complex organic compounds into simpler compounds mostly restored and available for plants are occurred during the conversion of manure into biogas. Thus, the fermented biomass from sludge digesters is in many ways several times better than other fertilizers [7].

Fermented organic-mineral fertilizers are environmentally friendly [8].

The anaerobic fermentation is a microbiological process where the organic matters, in an anaerobic environment, convert into gaseous methane (CH_4) and carbon dioxide (CO_2). The process is based on destruction of biomass macromolecules caused by bacteria of natural origin and consists of the next phases [9]:

1. Hydrolysis, when the stable substances (proteins, lipids and carbohydrates) are decomposed into simpler substances (amino and fatty acids, glucose).

2. Acidogenesis, when the obtained in the first stage components are decomposed by the acidogenic bacteria into other organic (acetic, propionic, butanoic acids, alcohols and aldehydes) and inorganic materials (H_2, CO_2, N_2, H_2S).

3. Acetogenesis, when the acetic acid is produced from the already formed acids under the influence of acetogenic bacteria:

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2,$$

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2.$$

4. Methanogenesis, when the acetic acid decomposes into methane, carbon dioxide and water:

$$CH_3COOH \rightarrow CH_4 + CO_2\ ,$$

$$CO_2 + H_2 \rightarrow CH_4 + H_2O\ .$$

Finally, biogas extracted from the production waste fermentation contains the following components [10]: CH_4 — 53...75 %; CO_2 — 20...44 %; H_2S — 1...5 %; H_2 — 0,5...2 %; NH_3, N_2 and O_2 — less than 1 %.

It should be emphasized, that plants much more easily absorb organic-mineral fertilizers obtained after the anaerobic fermentation, than the artificial fertilizers, such as urea, ammonium nitrate, nitrophoska. This is possible because the fermentation releases nutrients in such form which available for plants and they are readily soluble, and this is a very important moment in the development of new technologies.

The aim of the study is to identify the scientific regularities of organic-mineral fertilizers and biogas technologies from waste products and cattle manure with the addition of fermentation additive (whey).

Materials and Methods. Experimental studies have been conducted for three types of batches into the model anaerobic digester with the capacity of 1 dm^3 on dry basis, *g*: cattle manure with whey — 150, household waste (flour — 11 %, potatoes — 29 %, apples — 27 % and beet — 33 %) with whey — 150, cattle manure without additives — 155 (check sample).

Whey is used as fermentation additive with the next composition, %: water — 90; proteins (albumin and globulin) — 7; carbohydrates (milk sugar) — 2,95; fat — 0,05. Whey was added at the rate of 5 g per 150 g of raw material dry basis, i.e. in the ratio of 1:30.

In the course of experiments mesophilic (at 33 °C) digestion mode was used, which is technologically simplified and less costly compared with thermophilic mode, which is determined by temperatures over 52 °C.

The process of producing organic-mineral fertilizers and biogas was carried out in a glass digester with the capacity of 1 dm^3 and tightly closed rubber plug; airtight containers for biogas collection and cylinder to measure the volume of water displaced by biogas were attached to the digester.

A thermostat controlled heater maintained constant temperature (33 °C) of the mesophilic fermentation mode performed. Foam containment with the wall thickness of 20 mm was used to minimize heat loss of the bioreactor. Scheme of laboratory unit for the anaerobic digestion is shown in Fig. 2.

The experiment was conducted as follows. Reactor 2 was loaded with the studied mixture, sealed by cover 3 with the gas vent pipe 8 that connected reactor 2 and the biogas receiver 7. Biogas receiver 7 was filled with water. The heater with thermostat 4 connected to the current source 5 was attached to the reactor and covered by heat-sealed containment 1. Next, all the connecting channels were checked for leaks. Biogas volume was measured by volume of the displaced liquid (water) from the gas receivers 7 into the container 9. The experiment was conducted for three batches.

The volume of extracted biogas in a graduated cylinder with water was monitored every day.

Results. Figure 3 presents dependences of extracted biogas volume during the anaerobic fermentation on process duration and type of batch, obtained experimentally.

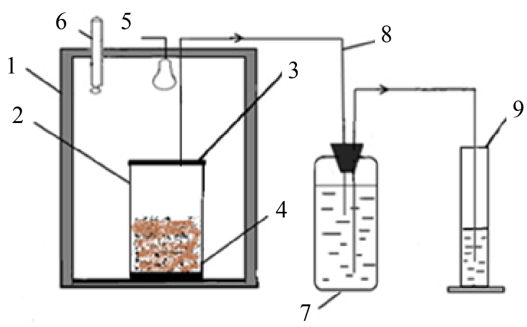

Fig. 2. The experimental setup: 1 — heat-sealed containment; 2 — bioreactor; 3 — hermetic cover; 4 — heater with thermostat; 5 — current source; 6 — thermometer; 7 — sealed glass to collect biogas; 8 — gas vent pipe; 9 — cylinder to measure the volume of water

It has been determined that biogas intensively generates when using cattle manure with whey as the input raw materials (Fig. 1, curve 1). The process lasted 16 days, biogas yield made 0,275 m^3/kg. Biogas yield from household waste with whey was 0,31 m^3/kg for 24 days (Fig. 1, curve 2). Based on the check sample (Fig. 1, curve 3), we can see that biogas extraction using cattle manure without fermentation additives was much slower and lasted 31 days, biogas yield made 0,26 m^3/kg.

The dependence of the average speed of biogas yield on the type of raw materials shows that the average biogas daily yield from cattle manure with whey is 0,017 m^3/day, from household waste with whey — 0,013 m^3/day, from cattle manure without additives — 0,008 m^3/day (Fig. 4). Thus, the addition of whey to the input raw materials accelerates the process of anaerobic digestion and biogas generation in 1,3...2,1 times.

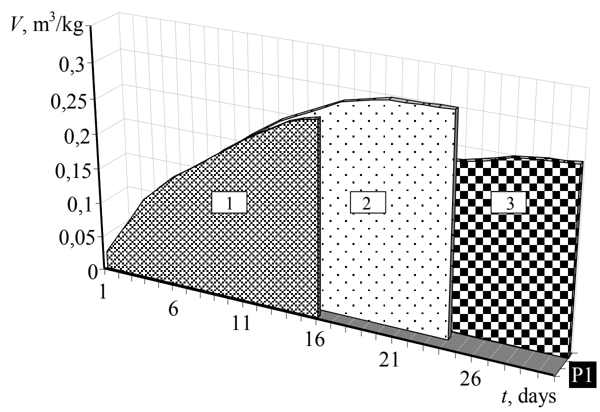

Fig. 3. Dependences of extracted biogas volume during the anaerobic fermentation on process duration and type of batch: 1 — cattle manure with whey; 2 — household waste with whey; 3 — cattle manure without additives (check sample)

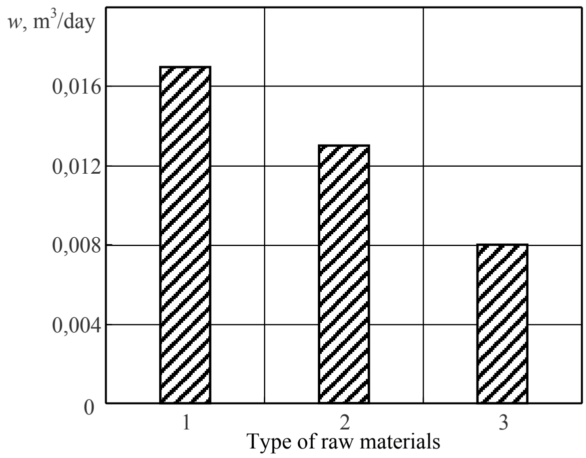

Fig. 4. The dependence of the average speed of biogas yield on the type of raw materials: 1 — cattle manure with whey; 2 — household waste with whey; 3 — cattle manure without additives

Fermented sludge can be used as an effective organic-mineral fertilizers.

Characteristics of the fermented sludge shows that the fermented sludge contains significant amount of organics — 83,57; 82,6; 80,75 %, respectively, as well as minerals (Table 1).

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

Table 1

Characteristics of fermented sludge

Raw materials	Content of organic and mineral substances after anaerobic fermentation, %	
	Minerals	Organics
Cattle manure and whey	16,43	83,57
Household waste and whey	17,40	82,60
Cattle manure without additives	19,25	80,75

Spectrometer "ElvaX mini" was used to determine the quality of fermented organic fertilizers.

Composition of the mineral part of the fermented organic-mineral fertilizers showed that the mineral part contains large amount of calcium and potassium (82,693 and 10,081 %, respectively, for the fertilizers based on cattle manure with whey; 41,905 and 48,911 % — for the fertilizers based on household waste), as well as microelements (Table 2), indicating their versatility and nutritional value for use in various farm cultures.

Table 2

Composition of the mineral part of the fermented organic-mineral fertilizers

Element	Content, %	
	Cattle manure with whey	Household waste with whey
MgO	0,099	—
SiO_2	2,364	6,945
P_2O_5	1,689	0,940
SO_3	0,255	0,090
Cl	0,123	0,629
K_2O	10,081	48,911
CaO	82,693	41,905
Cr_2O_3	0,074	—
MnO_2	0,268	0,093
Fe_2O_3	1,861	0,320
CuO	0,039	0,009
ZnO	0,115	0,037
As_2O_5	0,064	—
BrO	0,012	0,019
RbO	0,014	0,012
SrO	0,093	—
SnO	0,054	0,084
PbO	—	0,012

Technological scheme of producing organic-mineral fertilizers and biogas from waste was developed on basis of experimental research activities (Fig. 5).

The technological scheme operates as follows: container 1 is filled with raw materials and fermentation additives in the ratio 1:30 on dry basis; the mixture is stirred and pump 2 delivers it to bioreactor 3 where anaerobic fermentation is occurred. Heater 5 maintains constant temperature conditions (33 °C) of mesophilic mode in the bioreactor. Biogas, released from the bioreactor, enters the engine 4, where the gas is burnt. The fermented sludge (fertilizer) from bioreactor enters the centrifuge 6, where it is freed from the excess moisture. The final product (organic-mineral fertilizers) from centrifuge enters the warehouse 7 and further is transported to the consumer.

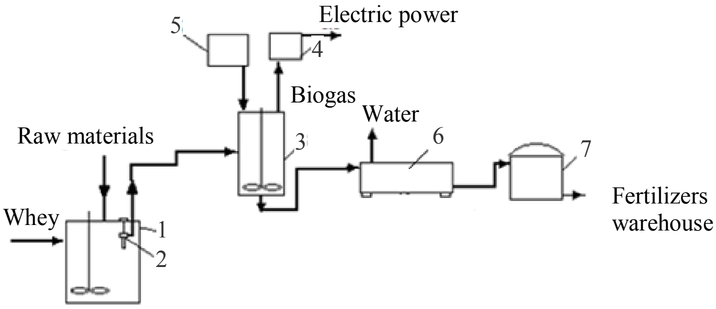

Fig. 5. Technological scheme of OMF and biogas producing from waste

The developed technology is recommended for implementation on farms and municipal waste treatment plants. Its implementation will reduce the run time for biogas plants by 1,3...2,1 times, and will boost their extensive application in Ukraine and abroad.

Conclusions. The author studied the technologies for producing organic-mineral fertilizers and biogas from cattle manure and waste products with whey. It has been shown that the addition of whey to the input raw materials accelerates the biogas generation in 1,3...2,1 times.

We conducted the analysis of organic-mineral fertilizers from cattle manure; and analysis showed the following percentage of components: organic matters — 83,57, calcium — 13,58, potassium — 1,65, silicon — 0,38; phosphorus — 0,27; based on waste, %: organic matters — 82,6, calcium — 7,29, potassium — 8,51, silicon — 1,2, phosphorus – 0,16.

Implementation of research results to farms and urban waste treatment facilities lead to increased energy potential of our country and expansion of high-quality organic-mineral fertilizers variety, which are well absorbed by plants.

Література

1. Мельников, Л.Ф. Органоминеральные удобрения. Теория и практика их получения и применения: монография / Л.Ф. Мельников; АН Респ. Узбекистан. Ин-т общей и неорган. химии. — СПб.: Изд-во Политехн. ун-та, 2007. — 304 с.
2. Пат. 14104 Україна, МПК C05F 11/02. Органо-мінеральне добриво / Мандрико Р.М., Кузьмін В.В., Скрильник Є.В.; заявники та патентовласники Мандрико Р.М., Кузьмін В.В., Скрильник Є.В. — № а200509237; заявл. 30.09.2005; надр. 15.05.2006, Бюл. № 5.
3. Иванченко, А.В. Возможности получения биофосфатного удобрения из осадков городских сточных вод после реагентно-адсорбционной доочистки от фосфатов / А.В. Иванченко, Н.Д. Волошин // Вісник НТУ «ХПІ». Хімія, хімічна технологія та екологія. — 2010. — № 10. — С. 141 — 147.
4. Якушко, С.І. Органо-мінеральні добрива. Переваги та способи виробництва / С.І. Якушко, В.П. Іванов // Хімічна промисловість України. — 2008. — № 3(86). — С. 38 — 43.
5. Бєлянська, О.Р. Технологія одержання комплексного добрива на основі диспергованого активного мулу / О.Р. Бєлянська, А.В. Іванченко, М.Д. Волошин // Восточно-Европейский журнал передовых технологий. — 2015. — № 3/6 (75). — С. 43 — 48.
6. Кучерук, П.П. Дослідження ефективності метаногенезу при анаеробному зброджуванні гною ВРХ з рослинними рештками / П.П. Кучерук, Ю.Б. Матвєєв, Т.В. Ходаківська // Відновлювана енергетика. — 2010. — № 1(20). — С. 83 — 89.
7. Утилізація відходів з отриманням біопалива та добрив / В.І. Карпенко, В.В. Козлов, Л.П. Городок, О.В. Горлінський // Проблеми екологічної біотехнології. — 2012. — № 2. — С. 97 — 123.
8. Очеретнюк, А.Р. Оптимизация методов получения экологически чистых биоминеральных удобрений / А.Р. Очеретнюк, Н.Д. Волошин, В.В. Кармазина // Науковий вісник Національного гірничого університету. — 2013. — № 6. — С. 104 — 111.
9. Добрынина, О.М. Технологические аспекты получения биогаза / О.М. Добрынина, Е.В. Калинина // Вестник Пермского национального исследовательского политехнического

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

университета. Охрана окружающей среды, транспорт, безопасность жизнедеятельности. — 2010. — № 2. — С. 33 — 40.
10. Визначення компонентного складу біогазу волюмометричним методом / Л.А. Хрокало, Т.І. Обушенко, Є.С. Перерва, О.А. Козловець// Наукові вісті НТУУ «КПІ».— 2013. — № 3. — С. 93 — 99.

References

1. Melnikov, L.F. (2007). *Organo-Mineral Fertilizers: Theory and Practice*. Saint-Petersburg: Saint-Petersburg Polytechnic University.
2. Mandryko, R.M., Kuzmin, V.V., & Skrylnyk, Y.V. (2006). *An organic and mineral fertilizer*. Ukraine Patent: UA 14104.
3. Ivanchenko, A.V., & Voloshin, N.D. (2010). The possibility of the production of the biophosphate fertilizers from sewage sludge after reagent adsorption on phosphates. *Bulletin of National Technical University "KhPI": Chemistry, Chemical Technology and Ecology*, 10, 141–148.
4. Yakushko, S.I., & Ivanov, M.P. (2008). Organic and mineral fertilizers: advantages and production technologies. *Chemical Industry of Ukraine*, 3, 38–43.
5. Belianskaya, A., Ivanchenko, A., & Voloshin, N. (2015). Production technology of complex fertilizers based on dispersed activated sludge. *Eastern-European Journal of Enterprise Technologies*, 3(6), 43–47. DOI:10.15587/1729-4061.2015.42137
6. Kucheruk, P.P., Matveev, Yu.B., & Khodakivska, T.V. (2010). Research on the effectiveness of methanogenesis in anaerobic digestion of cattle manure with plant remains. *Vidnovliuvana Enerhetyka*, 1, 83–89.
7. Karpenko, V.I., Kozlov, V.V., Golodok, L.P., & Gorlinskyy, O.V. (2012). Utilization of waste with biofuel and fertilizers obtaining. *Problems of Environmental Biotechnology*, 2, 97–123.
8. Ocheretnyuk, A.R., Voloshin, N.D., & Karmazina, V.V. (2013). Optimization of the methods of non-polluting biomineral fertilizers production. *Scientific Bulletin of National Mining University*, 6, 104–111.
9. Dobrynina, O.M., & Kalinina, E.V. (2010). Technological aspects of biofuel production. *Bulletin of Perm National Research Polytechnic University: Environmental Protection, Transport, Life Safety*, 2, 33–40.
10. Khrokalo, L.A., Obushenko, T.I., Pererva, Ie.S., & Kozlovets, O.A. (2013). Volumetric estimation of biogas content. *Research bulletin of National Technical University of Ukraine "Kyiv Polytechnic Institute"*, 3, 93–99.

Received November 1, 2015
Accepted December 9, 2015