Usage of Farm Animal Waste for Biogas Production

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Abstract. The article considers problems connecting with the development of cattle breeding in Russia, especially the utilization of animals and poultry waste products. Basing on the foreign scientists’ experience, it has been proposed different solutions to this problem in terms of the Russian Federation, conducted the study, and presented the results of the undertaken experiments. Recommendations on the use of substances, that speed up fermentation processes at certain temperatures, has been developed.

1. Introduction

In Russian economy farming is the fastest growing sector. It is continuously improving animal and poultry breeding enterprises, and intensifying crop production by increasing sowing areas and yield productivity, so agricultural enterprises perform diversified highly mechanized commercial farm unit. However, the current farming technology is not applicable to the utilization of waste products, such as animal and bird wastes, livestock manure, vegetable remains and other organic materials, which are an integral part of the agricultural sector and increase respectively to the growth of the farming sector.

Traditionally livestock manure, as a result of animal and poultry breeding enterprises activity, is collected and stored in giant artificial pits – “dung pits”. After being kept for 8-12 months it loses its dangerous qualities and gradually turns into a fertilizer that can be used to increase soil fertility. Although, many dung pits are outdated and even do not meet environmental standards. Most of the acting cattle-breeding complexes have been working for 25-30 years without upgrading their pollution control equipment; while such activity should be performed every 10-15 years due to its rapid wear. In addition, the ever-increasing number of livestock and poultry manure generates additional extra dung pits volume, which entails the removal of the "raw" manure on the fields and as a result lead to a number of problems.

Firstly, transportation of a huge waste quantity (solids content is 2-5%) requires additional resources. Secondly, raw litter and manure in soil are dangerous because of possible soil contamination with different infectious and parasitic diseases, ecotoxicants (heavy metals, pesticides, mycotoxins, etc.) and others. Soil largely seeds with microflora and weeds after application of organic manure, this situation can be environmentally and healthy dangerous too. Agricultural runoffs are one of the sources of pathogens that lead to over then 100 animal and human diseases. Such diseases include: aphthous fever, brucellosis, anthrax, leptospirosis, salmonellosis, encephalitis, erysipelas and swine fever, coccidiosis and many others. Animal waste is also a potential source of helminth eggs, molds and fungi. In addition it is continuously enriched with manure opportunistic pathogens, permanent inhabitants of animal digestible tract, such as Escherichia coli, Streptococcus, Pseudomonas Aureginosa and others. These microorganisms, passing through a lot of animal bodies,
enhance its pathogenicity and cause colibacillosis, streptococcosis, pseudomonosis and other diseases. In the third, raw manure application into the soil leads to the local accumulation of nitrates, copper and zinc in the grain, grass, and water sources.

Other countries produce biogas from various wastes, e.g. China uses food wastes for biomethane production [1]. Not only food waste can be used for this purpose; other organic and inorganic plants’ wastes can be transformed into biogas (as in Italy and Denmark) instead of being recycled as the law demands in many foreign countries [2, 3, 4]. Biogas production is economic due to the development of production system in foreign countries that minimize operating costs and cost of raw material transportation. Denmark biogas producing system is based on the use of fertilizers; Denmark researchers found that the benefits of a biomethane large-scale production and of its operating costs cover increasing transport expenses on the fertilizer and gas collection. To increase the yield, they use waste in biogas production [3].

One of the most rational solutions to this problem for Kuzbass and other regions in Russia could become a manure biotech processing in anaerobic conditions with a release of two by-products: alternate energy source (biogas) and environmentally friendly, plant readily available organic fertilizer (biosludge).

In the light of the above information, the development of biogas production technology in cold regions is very urgent and requires a detailed scientific approach.

2. Equipment and devices used in studies
The studies were held on the base of the Kemerovo State Agriculture Institute in the Scientific Research Laboratory “AgroBiotechnologies” with the use of 20 L Bio Gas Plants. The raw material for the study was cattle manure.

3. Results and discussion
Effect of different factors on the process of biogas release has been investigated several times by many researchers from different countries and covered in many scientific works, however, there is no consensus on this issue [5, 6, 7]. This is due to the fact that the studies were conducted in different climatic conditions and the raw materials were of varying quality and type.

A great number of strains of microorganisms produce biogas, but the most important of them are methane microorganisms because they emit methane that we are interested in. That is why the reproduction of such a complex and multi-step biological process as methanogenesis demands special attention to optimal environmental conditions for this group of microorganisms. But the other groups of bacteria participating in the process are also important; they gradually prepare a nutritious substrate for methane microorganisms in the process of anaerobic decomposition of organic matter and biogas release.

Thus, the process of biogas release is a complex multistep biological process, which involves a huge number of micro-organisms that differs by their nature, functional activities and even optimal living conditions, so it becomes complicated and practically implemented to create universal living conditions for all groups of bacteria.

Optimal temperature regulation is one of the most important factors in the fermentation process. Under natural conditions, the biogas formation takes place at temperatures from 0° C to 97° C. Most methane microorganisms are mesophiles, they grow at 30-40° C, while 25 °C is a lower limit for their functioning. But for some strains the optimal temperature zone is shifted down toward a lower limit (25 °C) or up to 55-65° C.

It is considered that the higher the ambient temperature is, the more rapidly chemical reactions proceed. But this is only partly true for the processes of decomposition and metabolism since involved in the process microorganisms exist at different optimum temperatures. The temperature abuse can lead to the microorganisms’ inhibition and even cause irreparable damage to them in extreme conditions.
Micro-organisms are very sensitive to temperature changes, in particular to its sudden drop, and slow down their metabolic and reproductive activity. The degree of the sensitivity, in turn, depends on the temperature boundaries of raw materials processing activity. The fermentation process can be performed at different temperature ranges:

- psychrophilic: ± 2 °C per hour;
- mesophilic: ± 1 °C per hour;
- thermophilic: ± 0.5 °C per hour.

This aspect performs a very big problem for the biogas production in the conditions of Siberian sharply continental climate, where winter temperature often shifts by 10-12 °C in two hours. Therefore, from this perspective it is advisable to use psychrophilic mode of anaerobic decomposition.

One more practical aspect should be mentioned, the self-heating effect, that was registered by the scientists the Kemerovo State Agriculture Institute during the experiments. This effect appears with adding substrates having in its structure carbohydrates, such as manure with particles of plant litter and roughage. Self-heating is explained by the fact that certain groups of micro-organisms in the process of decomposition of carbohydrates produce heat. This leads to the temperature increase from mesophilic mode up to 43-48 °C. Intensive analytical support and control over the process of temperature changes can be carried out with short-term, minor drop in gas produced. But without human intervention in the process, these microorganisms can not adapt to changes in temperature and even stop biogas producing.

An intensive analytical support and the process temperature changes regulation can make temperatures change be a short-term phenomenon to minimize the decrease of gas production. Absence of the temperature management leads to the microorganisms’ inadaptability to the temperature shifts and even to cessation of gas production.

The situation with pH value is similar to the situation with temperature. Different microorganisms need different pH values to ensure optimum growth, e.g. the optimum pH value for hydrolysing and acid-forming bacteria should be acid about 4.5-6.3, the bacteria forming acetic acid and methane can live only at a neutral or slightly alkaline pH level 6.8-8. At the same time, the metabolic activity and the level of reproduction of methane bacteria is lower than that of acid-forming bacteria. Increase in the amount of organic substances can turn out into an excess of volatile acids that reduces the methane bacteria activity as soon as the pH drops below 6.5. When pH reaches 4.3 methanogenesis stops as a result of poisoning of microflora with toxic undisassociated volatile fatty acids.

It is valid for all bacteria that the pH level exceeds the optimum rate, their vital activity slows down.

In the process of biogas production, the pH value within the system is established automatically under the influence of alkaline and acidic metabolic products that are formed during anaerobic decomposition, regardless of whether the process is single or multi-stage. But the degree of the balance sensibility to changes depends on the buffer capacity of the system itself.

The level of pH can be corrected by the amount and variety of added substrate. Rapidly oxidize substrates lead to a sharp pH drop; so they should be added gradually only in limited quantities.

Substrates differ in their ability to absorb the pH value. If the concentration of H⁺ increases, the substrates can align it in a limited amount and bind free ions to themselves. Due to this, the pH level in general remains stable. Only depletion of the binding and leveling capacity (when too many organic acids have accumulated), the pH value drops down.

As a result, the inhibitory effect of hydrogen sulphide and propionic acid increases, that can lead to the reactor’s overturning in a very short time. On the other hand, the pH can increase due to the decomposition of organic nitrogen compounds, that release ammonia from which ammonium is formed as a result of the reaction with water. As a result, the inhibitory effect of ammonia is increased. In any case, such a slowly measurable change in the content of H⁺ leads to delays in the development of bacteria and thus to a violation of gas generation. Regarding the process control, it should be mentioned that due to the pH value inertness it can be used only relatively. However, pH measurements, again due to inertia, lag behind the actual situation. While it is a cheap way to control
the system, the timely management of the process based only on measuring the pH level, is impossible. More effective is the measurement of buffer properties.

To maintain the stability of the anaerobic process, alkális can be used in concentrations up to 6000 mg/l. It is considered desirable that the ratio of the fatty acids number to the amount, for example, CaCO₃, should be at least 1:6.

For growth and vital activity of bacteria, it is necessary to have organic and mineral nutrients in the raw materials. Each variety of anaerobic microorganisms differs by a specific need for macr- substances, microelements and vitamins. The concentration and availability of these components affect the rate of growth and activity of different micropopulations.

There are minimal and maximum concentrations, depending on the type of microorganisms, which are difficult to determine due to the diversity of microorganisms and their adaptive capacity. To obtain methane as much as possible from the used substrates, it is necessary to ensure optimal supply of microorganisms with nutrients. As a result, the amount methane that can be obtained from the used substrates is determined by the content of proteins, fats and carbohydrates. These factors equally affect the specific nutritive requirement.

Stability of the process requires a balanced ratio of nutrient macro-substances and trace elements. In this case, the activity of the microbial reaction is largely determined by the ratio of carbon and nitrogen. Microorganisms require both nitrogen and carbon to assimilate them into their cellular structure. Therefore, the C / N ratio in the substrates is important. If this ratio is too high (many C and little N), the available carbon can not be completely processed due to insufficient metabolism, so that amount of methane do not reach its maximum. In the opposite case, the excess of nitrogen lead to excess amount of ammonia (NH₃), which even in small concentrations slows the growth of bacteria and can even result in death of the entire population of microorganisms.

Therefore, it is important to continuously maintain the C / N ratio in the range of from 10 to 30 to ensure the process stability. This can be achieved by the substrate supplying with a corresponding mass fraction of the missing substance to the reactor. Raw materials of different origin are significantly different from each other by the content of carbon and nitrogen and their ratio. An approximate ratio of carbon to nitrogen in different types of feedstock is given in Table 1.

**Table 1 – the C / N ratio in different types of raw materials for biogas production**

| Biofermentable material | Nitrogen N(%) | the C / N ratio |
|-------------------------|--------------|---------------|
| A. livestock manure     |              |               |
| cattle                  | 1.7 – 1.8    | 16.6 – 25     |
| poultry                 | 3.7 – 6.3    | 7.3 – 9.65    |
| horse                   | 2.3          | 25            |
| pig                     | 3.8          | 6.2 – 12.5    |
| sheep                   | 3.8          | 33            |
| B. plant dry wastes     |              |               |
| corn ear                | 1.2          | 56.6          |
| cereals straw           | 1            | 49.9          |
| wheat straw             | 0.5          | 100 – 150     |
| corn stover             | 0.8          | 50            |
| oat straw               | 1.1          | 50            |
| soya                    | 1.3          | 33            |
| lucern                  | 2.8          | 16.6 – 17     |
| sugar beet pulp         | 0.3 – 0.4    | 140 – 150     |
| C. others               |              |               |
| grass                   | 4            | 12            |
| sawdust                 | 0.1          | 200 – 500     |
| fallen leaves           | 1            | 50            |
Along with carbon and nitrogen, phosphorus and sulfur are also important nutrients. Sulfur is an integral part of amino acids, and phosphorus compounds are necessary for the formation of energy sources of ATP (adenosine triphosphate) and NADP (nicotinamide adenine dinucleotide phosphate). To ensure sufficient supply of microorganisms with nutrients, the C: N: P: S ratio in the reactor should be 600: 15: 5: 3 relatively.

Along with nutrient macro-substances for microorganisms, a sufficient availability of individual trace elements is vital. Most agricultural biogas plants cover the need for micronutrients by the use of animal excrement. Methanogenic archaea require cobalt (Co), nickel (Ni), molybdenum (Mo), selenium (Se), and partly tungsten (W). Ni, Co and Mo perform an essential part of cofactors in metabolic reactions. Also important micronutrients are magnesium (Mg), iron (Fe) and manganese (Mn), they are necessary for the transport of electrons and the functioning of certain enzymes.

In the world practice of biogas production [8, 9, 10], to accelerate the fermentation process or to increase the gas yield and improve its quality, various substances are added to the substrate during fermentation with a purpose to gain the best results. Origin and composition of these substances are the most diverse, ranging from simple chemical compounds to complex high-molecular organic systems. Regardless of their origin, composition and function in the process of methanogenesis, all these compounds can be determined as a catalyst.

All existing catalysts for biogas plants and their technological schemes have been developed and are being implemented in Europe, where the methods of anaerobic fermentation of organic waste processing are widespread and widely used. Currently there are very few such biogas plants in Russia, since such methods of utilization of organic materials are not widely used due to harsh climatic conditions. One of the options for solving the problem of inappropriate for the sharply continental climate technology of biogas producing is the use of catalysts.

In this regard, a group of scientists, graduate students and students of the Kemerovo State Agricultural Institute, basing on the data on the application of various catalysts in Germany collected by the University of Weihenstephan (Trisdorf, Germany), conducted a series of experiments to produce biogas from livestock waste with the addition of various catalysts under conditions of rigorous climate. The data of these experiments are given below.

Substrate before its introduction into the reactor was brought to the necessary humidity, taking into account the water contained in the whey, and subjected to preliminary dispersion to a particle size of 0.5-0.7 mm.

At loading the reactors, milk whey was added there in the volumes: 1, 5, 10 and 15% of the weight of the loaded substrate. For the fermentation of cattle manure, a psychrophilic fermentation regime with a temperature of 18 ± 1.5 °C was chosen. The test results are shown in Figure 1.

Milk whey due to its rich chemical composition, the presence of virtually all microelements and vitamins that are significant for the biogas release process has a significant impact on it. The results of the experiment showed that for the maximum production of biogas the most effective dose of whey application is 5%. At this concentration, the highest and constant biogas yields are observed, but the quality of the gas deteriorates significantly, the methane content in it is only 47%. Probably, this is due to the fact that this concentration of substances stimulates more hydrolytic microorganisms, which release carbon dioxide in large quantities in the course of their vital activity, that leads to an increase in the total biogas yield, as well as to its "dilution" and deterioration in its quality.

At the same time, small concentrations of milk whey influence directly on methanogenic archaea, partly inhibiting the remaining strains of microorganisms and increasing the proportion of methane, but with little effect on the overall yield of biogas during the first stages of fermentation, and subsequently depressing the whole process.
Figure 1 – Change in biogas yield during anaerobic processing of cattle manure with the addition of various concentrations of milk whey.

The most rational dose of milk whey is 10% of the weight of the raw material, since it showed an optimal combination of the gas yield and its quality. The methane content of the biogas sample from this reactor was 58%, and the volume released was only 0.2 m$^3$ less than when 5% of the whey was added. Probably, it is this dose of milk whey that combines the optimal ratio of nutrients, microelements and vitamins for all groups of bacteria involved in the process of biogas formation.

4. Conclusions
The work gives an observation of the process of biogas release, in which microorganisms are one of the most important factors, and one of the determining factors is the methanogens that directly release the final product. Metanogenesis, parameters and conditions of the technological environment of its production have been studied. Optimum temperatures of the fermentation process are examined: natural conditions and Siberian zone with sharply continental climate.

Stability of the anaerobic fermentation process is also ensured by using alkali in concentrations up to 6000 mg/l. For the growth and stability of the bacteria life, it is necessary to obtain organic and mineral nutrients in the raw material and a balanced ratio of nutrient macro-substances and microelements.

One of the solutions to the problem for the sharply continental climate is the development of technologies for producing biogas using catalysts. One of these catalysts is milk whey.

During the experiments whey was added in the reactors in volumes: 1, 5, 10 and 15% of the weight of the loaded substrate. For the fermentation of cattle manure, a psychrophilic fermentation regime with a temperature of 18 ± 1.5 °C was chosen.

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