

- CONFERENCES -

**TECHNICAL AND TECHNOLOGICAL SOLUTIONS TO INCREASE  
THE BIOGAS PRODUCTION EFFICIENCY IN THE AGRO-INDUSTRIAL  
WASTE WATERS TREATMENT**

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**ABSTRACT**

A modified biogas technology was elaborated for the treatment of agricultural wastewaters, using the phyto-catalysts for managing the biochemical processes (Covalov, V., Malina, J.F. et al. 2014). To implement the proposed technology, an integrated bioreactor design has been developed. To manufacture a pilot reactor, the available equipment at the “Bardar” Winery (Republic of Moldova) has been used and modernized. As a feedstock for the biochemical digestion a post-distillery vinasse in a mixture with cattle manure was used, to ensure rapid initiation and development of methanogenic process, due to the high contents in methanogenic microorganisms in manure. The ecological effect was due to the preventing of discharges of 15,7 m<sup>3</sup> biomass/day, or total amount of 24000 m<sup>3</sup> of untreated hazardous concentrated wastes into the natural water bodies (during the bioreactor operation period). Initial concentration of organics in feedstock was 27400 mg O<sub>2</sub>/l (COD), and after the anaerobic and following microfiltration treatment was approx. 187 mg O<sub>2</sub>/l.

**1. INTRODUCTION**

Production of biogas is an important part of the general concept of sustainable development, based on the production of high-energy fuel agents from the renewable plant raw materials, in view of the partial substitution and savings of nonrenewable hydrocarbon fuels – oil, coal, natural gas. The research has shown that under the anaerobic conditions, xenobiotic organic pollutants, non-biodegradable under aerobic conditions, may be converted biologically and then be removed under the aerobic conditions (Lema J.M. and Omil F., 2001). The development of anaerobic fermentation technologies using the liquid and solid wastes from the agricultural products processing industries is one of

perspective directions in the biogas production from plant raw materials and agricultural organic wastes (Speece R.E., 1996). The energy materials can serve the winery, brewery, yeasting and dairy wastes, different kinds of solid and liquid processing wastes of cereals, potatoes, sugar beets, fruits and vegetables, etc.

Anaerobic fermentation has been broadly used in wastewater treatment since 30-ies of the twentieth century, first to stabilize the sludge from wastewater, and later - even for the treatment of industrial polluted wastewater with high organic contents. However, due to high fermentation time needed (10-20 days under the mesophilic conditions at temperatures of ~ 30 ° C, and few months under the cryophile temperature conditions, at ambient temperature), the process was not very widespread because of high volume of reactors, although it had many advantages over the aerobic liquid waste treatment process. The problem is that the doubling time of strictly anaerobic metanogene microorganisms (the main of which are *Methanothrix* and *Methanosarcina*), which is between 10-20 days, and accordingly, the hydraulic retention time of sewage water or sludge subjected to anaerobic fermentation in bioreactors with suspended microflora, could not be less. This period may be reduced by recirculating of active microflora, but its separation from the treated medium is problematic because of its weak precipitability.

The significant reduction of the hydraulic retention time with regard to the microflora retention time in bioreactor (which must not be less than the doubling time of organisms - 10 to 20 days) became possible with application of biological treatment processes through the immobilization of active microflora on solid support inside the bioreactors (anaerobic filters), or growth and development of granular microflora (UASB bioreactors) and, more recently, the fluidized layer of material with fixed bacteria. In this case the biodestruction of organic pollutants was possible during the retention time ten times less, compared to the classical bioreactors with suspended microflora, this time ranging from 6 to 14 hours, and there was no longer need to recycle microflora. Such technology made it possible the broad application of anaerobic fermentation of wastewater (Lettinga G.L. et al. 1984).

The anaerobic treatment technology is most common for the industrial wastewaters, especially the food industry and in zootechnics, including in Moldova (Avicola, Vad-lui-Voda, cattle-breeding farm, Colonitsa - implemented with the assistance of Dutch companies). The most powerful company in this field is Biomethane, which has built over 500 reactors located in 40 countries, using the microflora granular UASB process for wastewater treatment in more than nine industrial branches.

The biochemical processes have high potential for the production of alternative renewable fuels, including biomethane and biohydrogen. However, the additional research is needed to identify the ways of intensification of biochemical processes, which would allow to reduce the dimensions and operation costs of bioreactors, to increase the yield of target products, to increase the valoric value of their combustion, to ensure the ecological safety due to the improving of treatment degree of waste waters and toxic wastes, and to obtain as a solid phase the useful products which may be used as fertilizers of forage additives in cattle breeding.

### **PERSPECTIVES OF BIOGAS TECHNOLOGY**

The experience in using and building of biogas plants in Moldova is not sufficient. One explanation for this is lack of scientific and technical knowledge and experience of construction and operation of biogas plants. No real technical concepts in this area, and lack of reliance on scientific personnel, has resulted, for example, built on the foreign investment the only two biogas plants at poultry factory «Vinicola» in the village Vadul-lui-Voda, and cattle-breeding complex in the Colonitsa village practically not exploited because of the approved administrative and technical errors.

Despite the seeming simplicity of the technical solutions, this technology is fraught with many subtle biochemical aspects depending on the type of biochemically of feedstock and other factors. At the same time, technological advances pose new challenges to improve the technology so as to obtain economic benefit from the implementation of secondary mineral products, including biogas with high methane content in it, the improved performance of wastewater treatment for the prevention of environmental risks in their discharge, sediments with their high yield characteristics for recycling. This requires the improvement of biogas technology, with the highest possible automation of these processes, in that directed this project. This is a necessary condition of increasing the competitiveness of such plants, which can be achieved continuous improvement of biochemical technology and enhancing its efficiency, reduce their costs, primarily - by reducing the payback period and obtain economic benefits through the use of reproducible energy plant resources, with the implementation of secondary mineral products - biogas.

A similar situation is observed in other Black Sea countries: Russia, Romania, Bulgaria, Turkey, Georgia, Greece. Thus, the market of biogas technology in Moldova and other countries in the Black Sea region urgently needs an effective, low-cost autonomous biogas plants for treatment of various types of organic waste and sewage. These settings are of interest, both for the collective consumers (farms, etc.), and for industrial processing enterprises.

### **CONCEPT OF BIOCHEMICAL TREATMENT OF AGRO-INDUSTRIAL WASTE WATERS**

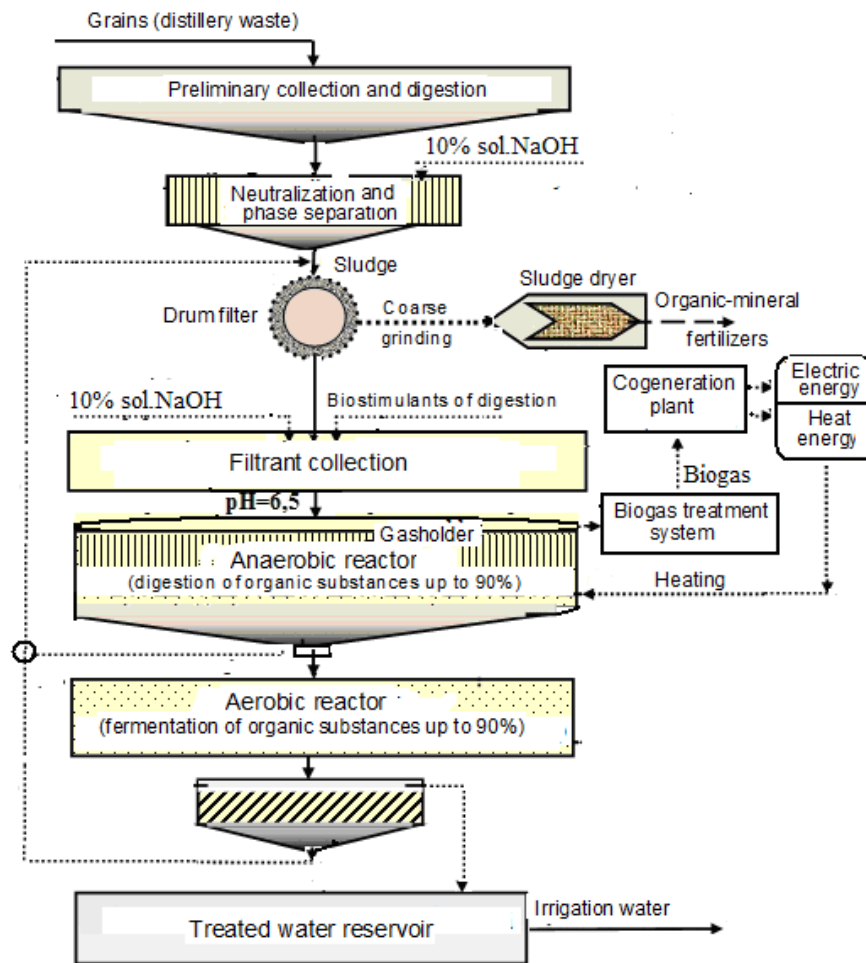
The new technology of anaerobic digestion of the distillery grains is based on the using of biostimulators and special equipment for the intensive biochemical treatment, with the enhancing of biogas or biohydrogen yield, with high caloric contents of the produced biomethane, and high efficiency of its using in the cogeneration systems of heat and electric energy, as well as the production of vitaminized sludge that can be used as the additive for cattle feeding or as an organic fertilizer for agricultural crops. The proposed technology also makes it possible to partially reuse the treated water for technological needs or irrigation.

The technology involves the following technical solutions, some of them having no analogs in the world:

- new stimulating microadditives of anaerobic fermentation and methanogenesis processes, among them the vegetal oils with the contents in phyto-regulators of isoprenoid nature with work concentrations within the range  $1 \cdot 10^{-3} \div 1 \cdot 10^{-4} \%$ , isolated from the vegetable sources;
- novel industrial method of the production of new biostimulators of anaerobic digestion of BIOSTIM-CH<sub>4</sub> or BIOSTIM-H<sub>2</sub> type, and creation of the sectors for cultivation of vegetable raw materials and production of the commercial compositions of the proposed preparations;
- manufacturing of the new integrated bioreactor with the improved mass-exchange, separation and isolation of formed gases, solid and liquid phases;
- equipment for optimization of operation conditions and ensuring the technological control and management of biochemical process;
- cheap and available raw materials on the base of the wastes: melusa - the wastes of the limestone sawing for the neutralization of winery grains; the substrate for microflora fixing – grapevine, etc.

As a result of using of the new biologically active additives, combined raw materials and new equipment proposed for intensification of anaerobic digestion and methanogenesis, at the distillery grains and winery wastewater treatment (with the initial COD 60-80 g/l), the following ecological-economic outcomes will be reached:

- a significant decrease in power consumption for the treatment of mentioned liquid wastes, due to the intensification of biochemical processes through modification of thermophilic conditions in mesophilic ones and using of the produced biogas as an energy agent;
- intensification of anaerobic digestion of organic wastes using the biologically active microadditives in 2-2,5 times, due to the shortening of methanogenic fermentation time up to 18-36 hours and the essential reducing of capital investments;
- due to the intensification of biochemical processes, the bioreactor construction costs will be up to 1,5-2 times decreased;
- increase in the biomethane contents in biogas from 55-70% to 80-90%, as well as the increase in the caloric value from 5000-5500 kkal/m<sup>3</sup> to 7000-8000 kkal/m<sup>3</sup>;
- more intensive treatment of the distillery grains, by 15 - 20% more intensive compared to the conventional methods, with the possibility to reuse up to 50-80% of purified water for the technical needs of an enterprise;
- the dried stabilized sludge, enriched with vitamin B<sub>12</sub>, can be used as a supplement for cattle forage or as an organic fertilizer.



**FIGURE 1.** General scheme of the waste water treatment from the alcohol production.

The developed Concept (Fig.1) makes it possible to transform the technology of the distillery grains treatment into the practically wastes-free technology, and cardinally decrease the negative impact on the natural environment, as well as to produce the following useful products:

- Purified water, up to 80% of which may be reused for the technical or production needs at the enterprise;
- Dried stabilized sludge enriched with vitamin B<sub>12</sub> that can be used as the supplement for cattle forage or as an organic fertilizer;
- Biogas with the contents in 80-90 % of biomethane, with the volume exceeding 0,5-0,6 m<sup>3</sup> per 1 kg of COD, which can be realistically used in place of the natural gases for cogeneration of heat and electric energy, or can be used for technical needs;
- A possibility to purify the biogas from the aggressive admixtures of H<sub>2</sub>S and CO<sub>2</sub>, that can enlarge the spheres of its utilization;
- Production of cheaper electric and heat energy, using biogas;

- Appearance of a new perspective method aimed at the selective production of biohydrogen with the cheaper biochemical method, for the development of hydrogen power engineering.

### **TESTING OF PILOT ANAEROBIC BIOREACTOR**

The proposed technology of wastewaters anaerobic treatment in the bioreactors with fixed microflora (anaerobic biofilters) was tested at the „Bardar-Vin” S.A. Company in Moldova. The 36-m<sup>2</sup> pilot anaerobic biogas reactor has been constricted (Fig.2), at which the regimes of biogas technology of anaerobic fermentation of winery vinasse have been tested in view to determine the optimal operation parameters. To make the construction cheaper, the reservoirs and other auxiliary equipment are available at the winery. This made it possible to reduce the capital costs. As a substrate for microflora fixation, the dried grapevine was used with the diameter of 2-3 mm and package density under the compression 3-5 kg/dm<sup>2</sup>. The grapevine had the composite curved form, is stable under the conditions of anaerobic fermentation of winery wastewaters, ensures the good adhesion of microflora on its surface. Its active summary surface was 100-120 m<sup>2</sup>/m<sup>3</sup> of bioreactor bulk. As a gasholder, the elastic polypropilene tissue (thickness 1 mm) was used.



**FIGURE 2.** General view of the biogas reactor at Bardar Winery, Moldova

As a feedstock for the biochemical digestion a post-distillery vinasse in a mixture with cattle manure was taken, to ensure rapid initiation and development of methanogenic process, due to the high contents in methanogenic microorganisms in manure. As a result of the pilot bioreactor

operation under the mesophylic regime, the biogas yield per 1 kg COD made in average 0,5 m<sup>3</sup> with 60-70% contents in methane with the calorificity of 25,9 mJ/m<sup>3</sup>. The summary amount of biogas made 79,65 m<sup>3</sup>/day. The biogas thus produced can be used for different scopes, although its application depends on its composition and quality. Its using for cogeneration of heat and electric energy is especially profitable, as well as for the heating of sludge during the digestion and optimization of temperature regime of biochemical processes, and also for other scopes. To improve the energetic efficiency of biogas equipment, it was recommended to use the systems of the combined production – cogeneration of electric and heat energy. By the assessments, the amount of produced electric energy will make 141,7 kWt/h, and the heat energy – 0,244 Gkal/day. The operation time of the biogas reactor (considering the seasonal operation of winery) was 102 days within a year.

The ecological effect was due to the preventing of discharges of 15,7 m<sup>3</sup> biomass/day, or total amount of 24000 m<sup>3</sup> of untreated hazardous concentrated wastes into the natural water bodies (during the bioreactor operation period). Initial concentration of organics in feedstock was 27400 mg O<sub>2</sub>/l (COD), and after the anaerobic and following microfiltration treatment is was apprx. 187 mg O<sub>2</sub>/l.

It was shown that the proposed technology of wastewaters anaerobic treatment in the bioreactors with fixed microflora (anaerobic biofilters) makes it possible to reduce the treatment time to 1-2 days, and in case of the low initial concentrations of biodegradable organic substances (specific for the household wastewaters) - even to 4-8 hours, which is 5-30 times less than the appropriate time in the conventional metatanks with the suspended microflora (anaerobic active sludge). This means that the volumes of bioreactors can be reduced essentially. The long-term experiments (2 years) of pilot in Bardar, Republic of Moldova, has shown that this type of bioreactors is less sensible towards the temperature variations, organic loads and even the long-term interruptions (from one day to several months) of feeding with wastewaters. This imparts to this process the very high durability and flexibility in operation.

**Acknowledgement:** This research has been performed under the STCU (American Science and Technology Center in Ukraine) grants # 5832 and # 5998.

## **REFERENCES**

1. Covalov, V., Malina, J.F., Duca, Gh., Covaliova, O., Bobeica, V. (2014) 'Application of Bioactive Substances in the Biogas Technology'. In: Management of Water Quality in Moldova. Ed. Gh.Duca. Springer, pp. 225-241.
2. Lema J.M. and Omil F. (2001). 'Anaerobic Treatment: a key technology for a sustainable management of wastes in Europe' **Water Sci. and Tech.**, Vol. 44, No.8, pp. 133-140.
3. Lettinga G.L. et al. (1984). 'High-rate Anaerobic Wastewater Treatment Using the UASB Reactor under a Wide Range of Temperature Conditions' **Biotech. and Genetic Eng. Rev.**, Vol.2, pp. 253-284.
4. Speece R.E. (1996). 'Anaerobic Biotechnology for Industrial Wastewaters' Vanderbilt University, 416 p.