Sylwester BOROWSKI[1], Piotr DOROSZEWSKI[2], Jerzy KASZKOWIAK[1], Edmund DULCET[1], Jan MIKOŁAJCZAK[2]
Uniwersytet Technologiczno-Przyrodniczy w Bydgoszczy, Wydział Inżynierii Mechanicznej
[1] Zakład Techniki Rolniczej, [2] Katedra Żywienia Zwierząt i Gospodarki Paszowej
ul. Prof. S. Kaliskiego 7, 85-789 Bydgoszcz, Poland
e-mail: sylwa@utp.edu.pl

APPLICATION OF THE ADDITIVES WHICH INCREASE THE BIOGAS PRODUCTION IN THE CONTEXT OF IMPROVEMENT OF THE BIOGAS PRODUCTION PROCESS

Summary

This paper presents the review of the latest additives which are used for ensiling the substratum used in the biogas production process. Moreover, the influence of the additives' proper usage on the improvement of the ensilage productivity has been valued. What is more, the research shows that these kinds of additives are very useful to be put into practice. It results not only from leading the fermentation process in a way that would increase the biogas output, but also from reducing the energy losses caused by the secondary heating of the ensilage after opening of the silos. This thesis also points out the opportunity to limit the amount of employed additives through improvement of the quality of their usage.

***Key words**: biogas, production, substratum ensiling*

1. Introduction

Renewable energy sources are an important branch of economy considering present financial and legal realities. One of the most important sources of renewable energy is the biomass. It occupies a significant percentage in global energy production. The methods of its conversion into the energy used by men are constantly in demand. One of the methods is generation of the electric and thermal energy in agricultural biogas works. In order to ensure the biogas works with constant material and make them independent of the seasonal occurrence of the substratum, the ensilage is being used to supply them. In European terms, the basis plant used as a substratum for biogas works is maize. The maize is harvested by the use of collecting chaff-cutter. Then the chaff is brought to the storage places and formed into silos [3, 4].

2. Results of the preservatives

Lactic fermentation, which is produced by lactic acid bacteria, is a common method of preservation of the vegetable material, which is designed for fodder production and for gaining the substratum for the biogas works [9, 10]. The technology of making ensilages, which are used as a batch-coenzyme in the biogas production in agricultural biogas works, is almost the same as the one used in ensiling fodder for ruminant animals (cattle and sheep). The purity of the ensiling material has a great influence on the fermentation process itself, as well as on the quality of the given ensilages. It is not allowed to feed animals with bad and mouldy ensilages. Moreover, bad ensilage is not suitable for the biogas production, because it is its quality that is crucial for the amount of the obtained gas which contains bioethane [27]. Strong contamination of the biomass with soil causes that the biomass contains a lot of clostridium bacteria. Those bacteria cause the secondary fermentation (butyric fermentation) in the stable phase of ensiling. Sacharalytic species crack sugars that are indispensable for the lactic bacteria, while proteolysis species crack protein [16]. Disintegration of this alimentary ingredient leads to the creation of amine and aminoacids which hamper the growth of methanogenic bacteria. Whereas mould produces mycotoxins (secondary metabolites), which also hamper the growth of those bacteria which causes the reduction of the biogas production efficiency [27].

However, there are two basic differences considering grinding the material for ensiling and the fermentation's volatile products composition of ensilages. The browse which is ensiled as a fodder should be cut into chaff 15-30 mm long. It comes out of the physiological needs of ruminants (proper saliva secretion, masticator fermentation stabilization, etc). However, when it comes to the material for biogas works, the cut should be smaller 4-8 mm which increases the surface available for the bacterial enzymes, thereby improves the amount of the biogas production [27].

In view of the fermentation process conducted by the lactic bacteria, they are divided into homo- and hetero-fermentative. The first group, above all, produces lactic acid and marginal amounts of acetic acid. The later produces lactic, acetic and propionic acids and other fermentation products as alcohols [15]. Yet, vegetables usually contain insufficient amount of the lactic acid's epiphytic bacteria. They would have provided a proper course of fermentation [11, 14] which can be supported by ensiling supplements f. ex microbiological [12, 26].

There have been two groups of the ensiling supplements distinguished: fermentation inhibitors and fermentation stimulants. Both contain chemical preservatives, biological supplements or mixed [5, 6, 15]. First ones quickly acidify the biomass and break the natural process of lactic fermentation and prevent the growth of injurious micro flora. The second group concerns biological supplements that are supposed to support and direct the ensiling process. The third group concerns combined Additives compound of a biological and chemical part. The biological part helps in the fermentation process, while the chemical part prevents the ensilage from stability loss during its growth and picking [5, 6, 9, 15]. Selected ensiling supplements are presented in the Table 1.

Considering the production of the ensilage for the ruminants, it is important that the given fodder has a lot of lactic acid and smaller content of the acetic acid. Natural fermentation process intended for the ruminant fodder leads to the formation of a large amount of lactic acid. Supporting the process with different ensiling additives, which contain homofermentative bacteria, causes the fermentation to produce large amounts of these acid and smaller amounts of acetic acid. It makes the ensilages useful for the animals, however they have small oxygen durability [5, 9, 15, 20, 24, 29, 30]. This kind of ensilage used as a batch-coenzyme in biogas work has a limited application because methane bacteria can only poorly decompose lactic acid, while volatile products of fermentation, such as acetic and propionic acids and alcohols are decomposed better [9, 10, 24, 32]. That is why, for ensiling vegetables for this purpose, it is recommended to use ensiling additives which contain lactic heterofermentative bacteria, especially *lactobacillus buchneri*. They will not cause the future batch- coferment to be excessively acidified with lactic acid but with acetic acid [9, 22]. Nevertheless, heterofermentative process causes fermentative loss [1, 20, 28].

One of the basic parameter for the rating of the quality of the ensilages is the content of the acetic acid, which is fungistatic compound and it increases the oxygen durability of the ensilages. Concentration of the undissociated acetic acid on the 8 g kg^{-1} level of the fresh mass hampers the growth and development of the fungi and yeast [16, 23]. However, dry mass should not contain more than 3,5% [31]. In the ensilage production for energetic purposes, the quality of the gained substratum has to be very high in order to ensure good efficiency of methane [9]. What is more, it should contain more acetic acid which is essential in the acetic stage of the biogas production [2, 9, 19]. Nevertheless, Plöchl et al. [25] claim that at this stage, the acetic acid's concentration in the ensilage is not so important as the size of its production. Products such as lactic, acetic, butyric acids, ethanol and propylene glycol made during the fermentation have to improve the conditions of the methanogenesis and increase methane efficiency [19, 25], however the lactic acid bacteria have little influence on the efficiency of this gas [9, 20]. Ensiling supplements usage effect may also depend on the ensiling material [1, 7, 13, 21, 24, 25, 28].

Formic acid, enzymes and inoculant have increased the productive potential of methane from ensiled beetroot's heads and grasses by 19-22% [13]. Concidering maize, the growth was by 16%, hemp 50%, yet there were no effect concidering beans. While urea has increased the methane production from hem ensilage by 25-42% [24]. The use of the additive of the homo- and heterofermentative bacteria or their mix for ensiling different materials have increased the efficiency of methane comparing with the control ensilage [1, 2, 20]. Lactobacillus buchneri bacteria PTA 6138 increased the methane production from grasses and maize by 8% and improved its viscosity suspension in the fermenter. It resulted in lowering the intensity of blending, which cut the cost of electricity used to the process and it decreased the mechanic use of the agitator [28]. This strain consists of an enzyme – ferulic esterase, which decompose lignin which is a part of a plant's cell wall. It improves the availability of substratum that are needed for methane fermentation [18].

The research demonstrated that lactic homofermentative bacteria and chemical additives (i.e mixture of sodium nitrite, sodium benzoate, sodium propionate, potassium sorbate and hexamine) have a positive influence on the quality of ensilages from lucerne.

Table 1. The efficiency of the methane depending on the used materials and additives

Additive	Raw materials	Efficiency methane gas	Author
lactobacilli homo- + hetero-	corn plant, all	97,6 l kg^{-1} silage	Banemann et al. (2008) [1]
name not given	corn plant, all	309-339 m^{3} t^{-1} DW$_{C}$	Banemann et al. (2009) [2]
Mais Kofasil® liquid	corn plant, all	~320 l kg^{-1} DWO	Heiermann et al. (2007) [7]
Biosil		~340	
Bonsilage Plus		~345	
Silasil Energy		~360	
Formic acid	grasses	0,26 - 0,28 m^{3} kg^{-1} VCO	Lehtomäki (2006) [13]
xylanase, cellulase		0,21 - 0,22	
AIV		0,20 - 0,21	
mixture of bacteria from the biogas reactor		0,20 - 0,21	
Formic acid	heads of sugar beet	0,24 - 0,36	
xylanase, cellulase		0.22 – 0,27	
AIV		0,25 - 0,32	
mixture of bacteria from the biogas reactor		0,28 – 0,37	
lactobacilli homo-	ryegrass	311,4 kg^{-1} DWO$_{C}$	Nussbaum (2012) [20, 21]
lactobacilli hetero-		312,0	
Formic acid	corn plant, all	~375 - ~450 dm^{3} CH_4 kg^{-1} VC$_{C}$	Pakarinen et al. (2011) [23]
Formic acid	cannabis	~335 - ~360	
Urea		~300	
Formic acid	faba bean	~290 - ~360	
Kofasil® liquid	grasses	251,9 m^{3} t^{-1}	Plöchl et al. (2009) [25]
lactobacilli homo-		337,6 - 369,8	
Kofasil® liquid	lucerne	~ 225	
Kofasil® life		201,5	
Mais Kofasil® Liquid	corn plant, all	308,2	
Kofasil® stabil		324,7	
Kofasil® lac		319,7	
Pioneer 11CH4	corn plant, all grasses	~90-~330 ml kg^{-1} DWO$_{C}$	Ruser et al. (2009) [28]

DWO - dry weight organic; DWO$_{C}$ - dry weight organic corrected; DW$_{C}$ - dry weight corrected; VC$_{C}$ - volatile components corrected; VCO - organic volatile components

Nevertheless, increased methane efficiency does not cover the costs of the additives. Maize has given the opposite results. Moreover, there is no clear correlation between the amount of acetic acid in the ensilage and the efficiency of the biogas made from dry organic mass. However, that relation exists between the sum of all fermentative acids (acid concentration: lactic, acetic, butyric, propiane in the dry mass) and the methane efficiency from dry organic mass. Ensiling additives should increase the amount of organic acids and lower the risk of losses in the oxygen conditions [25].

The preservation of the productive potential of the biogas made from the grass and white beet's head ensilage ensured the usage of the mixture of bacterial cultures from biogas production in agricultural bioreactor. This solution occurred to be economically beneficial.

Ensiling supplements used in the above mentioned research were mostly used in the ensilage production for the animals. That is why some authors claim, that it is necessary to run some research considering the influence of the ensiling process of the crops on the methane efficiency and the development of special ensiling additives predestined for the production of the ensilage as a substratum for the biogas work [7, 25]. German Agriculture Society (DLG) has designed a test procedure for evaluating the influence of ensiling supplements on the methane efficiency. It consists in the analysis of the fermentative loss in the oxygen and oxygen-free conditions and the evaluation of the efficiency of the biogas obtained from the analyzed ensilage on the basis of the HBT test (Hohenheim Biogas Yield Test according to [8]). The evaluation is completed by the static analysis [20, 21].

3. Research – losses of additives

For the sake of the experiment, the finish applicator Junkkari HP 5 has been used. It is built out of (fig. 1) centrifugal pump with the 12 V electric motor powered from the tractor's wiring system, mechanical flow regulator, antisewer valve and beam with two slotted atomizers of the RS MM 110o/04 type, red color.

The applicator is mounted on Silage trailers JUMBO Pottinger.

Fig. 1. JUNKKARI HP5 applicator

Additives application inequality indicator did not exceed 2% for the atomizers used in the analysis.

The beam with the atomizers of the Junkkari HP 5 applicator has been placed at two different points on the collector trailer:

- in front of the pickup unit (a shaft of browse has been watered),
- above the pickup unit.

A 5% aqueous solution of sodium chloride has been used as an additive. It was added in the amount of 2,5 dm^3 t^{-1} of the browse. The size of the loss of the additive (5% aqueous solution NaCl) has been estimated on the basis of concentration marks of Cl$^-$ ions. The size of these losses has been estimated in the ratio of the amount of the additive which remained on the measurement plates to the set amount according to formula:

$$S = \frac{V_p}{V_z} \cdot 100\,\%$$

where: S – additive loss, %

V_P – the amount of the additive that remained on the control plates, dm^3 t^{-1},

V_Z – the additive set amount, dm^3 t^{-1}.

The aggregate moved with the speed that was congruent with the agrotechnical specifications for the browse collection for the ensilage. Three plates with vinyl polycarbonate, which ensured that the whole operating width of the aggregate has been measured.

When the aggregate had driven, the additive that remained on the measurement plates was rinsed with the use of distilled water. A solution received as a result of rinsing the remained substratum from the basic (plate) has been placed in the glass containers. Cl$^-$ ion marks have been done by the mercurimetric method with the use of mixed diphenylocarbazone with bromephenol blue in the acid environment [17].

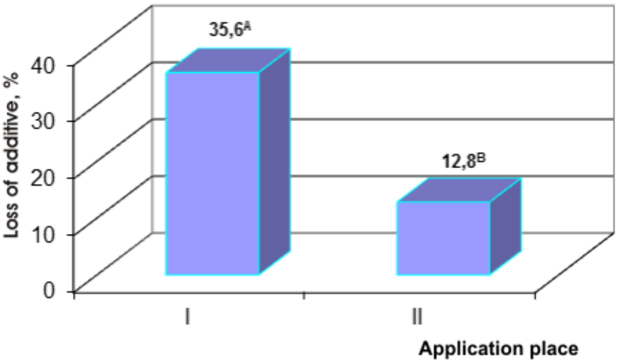

Fig. 2. Losses of the preparation depending on the place of its application: I - in front of the pickup unit (a shaft of browse has been watered), II - above the pickup unit. Values marked with letters vary considerably in terms of statistics ($p \leq 0.01$)

Based on the research and the statistical analysis of the obtained results say that the installation place of the applicator's atomizers has a great influence on the size of the additive loss. The lowest additive loss occurred when it was applying into the vegetable material above the pickup unit. It comes out of the fact that, the additive which does not cover the browse falls down on the working units. There the additive is successively taken away with moving groups of vegetable material.

4. Conclusion

The conversion of the biomass into electric and thermal energy should take place with the highest efficiency. One of the ways is reduction the loss connected with ensiling and storing the substratum as the ensilages. There are plenty Additives available on the market which can help in obtaining a good quality ensilage. In practice, farmers use supplements that facilitate ensiling for the fodder as well as for the substratum production. However, in that case, only those additives should be used which would guarantee obtaining greater amount of biogas during processes conducted in a pile.

The other way is to cut the costs of using Additives. The simplest procedure is to limit the additive loss, because the losses could be significant, as it was presented in the discussed experiment.

5. References

[1] Banemann D., Mayrhuber E., Schein H., Nelles M., 2008. Effect of homo- and heterofermentative silagen additive on the methan yield of mais silage. Proc. of 13th Int. Conf. Fooder conservation, Nitra, Slovak Republic, 156-157.

[2] Banemann D., Nelles M., Thaysen J., 2009. Silages as feedstock for biogas: Novel perspectives for silage additives. Proc. of XVth Int. Silage Conf., Madison, Wisconsin, USA, 355-356.

[3] Borowski S. 2012. Controlling Rate Of Delivery Of Applicators At The Harvest Of Substrates Biogasworks - Preliminary Issues, Journal of POLISH CIMAC, Vol. 7 No 3, pp: 17-22.

[4] Borowski S., Dulcet E., Kaszkowiak J., Bujaczek R., Chojnacki J. 2012. Ballers For Molding Bales Of Shredded Material, Journal of POLISH CIMAC, Vol. 7 No 3, pp: 23-28.

[5] Dorszewski P.A., 2009. Efektywność stosowania dodatków kiszonkarskich w konserwacji zielonek z mieszanki motylkowato-trawiastej oraz z całych roślin kukurydzy. Rozprawy nr 136. Wyd. Ucz. UTP, Bydgoszcz.

[6] Dorszewski P., Grabowicz M., 2010. Kiszenie pasz i dodatki kiszonkarskie. [W:] Biochemia i biotechnologia w produkcji rolniczej. Red. E.R. Grela. PWRiL, Warszawa, 248-260.

[7] Heiermann M., Herrmann C., Idler C., Scholz V., 2007. Optimisation potential of the supply of crops as feedstock for biogas production. Conf. Proc. Zemědělská technika a biomasa 4, 42-50.

[8] Helffrich D., Oechsner H., 2003. The Hohenheim Biogas Yield Test. Agric. Engineering 58, 148-149.

[9] Kalač P., 2011. The required characteristics of ensiled crops used as a feedstock for biogas production: a review. J. Agrobiol. 28, 85-96.

[10] Köfinger P., Grabherr R., Eikmeyer F.G., Zakrzewski M., Schlütter A., Mayrhuber E., Schwab H., 2012. Metagenomic analysis of a microbial community isolated from silagen. Proc. of XVIth Int. Silage Conf., Hämmenlinna, Finland, 350-351.

[11] Kung L.Jr., 2010. Understanding the biology of silage preservation to maximize quality and protect the environment. Proc. California Alfalfa & Forage Symp., Visalia, CA, 41-54.

[12] Kung L.Jr., Myers C.L., Neylon J.M., Taylor C.C., Lazartic J., Mills J.A., Whiter A.G., 2004. The effect of buffered propionic acid-based additives alone or combined with microbial inoculation on the fermentation of high moisture corn and whole-crop barley. J. Dairy Sci. 87, 1310-1316.

[13] Lehtomäki A., 2006. Biogas production from energy crops and crop residues. PhD Thesis, University of Jyväskylä, (SF). Jyväskylä Studies in Biological and Environmental Science 163, Jyväskylä (SF).

[14] Lin C., Hart R.A., Bolsen K.K., Dickerson J.T., Curtis J.L., 1990. Indigenous microflora on alfalfa and corn, and populations changes during ensiling. Proc. Cattlemen's Day, Kansas State University, Manhattan, KS, 118-122.

[15] McDonald P., Henderson A.R., Heron S.J.E., 1991. The biochemistry of silage. Chalcombe Publications, Bucks.

[16] McEniry J., O'Kiely P., Clipson N.J.W., Forristal P.D., Doyle E.M., 2006. The microbiological and chemical composition of baled and precision-chop silages on a sample of farms in County Meath. Irish J. Agric. Food Res. 45, 73-83.

[17] Minczewski J., Marczenko Z. 1978. Chemia analityczna, PWN, Warszawa.

[18] Nsereko V.L., Smiley B.K., Rutherford W.M., Spielbauer A., Forrester K.J., Hettinger G.H., Harman E.K., Harman B.R., 2008. Influence of inoculating forage with lactic acid bacterial strains that produce ferulate esterase on ensilage and ruminal degradation of fiber. Anim. Feed Sci. Technol. 145, 12-13.

[19] Nussbaum Hj., 2009. Effects of different fermentation products on dynamism and yield of biogas. Proc. of XVth Int. Silage Conf., Madison, Wisconsin, USA, 435-436.

[20] Nussbaum Hj., 2012. Effects of silage additives based on homo- and heterofermentative lactic acid bacteria on methane yields in the biogas processing. Proc. of XVIth Int. Silage Conf., Hämmenlinna, Finland, 452-453.

[21] Nussbuam Hj., Staudacher W., 2012. Methane yield – a new DLG-test scheme for silage additives. Proc. of XVIth Int. Silage Conf., Hämmenlinna, Finland, 450-451.

[22] Oude Elferink S.J.W.H., Dreihuis F., Krooneman J., Gottschal J.C., Sierk F., 1999. Lactobacillus buchneri can improve the aerobic stability of silagen via a novel fermentation pathway: the anaerobic degradation of lactic acid to acetic acid and 1,2-propanediol. Proc. 12th Int. Silage Conf., Uppsala, Sweden, 266-267.

[23] Pahlow G., 2004. Erfahrungen mit Mikroorganismen in der Silierung. 20. Hülsenberger Gespräche. Mikrobiologe und Tierernährung. Lübeck, 85-93.

[24] Pakarinen A., Maijala P., Jaakkola S., Stoddard F.L., Kymäläinen M., Viikari L., 2011. Evaluation of preservation methods for improving biogas production and enzymatic conversion yields of annual crops. Biotechnol. Biofuels 4:20.

[25] Plöchl M., H. Zacharias, C. Herrmann, M. Heiermann, A. Prochnow., 2009. Influence of silage additives on methane yield and economic performance of selected feedstock. Agric. Eng. Int.: the CIGR Ejournal XI., 1-16.

[26] Polan C.E., Stieve D.E., Garrett J.L., 1998. Protein preservation and ruminal degradation of ensiled forage treated with heat, formic acid, ammonia, or microbial inoculant. J. Dairy Sci. 81, 765-776.

[27] Agrobiogazownia, 2010. Red. K. Węglarzy, W. Podkówka. IZ PIB, Grodziec Śląski, Zespół Wydawnictw i Poligrafii Instytutu Zootechniki PIB.

[28] Ruser B., Pahlow G., Kräft A., Rutherford W., 2009. Improved biogas production from silage treated with an esterase producing inokulant. Proc. of XVth Int. Silage Conf., Madison, Wisconsin, USA, 455-456.

[29] Sucu E., Filya I., 2006. Effects of homofermentative lactic acid bacterial inoculants on the fermentation and aerobic stability characteristics of low dry matter corn silage. Turk. J. Vet. Anim. Sci. 30, 83-88.

[30] Sucu E., Filya I., 2006a. The effect of bacterial inoculants on the fermentation, aerobic stability and rumen degradability characteristics of wheat silages. Turk. J. Vet. Anim. Sci. 30, 187-193.

[31] Thaysen J., 2004. Die Produktion von qualitativ hochwertigen Grassilagen. Übers. Tierernährg. 32, 57-102.

[32] Weissbach F., 2009. Prediction of biogas production potential of silages. Proc. of XVth Int. Silage Conf., Madison, Wisconsin, USA, 189-190.