Natural Resources and Sustainable Development | **Volume 10, Issue 1, 2020**
DOI: 10.31924/nrsd.v10i1.044

ANALYSIS OF NUTRITIONAL PARAMETERS OF BIOGAS SLURRY

Kiss Nikolett Éva*#, Tamás János*, Gorliczay Edit*, Gálya Bernadett*, Nagy Attila*, Jóvér János, Riczu Péter*****

*University of Debrecen, Faculty of Agricultural and Food Sciences and Environmental Management, Institute of Water and Environmental Management, Debrecen, Hungary,
e-mail: kiss.nikoletteva@agr.unideb.hu
**Zal-Agro Corporated Company, Türje
***KITE Zrt., Hungary

Abstract

Large amount of waste and by-products generated during livestock processes requires urgent treatment and disposal. The energy recovery of wastes and by-products can be a solution for the problem, since the biogas production is an obvious way of recovery. As a by-product of biogas production biogas slurry is produced and it is to be suitable for nutrient supply.

The samples of the biogas slurry originate from the Nyírbátor Regional Biogas Plant. The plant is used for the disposal and recovery of plant residues, manure of cattle and poultry, poultry slaughterhouses and other animal wastes. The organic matter from the fermenter is separated. After separation, the dilute phase is transferred to the manure storage and the solid phase is transferred to a drying plant or composting plant. Aims of the study were the analysis of filtering efficiency of the separator, comparison of properties of the pre-separator and the separated fermentation residue, since the company wants to spread the biogas slurry to arable land and pasture in a frame of complex precision irrigation system. For this reason, the sampling points were planned to set both before and after separator processes. Samples were taken twelve times between February and June 2018. Among other properties, the dry matter content of the biogas slurry, C and N content, element content, pH, conductivity, biological and chemical oxygen demand were measured.

Based on the element content and the N content, the biogas slurry is suitable for nutrient supply. The average dry matter content values of the samples show that the result of the separation process the dry matter content is significantly reduced ($P<0.05$). The salt content was very high in the samples both before and after separation. In order to prevent environmental stress, it is recommended to reduce the salt content before applying the biogas slurry.

Key words: biogas slurry, nutritional parameters, separator, precision irrigation

INTRODUCTION

Due to their environmental impact, non-recyclable secondary products formed during animal husbandry processes, such as untreated manure or slaughterhouse waste, are a major problem for the livestock sector. There are two forms of by-product recovery, material recovery and energy recovery. In the latter case, anaerobic fermentation produces biogas from a large amount of slurry, litter manure and slaughterhouse waste. The anaerobic fermentation process is suitable for the disposal of bio-waste and for the production of "green energy" (Mézes et al., 2007; Tamás, Kovács, 2008; Mézes, Tamás, 2015). The stages of anaerobic fermentation are naturally inseparable, since the microbiological activities are based on each

Corresponding author

other. The four stages of anaerobic fermentation are as follows (Gijzen, 1987; Bitton, 1994; Angenent, Wrenn, 2008; Wilkie, 2008):

1. Hydrolysis. Conversion of polymers into monomers (sugars, amino and fatty acids).

2. Acidogenesis. Conversion of the monomers into alcohols, ammonia, carbon dioxide, hydrogen gas and volatile fatty acids.

3. Acetogenesis. Conversion of alcohols and volatile fatty acids into acetate, carbon dioxide and hydrogen by acetogenic bacteria.

4. Methanogenesis. Conversion of acetate, carbon dioxide and hydrogen by methanogenic bacteria into methane and carbon dioxide.

Biogas production can produce 50 % or even 75 % of methane, which can be used as heat and/or electricity. Biogas production highly depends on the raw materials used (Table 1).

Table 1

Biogas production for various manures and other feedstocks (Surendra et al., 2013)

Feedstock	Biogas production (m^3/ton dry solids)
Cattle manure	200-300
Pig manure	250-500
Chicken manure	310
Sheep manure	300-400
Human excreta (night soil)	380
Vegetable wastes	400
Grass lawn cuttings	700-800
Rice straw	550-620
Maize silage	600-700
Maize straw	400-1000
Kitchen waste	400-1000

Two products are produced during the fermentation process: the methane gas, which is suitable for energy production and the biogas slurry suitable for fertilization, the fermentation broth. Szegi, 1967 and Bíró, Pacsuta, 2002, emphasize in their publication that fermented material is capable of regenerating soil fertility, increasing agricultural production and replacing fertilizers (Szőllősi et al., 2008).

The composition of the biogas slurry is influenced by the raw materials used for biogas production and the digestion technology (Monnet, 2003).

Fermentation reduces the carbon content in the slurry, but not the nitrogen content and other nutrients. Thus, the resulting material is rich in macro-, micro-nutrients, trace elements and organic compounds (Holm-Nielsen et al., 1997; Ishikawa et al., 2006; Alam, 2006).

The samples of the biogas slurry originate from the Nyírbátor Regional Biogas Plant. The plant is used for the disposal and recovery of

plant residues, manure of cattle and poultry, poultry slaughterhouses and other animal wastes. Since to biogas production uses mixed raw materials, a combination of mesophilic and thermophilic fermenter is used for more perfect organic matter decomposition. The raw materials are pumped in every four hours into mesophilic fermentors (32-38 °C) and then into thermophilic digesters (55-60 °C). The organic material from the thermophilic fermentor is stored in containers, where it is being cooled down to 35-38 °C and its decomposing continues, then by gravity it goes into a tank. With pump, the biogas slurry is transported to the separators, where the dilute phase is transferred to the manure storage and the solid phase goes to a drying or a composting plant.

The fermentors produce 20 000 – 25 000 m^3/day of biogas with a methane content of 60-65 %, which is used for electricity generation and heating. The fermentation residue of biogas production at the factory is 100000 t biofertilizer or biogas slurry, which is utilized for irrigation for nutrient supply. In order to ensure sustainable and environmentally friendly management and to maintain biogas production, it is essential to study the nutritional parameters and safe disposition of the slurry.

The aim of our research was to analyze the filtering efficiency of the separator and to compare the properties of the pre-separator and the separated dilute phase.

MATERIAL AND METHOD

The sampling points were located before (pre-separator samples) and after the separator (separated samples). Samples were taken twelve times between February and June 2018.

The analysis of the nutrient parameters (pH, EC, TDS, COD, BOD, dry matter content and sedimentation, micronutrient and nutrient content) was carried out at the University of Debrecen, Faculty of Agriculture, Food Science and Environmental Management, by the Water and Environmental Management Institute and other tests (C, N content, C/N ratio, Kjeldahl N content) was carried out by the microbiological laboratory of Gastor Foods Kft. The tests were performed in 3 replicates for statistical evaluation.

Evolution of C content and N forms of the biogas slurry

The pre-separator and the separated slurry samples were first dried at 105 °C, then grind to a small grain size and finally the samples were sieved for homogeneity. The C and N contents of the prepared samples were analyzed with the Vario EL Elementar universal elemental analyzer, which is also suitable for the analysis of H, S and O elements.

To measure the recoverable N content of the biogas slurry Kjeldahl N content was also determined in three steps: digestion (in a Kjeldahl flask),

distillation (in a Wagner-Parnas apparatus) and then titration. As a first step, the nitrogen content of the slurry was converted to ammonium sulfate by sulfuric acid digestion. The sulfuric acid solution was basified in a Wagner-Parnas apparatus, the liberated ammonia is distilled and trapping in boric acid. The final step was the titration with hydrochloric acid. In this way, the amount of bound ammonia was obtained, and from this the nitrogen content of the protein sample could be calculated.

The nitrite and nitrate contents of the samples were measured with Photometer PF-12 Plus. Before measurement biogas slurry samples were sedimented for 3 minutes using a Rotofix 32A centrifuge, then diluted 100-fold and finally the required Visocolor ECO reagents were added to the samples.

Element content of biogas slurry

The biogas slurry samples were dried at the temperature of 105 °C until reaching the constant weight, shredded and the particle fraction below 2 mm was placed in a sampling bag. The elemental content of the samples were determined with Niton XLt 700 field X-ray spectrometer.

Dry matter content and determination of the amount of sediment

One liter of the pre-separator and the separated samples were weighed into measuring cylinders in three replicates. Samples were taken daily at 10, 20 and 30 cm depths using a pipette for 5 days. The wet weight of fresh samples was weighed and then dried in drying oven at 105 °C for 24 hours. After drying the dry sample weight was also measured. The dry matter content was calculated to determine the amount of sediment using the following formula:

$$\text{Dry matter content (\%)} = \frac{\text{wet weight} - \text{dried weight}}{\text{dried weight}} * 100$$

Measurement of pH, electrical conductivity (EC) and total dissolved solids (TDS)

The biogas slurry and deionized water were mixed in a ratio of 1:9 and shaken for 24 hours. The pH, EC and TDS of the samples were measured with a HANNA HI 2550 combined pH, ORP EC, TDS, NaCl meter.

Evolution of Biological Oxygen Demand (BOD)

BOD refers to the amount of oxygen needed to decompose biodegradable organic matter in water, thus suggesting the organic nutrient load to water. During the measurement, 43.5 ml of the fermentation broth sample was weighed into the BOI bottles. A magnetic stirrer was placed in

the bottles, and a rubber basket collar was placed on the neck of the bottle, in which 2 NaOH granules were placed. The bottle was sealed with the OxiTop probe, started the measurement, and placed in a thermostat cabinet at 20 °C for 5 days.

Measurement of Chemical Oxygen Demand (COD)

Since the COD value is related to the organic matter content, it is a very important point in the analysis of slurry. The measurement was carried out according to ISO 15075: 2002 as follows: 2.0 ml of a 100-fold dilution of the biogas slurry was weighed into test tubes which is containing sulfuric acid (80-98 %), potassium dichromate (0.28-0.56 %) and mercury (II) sulfate (0.74-1.50 %). The test tube was placed in a thermoblock at 148 °C for 2 hours after sealing and shaking. After the sample had cooled to room temperature, we began the measurement with the PF-12 Plus photometer.

Statistical analysis

Statistical analysis of the data was performed using R software in R Studio user environment.

The normal distribution of the data was examined by the Shapiro-Wilk test. If the data were found to be normal, the Duncan test was applied to quantify statistical differences at a 5 % significance level ($p = 0.05$). In some cases, the normality was not fulfilled for the groups, in which case the Kruskal-Wallis test was applied.

RESULTS AND DISCUSSION

Evolution of C content and N forms of the biogas slurry

The C and N contents of the samples were analyzed with the Vario EL Elementar universal elemental analyzer (Table 2).

Table 2

C and N content, C:N ratio of the samples

	Pre-separator samples	Separated samples
C content (mg/l)	19851.35[a]	9595.48[b]
N content (mg/l)	1846.86[a]	1004.17[b]
C:N ratio (%)	12.03[a]	9.5[b]

The C and N content of the biogas slurry and thus the C:N ratio decreased as a result of the separator, of which significantly decreased value could be detected.

The Kjeldahl's N content has also been defined to map accurately the usable N content (Table 3).

Table 3

Kjeldahl N content

	Pre-separator samples (mg/l)	Separated samples (mg/l)
Kjeldahl N content	4326.66[a]	3860[b]

The N content determined by the Kjeldahl method was higher than the N content measured by the elemental analyzer. This is due to the two methods of sample preparation, since the CNS elemental analyzer requires a solid sample, whereas the Kjeldahl N content was determined from the dilute phase. The difference is due to the nitrite and nitrate nitrogen content in the dilute phase. The Kjeldahl method also showed a significant decrease in the nitrogen content.

Since the nitrite and nitrate contents can not be detected in the Kjeldahl nitrogen determination, they were subjected for photometric measurements using Visocolor ECO tests.

Of the two parameters, only the nitrate content decreased, but no significant difference could be detected (Table 4).

Table 4

Nitrite and nitrate content of biogas slurry

	Pre-separator samples	Separated samples
NO_2 (mg/l)	22.69[a]	22.75[a]
NO_3 (mg/l)	2445.9[a]	1895[a]

The sum of the N content measured with the elemental analyzer and the photometrically determined nitrite and nitrate content is close to the Kjeldahl N content.

Element content of biogas slurry

For the Rb, Cu and Zn elements, some increase was observed as a result of the separation, while the amount of the other elements decreased after the separator (Table 5).

Table 5

Element content of biogas slurry

	Rb	Cu	Zn	Sc	Mn	Fe	S	Cl	Ca	K
Pre-separator simples (mg/kg)	0.8[a]	9.2[a]	15.1[a]	29.1[a]	31.2[a]	111.8[a]	304.8[a]	485.5[a]	2172.7[a]	2983.8[a]
Separated simples (mg/kg)	1.0[b]	9.3[a]	15.8[a]	12.0[b]	20.6[b]	98.3[a]	167.6[b]	452.4[a]	974.3[b]	2678.3[b]

Significant difference was found for Rb, Mn, Sc, Ca, K and S elements. Despite the change due to separation, the amount of micro- and macro-nutrients in the biogas slurry does not exclude agricultural use.

Dry matter content and determination of the amount of sediment

The dry matter content was checked daily. Pre-separator and separated samples were sampled at 10, 20 and 30 cm depths for 5 days. After measuring the wet and dry mass, the dry matter content was calculated. The results are presented by the following figures (Fig. 1, Fig. 2).

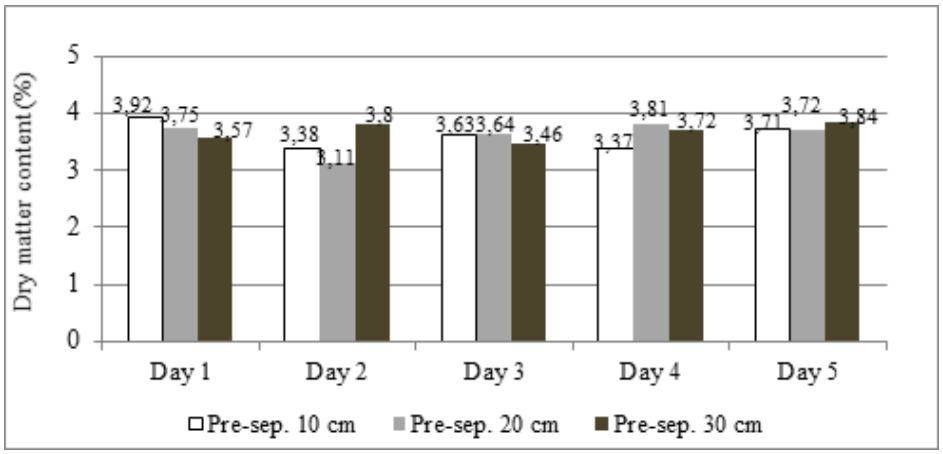

Fig. 1. Dry matter content of pre-separator samples

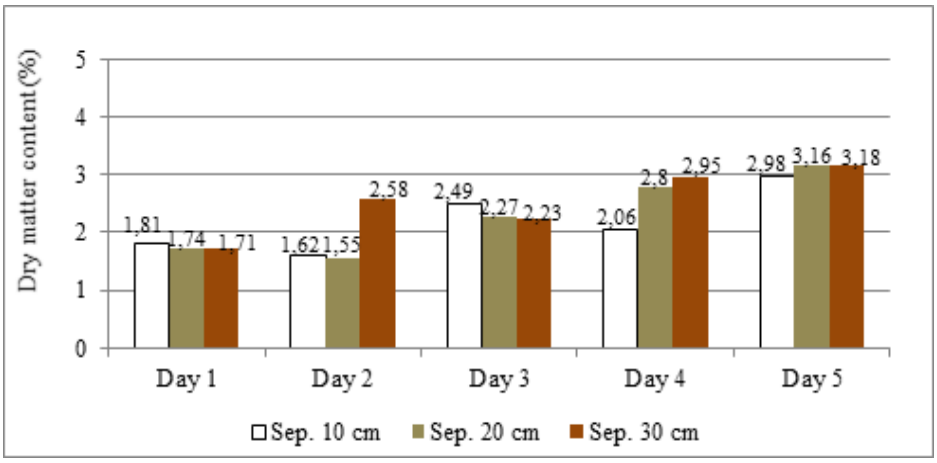

Fig. 2. Dry matter content of separated samples

In the pre-separator samples the dry matter content ranged from 3.11 to 3.92 % and from 1.55 to 3.18 % in the separated samples. The values decreased significantly due to separation, however the biogas slurry still contains a significant amount of floating material which must be removed in case of rainy irrigation.

Measurement of pH, electrical conductivity (EC) and total dissolved solids (TDS)

The pH of the biogas slurry, both before and after the separator, ranges from 8.2 to 8.4, so it is slightly alkaline. No significant difference was observed in the effect of the separator (Table 6).

Table 6

The pH, electrical conductivity and total dissolved solids of the biogas slurry

	Pre-separator samples	Separated samples
pH	8.33[a]	8.45[b]
EC (mS/cm)	19.79[a]	21.17[b]
TDS (mg/l)	9940.56[a]	10727.78[b]

During the measurements, the biogas slurry both before and after the separator, had very high salinity based on electrical conductivity (EC). According to Stefanovits et al., 1999, no salinization occurs if the irrigation water should not exceed 500 mg/l, which corresponds to 0.78 mS/cm. Accordingly, the salt concentration of the biogas slurry is very high and should be reduced in order to prevent environmental loading.

The total dissolved solid (TDS) content showed a slight increase due to separation (Table 6).

Evolution of Biological Oxygen Demand (BOD)

Biological oxygen demand was measured using a five-day incubation period.

A continuous growth in biological oxygen demand was traceable both before and after the separator. The biological oxygen demand of the separated biogas slurry was lower all the time, but no significant difference ($p = 0.05$) was observed (Fig. 3).

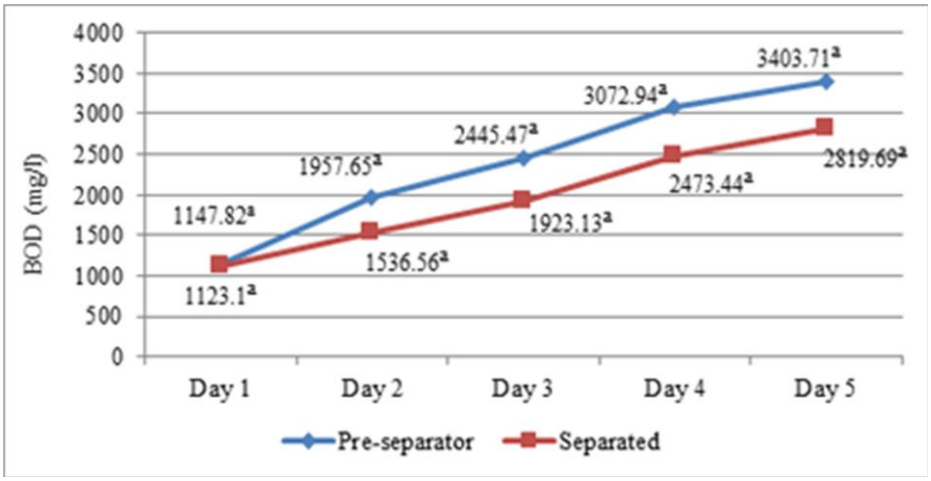

Fig. 3. Evolution of biological oxygen demand in the biogas slurry

Measurement of Chemical Oxygen Demand (COD)

According to other authors the chemical oxygen demand generally shows a downward trend in the effect of the separator. This is reported by Gamze, Göksel, 2003, who have experienced a 32 % reduction in some cases and up to 50 % in other cases as a result of separation.

During the study the average oxygen demand was 53737 mg/l in pre-separator samples and 52273.33 mg/l in the separated samples (Table 7).

Table 7

Evolution of chemical oxygen demand due to the separator

	Pre-separator simple	Separated simple
COD (mg/l)	53737[a]	52273.33[a]

Based on this, in our case the decreasing tendency was the effect of the separator, which was 2.7 % based on the average COD values. However, we could not detect a significant change.

CONCLUSIONS

Based on our results, it can be concluded that the decrease in C, N and other elemental contents due to separation does not exclude agricultural utilization.

However, utilization by irrigation may be difficult because significant amounts of suspended solids remain in the slurry despite separation. In addition, the biogas slurry has a very high salt content, which has not been reduced despite the separation, so it can be a burden on the environment.

The further studies are mainly aimed at reducing high suspended solids and also high salt concentrations.

Acknowledgment

This research was supported by EFOP-3.6.2-16-2017-00001 project (Research of complex rural economic and sustainable development, elaboration of its service networks in the Carpathian basin).

REFERENCES

1. Alam S., 2006, Production of organic manure in Bangladesh. Bangladesh Livestock Research Institute's Report, Savar, Dhaka, Bangladesh;
2. Angenent L.T., Wrenn B.A., 2008, Optimizing mixed-culture bioprocessing to convert wastes into bioenergy. In: J. Wall (Ed.), Bioenergy. ASM Press, Washington, pp.179-194;
3. Bíró B., Pacsuta A.J., 2002, Újgenerációs szemlélet és lehetőségek a talajbiológiai aktivitás és a talajtermékenység irányított fokozására. Gyakorlati Agrofórum. 13, pp.72-74;

4. Bitton G., 1994, Anaerobic digestion of wastewater and sludge. Wastewater Microbiology, Wiley-liss. New York, pp.229-245;
5. Gamze G.D., Göksel N.D., 2003, Effect of initial COD concentration, nutrient addition, temperature and microbial acclimation on anaerobic treatability of broiler and cattle manure. Bioresource Technology, Volume 93, pp.109-117;
6. Gijzen H.J., 1987, Anaerobic digestion of cellulosic waste by rumen a rumen-derived process. University of Nijmegen, The Netherlands;
7. Holm-Nielsen J.B., Halberg N., Hutingford S., Al Seadi T., 1997, Joint biogas plant. Agricultural Advantages – circulation of N, P and K. Report Made for the Danish Energy Agency, Revised and Emendted Edition, August 1997;
8. Ishikawa S., Hoshiba S., Hinata T., Hishinuma T., Morita S., 2006, Evaluation of a biogas plant from life cycle assessment (LCA). International Congress Series, 1293, pp.230-233;
9. Mézes L., Bíró T., Tamás J., Petis M., 2007, The examination of poultry feather digestility for biogas production. Acta Agraria Debreceniensis, 26, pp.113-118;
10. Mézes L, Tamás J., 2015, Feather Waste Recycling for Biogas Production, Waste and Biomass Valorization 5:(6) pp.899-911;
11. Monnet F., 2003, An Introduction to Anaerobic Digestion of Organic Wastes. Final Report Biogasmax. Remade. Scotland;
12. Stefanovits P., Filep Gy., Füleky, Gy., 1999, Talajtan. – Mezőgazda Kiadó. Budapest;
13. Surendra K.C., Takara D., Jasinski J., Khanal S.K., 2013, Household anaerobic digester for bioenergy production in developing countries: opportunities and challenges. Environmental Technology 34(13-14), pp.1671-1689;
14. Szegi J., 1967, Nitrogénkötő mikroorganizmusok jelentősége a talaj termékenysége szempontjából. Agrokémia és Talajtan. 16, pp.477-486;
15. Szőllősi N., Mézes L., Bíró Gy., Petis M., 2008, Evaluation of landuse, based on recycling of liquid biogas by-product. Növénytermelés, 60, pp.459-462;
16. Tamás J., Kovács E., 2008, Environmental technology. University of Debrecen, Centre for Agricultural and Applied Economic Sciences;
17. Wilkie A.C., 2008, Biomethane from biomass, biowaste and biofuels. In: J. Wall (Ed.), Bioenergy. ASM Press, Washington, pp.195-205.

Received: October 31, 2019
Revised: April 02, 2020