NOVEL APPROACH ON THE BASIS OF FOS/TAC METHOD

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Abstract
The research takes place in a biogas plant based on mixed agricultural composition in Nyírbátor. The problem is the seasonal, periodical and optional changes of the input materials. The aim of the research is to apply a relative new FOS/TAC method as process control in the biogas plant. Input materials determine the composition of the examined substrate variations and a continuously operating biogas plant demands fast reaction time. Till now applied methods require examination of several parameters (pH, alkalinity, VFA, dry- and organic material content and C/N ratio), but measurement of quality is expensive and time consuming. In contrast with other methods the FOS/TAC method has several advantages. The stability of anaerobic degradation process can be determined early, easily and continually. The result is a single value depending on the relation of two parameters, which are Volatile Organic Acids content (FOS) and buffer capacity (TAC). The mean pH value was 7.9±0.22. The FOS/TAC ratio changed between 0.14 and 0.29. This value means a low biomass feeding.

Key words: agricultural biogas plant, biogas production, FOS/TAC method.

INTRODUCTION

The degradation process is complex and depends on a balanced action of several microbial groups (Gujer W. and Zehnder A., 1983). The process of anaerobic digestion consists of three steps – solubilization, acidogenesis and methanogenesis (Kim M. et al., 2003). In the first hydrolysis step the complex organic polymers (proteins, carbohydrates and fats) are degrading into simple sugars, amino acids and fatty acids by heterogeneous microorganism. As the second step, acidogenic bacteria produce fermentation intermediates, mainly volatile fatty acids (VFAs), and lastly, in the methane step, methane and carbon dioxide are produced from these intermediates by methanogenic bacterial metabolism. In each step of the process, the gas production and decomposition rates of organic waste are influenced by environmental factors such as temperature, pH and hydraulic retention time (HRT) and substrate concentration (Mata-Alvarez J., 2003; Edgar F. et al, 2006; Gamze G. and Demirer G., 2004).

The produced volatile fatty acids (VFAs) are mostly acetic acid, propionate and butyrate, and in lesser proportion formic acid, lactic acid, valerate and isobutyrate. The VFAs might have a promoter (low concentration) or inhibitor (high concentration) effect on the multiplication of bacteria, depending on concentration (Hanaki K. et al, 1987). The results also showed that the methane production, pH or the propionate:acetate ratio cannot be used as a single reliable parameter for indication of process imbalances in biogas plants treating manure together with industrial waste (Nielsen B. et al, 2007).

Input materials determine the composition of the examined substrate variations, but measurement of quality is expensive and time consuming. Therefore, another method is needed for process control. FOS/TAC-ratio has been applied with good results. Applying FOS/TAC method the stability of anaerobic degradation process can be determined easily and continually. The result is a single value depending on the relation of two parameters, which are Volatile Organic Acids content (FOS) and buffer capacity (TAC).

TAC is the abbreviation for total inorganic carbon (basic puffer capacity) (mg $CaCO_3/dm^3$) (Rieger Ch. and Weiland P., 2006; Pfeifer B., 2007). The stability of the anaerobic process can be assessed either through knowledge of the single parameters (volatile organic acids and buffer capacity) or through the relation of these parameters to each other. If, for instance, the ratio of organic acids is very high (e.g. > 10 g/L), this indicates that the metabolism is incomplete, which can lead to inhibition of the process. However, this effect is not as marked if at the same time there is an adequate buffer capacity in the system. According to the hydro-analytical parameters acid and alkaline capacity and the analyses run by Nordmann (Nordmann W., 1977). The titration method which today is applied for the determination of FOS and TAC also in biogas plants was introduced by the Scot McGhee T. in 1968. In order to determine the fatty acid concentration in the fermentation water, McGhee ran several test series to develop a method in which the acid consumption per changes of the pH-value is measured between certain titration end points (Voß E. et al, 2009). The FOS/TAC analysis was developed by "Bundesforschungsanstalt für Landwirtschaft/FAL" from a titration method (Nordmann-method).

$$FOS = ((B * 1.66) - 0.15) * 500 [mg/L HAc]$$

Nordmann W. (1977) developed the determination of the volatile organic acids (FOS) through titration from pH-value 5.0 to pH-value 4.4 of 0.1 N sulphuric acid into a 20 ml sample volume of the filtered sludge sample, with B as acid consumption in [ml].

The buffer capacity of the system is determined through titration of the 20 ml sample from its original pH-value to a pH-value of 5.

$$TAC = A * 250 [mg\ CaCO_3/L]$$

With A as acid consumption of 0.1 N H_2SO_4 in [ml] for this pH-value range. The relation of both parameters – rendered as FOS/TAC – has by now become a very popular application for the evaluation of the process stability of biogas plants. The described method to determine the FOS/TAC relation is a low-cost and fast method to presently obtain high-quality information about the stability of the degradation processes in a biogas plant or an anaerobic wastewater treatment plant on location (Voß E. et al, 2009).

MATERIAL AND METHOD

Assessment of the Agricultural Biogas Plant (BP)

The biogas plant was established by BátorTrade Ltd. in 2002. The regional plant forms a multi-role system, which besides carrying out conventional agricultural activities is also producing biogas of high methane content (Bíró T. et al, 2008; Mézes L. et al, 2008). The biogas is produced in low digesters optimized for mixed combination of raw materials, and then it is consumed in gas engines in order to generate both electricity and heat energy. The available capacity involves 17 000 m^3 of digester volume, 2600 kW electric energy output, a daily yield of 20-25 000 m^3 biogas and 110 000 tons of raw material consumption. As the plant is consuming mixed materials, the 6 mesophilic – and 6 thermophilic digesters are operated in linked sequence (Mézes L. et al, 2008). The installation of an additional digester-pair is currently in progress. From the pressurized gas chamber of the digester the biogas gets to the gas-cleaner, then into the gasbag through a pipe system. The quality and quantity of biogas is being monitored continuously throughout the process. Solid and liquid phases are stored separately and utilized to supply nutrient content on farmlands.

Assessment of an analyze method

Dry material - and organic material content were examined according to MSZ 318-3:1979 and MSZ 318-3:1979. The pH was measured daily by a WTW 340i pH-meter (Accuracy: +/-0.005, Range: -2 to 20 pH). In the Regional Biogas Plant samples were gathered from the mesophilic reactor with a special method. We applied the laboratory FOS/TAC method (Nordmann W., 1977). In the FOS/TAC determination can be a massive difference in the acid consumption of differently pre-treated samples. Samples which were not filtered, but only sieved showed a considerably higher acid consumption than filtered (folded filter) or centrifuged samples (Voß E. et al, 2009). Because of this, after the representative sampling (twice a week), the samples were filtered in order to remove the main contamination. The 20 cm^3 sample was titrated to pH 5.0 using H_2SO_4 0.1 N besides a continuous stirring. The H_2SO_4 consumption up to pH-value 5.0 reflects the buffer capacity of the carbon buffer system as lime reserve

(TAC). Between pH-value 5.0 and pH-value 4.4, the protons are absorbed by the organic acids (Voß E. et al., 2009). The pH was measured on 25 °C. The FOS/TAC ratio was calculated under an empirical formula:

TAC= ("A" ml N/10 H_2SO_4 down to pH 5.0) x 250 = mg $CaCO_3$/Liter

FOS = [("B" ml n/10 H_2SO_4 from pH 5.0 down to pH 4.4 x 1.66) – 0.15] x 500 = mg free fatty acids (as CH_3COOH) / Liter (Nordmann W., 1977).

Evaluation of FOS/TAC ratios (empirical values provided by Deula-Nienburg) *(Table 1).*

Table 1

Evaluation of FOS/TAC ratios according to empirical experience

FOS/TAC ratios	Background	Suggestion/Counter Action
>0,6	Highly excessive biomass input	Stop adding biomass
0,5-0,6	Excessive biomass input	Add less biomass
0,4-0,5	Plant is overflowing	Monitor the plant more closely
0,3-0,4	**Biogas production at the maximum**	**Keep biomass input constant**
0,2-0,3	Biomass input is too low	Slowly increase the biomass input
<0,2	Biomass input is far too low	Rapidly increase the biomass input

RESULTS AND DISSCUSIONS

The mean dry material contant was 6.5±1.8% and the organic material contant was 2.5±0.7% in the mesophilic digester. The FOS/TAC ratio and the pH value (25 °C) was continously measured in the mesophilic digester (between July and October 2011) *(Figure 1.).*

The mean pH value was 7.9±0.22, but fluctuated between 7.6 and 8.3 during the examined period. The most favorable pH value for methane production is between 6.5 and 7.5 (Karpenstein-Machen M. 2005; Deublein D. and Steinhauser A., 2008). Under pH 6.0 and over 8.0 the methan production will be slower. The pH value can change significantly, if the system not has enough puffer-capacity, therefore in the examined biogas plant the pH value should be decreased, or the composition of input materials should be changed.

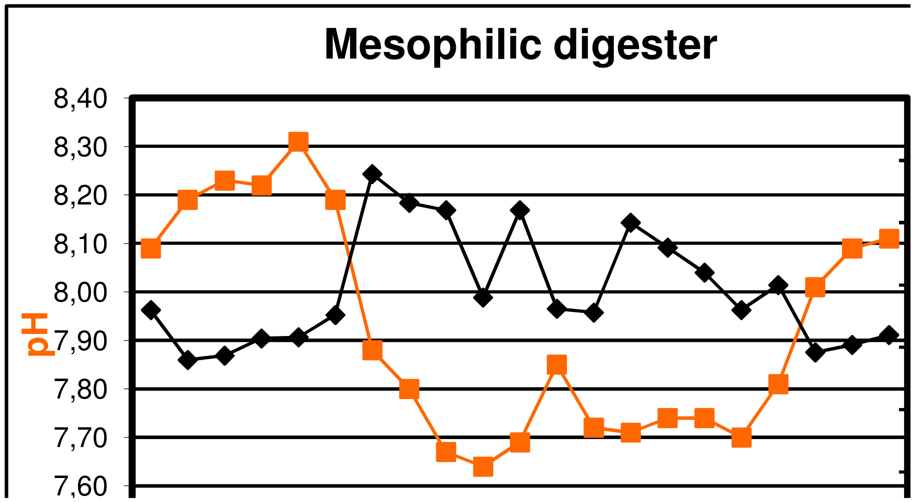

Fig. 1 Relationship of FOS/TAC ratio and pH in the Regional Biogas Plant in Nyírbátor

The FOS/TAC ratio changed between 0.14 and 0.29. The mean of FOS/TAC showed a value of 0.2±0.05. This value means a low biomass feeding according to the *Table 1.* Biogas system is stabile between FOS/TAC 0.3-0.4 values based on practice; therefore the quantity of input materials could be increased. The status of anaerobic degradation process is correct according to the results of Voß E. et al. (2009), who determinated another optimal intervall between 0.15 and 0.45. All biogas system has an own optimal FOS/TAC value, what long-term analysis and regular monitoring can define.

CONCLUSIONS

Decreasing the pH would be useful, because of retaining the stability of the biogas plant. Applying food industrial by-product such as whay would be a good solution. While the FOS/TAC value strongly depends on the quality of raw materials, the raw material base of the examined biogas makes the accurate prediction very difficult. As a summary, in the Regional Biogas Plant in Nyírbátor the measured value was lower than the optimal 0.3 value, but this does not mean that, there will be an imbalance in the biogas plant.

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