# MAINTAINING AND IMPROVING THE TRACE ELEMENTS PARAMETERS RATIO OF THE MICROBIAL POPULATION IN A BIOGAS PLANT

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#### Abstract

The purpose of this research is to identify the influence of trace elements concentrations in fermentation tanks on the biogas yield and plant efficiency. In order to make Anaerobic Digestion more efficient and optimized, measures of the process are often made. In this way the biogas plant managers are trying to produce as much biogas from the given substrate as possible, while at the same time maintaining a reasonable level of process stability. Trace elements (ex. Cobalt, Iron, Selenium, Zinc, etc.) are needed for the growth of the microorganisms involved in biogas biosynthesis. This is mainly related to the fact that most of them are situated in active parts of enzymes, thus having a strong influence on their activity. Maintaining a normal concentration of those elements inside the Fermentation medium is a vital part of the Anaerobic Digestion process and adding supliments of trace elements in the biogas fermenter has often proved beneficial by increasing the biogas production, resulting in a more stable and efficient methane production. The importance of the biogas production and its components are well known because they are strictly related to the operation of othe Cogeneration Module which uses it as a fuel. Also very important is to increase the CH4 percentage contained in one cubic meter of biogas in order to have a superior calorific power and a good cogeneration efficiency.

Key words: Anaerobic Digestion, Biogas Production, Cogeneration.

# INTRODUCTION

The anaerobic metabolism takes place in four big steps with specific enzymes and bacteria: hydrolysis, acidification, acetonogenesis and methanogenesis. The supply with nutrient powder is crucial for the biogas production in Anaerobic Fermentation because they contain elements like cobalt, nickel, iron, zinc, molybdenum which are important to be apart of the biogas plant substrate in order to have an efficient and continuous biogas production<sup>[4]</sup>. The limitation or undersupplied of these elements influences the conversion considerably, resulting in a disturbed process.

This limitation leads to reduced methan yields and considerable problems due to increasing process instability <sup>[1]</sup>.

The bioavailability of trace elements for metabolic pathways of the anaerobic bacteria it is strictly related to the feeding plan of the biogas plant. Also, many parameters such as variations of the pH-value or the working temperature inside the Fermentation tanks may lead to a diminish of trace elements. The biogas plant which is operating only with energy crops (in our research, maize silage) as single substrates in the feeding plan, after a short period since its startup, show lack of trace elements and an inefficient biogas production. In this work, we studied the influence of the macro/micro elements inside a biogas plant substrate which uses only maize silage and the results after correcting the values with supliments.

# MATERIALS AND METHODS

Many biogas plants in Europe are operating with maize silage as solo substrate. Often these plants are suffering from a dramatic drop of biogas production after a certain time of operation. This phenomenon is usually related due to the lack of trace elements such as nickel and cobalt which are essential factors of the enzymes involved in the anaerobic digestion of the biomass inside the fermentation tanks<sup>[1]</sup>.

We have studied this issue in one Romanian biogas plant (1MW<sub>el</sub> plant), where after one year of operating with maize silage (32-35 %

dry matter and 95% organic dry matter) the effiency of the biogas production dropped considerably and the operator was forced to increase the feeding amount in order to maintain a 100% biogas production for the needs of the CHP (Combined Heat and Power) with 10 % from 53 tons to 59 tons per day of maize, resulting in an inefficient input-output economic calculation and also increasing the FOS/TAC ratio.

The  $CH_4$  percentage was analysed and it's value was 52 % in accordance with Pronova SM6000 gas analyser.

It was necessary to make some analysis of the substrate inside the fermenters in order to see what is missing from the Fermentation medium and to apply as soon as possible the needed trace elements supliments. We made those analysis with 2 different laboratories from Germany: MT-Energie GmbH and bonalytic GmbH. They determined our trace elements results in accordance with test methods ICP-OES (inductively coupled plasma atomic emission spectrometry): EN ISO 11885:1997; DM (Dry Matter): EN 122880:2000 accredited test methods.

#### **RESULTS AND DISCUSSIONS**

The samples were analysed in two separated months, January and March in order to see the concentration of the elements. The results are listed below and in Table 1:

DM content: 9,15 k/kg pH: 7,50 FOS: 4.336 mg/l TAC: 10.891 mg/l

		Content of DM		
Element	Unit	bonalytic (January)	MT-En. (March)	
Cobalt (Co)	mg/kg	1.11	0,88	
Copper (Cu)	mg/kg	32.1	31	
Iron (Fe)	mg/kg	2530	1730	
Manganese (Mg)	mg/kg	491	229	
Molybdenum				
(Mo)	mg/kg	1.95	2	
Nickel (Ni)	mg/kg	8.84	8.4	
Sulphur (S)	mg/kg	4870	4860	
Selenium (Se)	mg/kg	<15	0.25	
Zinc (Zn)	mg/kg	196	181	

Table 1.Analysis results regarding the concentration of trace elements in medium digester

According to both of the laboratories knowledge, there was a partial lack of trace elements inside the microbial population. The analysis shown low contents of the elements iron, molybdenum, selenium and especially cobalt. The high acid concentrations in the digester illustrates that the microorganisms do not have an optimal nutrient supply. To improve the nutrient concentrations the laboratories recommended to add a special trace elements powder for biogas plant customized to our needs and based on the analysis.

The issue we were dealing with was normal because we feed only maize silage and , in accordance with the analysis of maize silage <sup>[3]</sup> and shown in Table 2, the values of the elements containted in it will be everytime in an 'undersupplied' range.

Table 2. Maize silage nutrients content of Fresh Mass

Element	Nutrient content [mg/kg DM]	
Cobalt	0.84	
Copper	4	
Iron	111	
Manganese	32	
Molybdenum	0.78	
Nickel	<1	
Zinc	38	

These values show lack of the nutrients needed for a normal anaerobic microbial digestion<sup>[2]</sup>, that is why we complied with their recommendations and started to use the supliments which contained concentrations as Table 3:

Table 3.	Elements and concentrations for the trace
	elements powder supplied

Element	Amount	Unit
Iron	21.7	%
Cobalt	200	ppm
Copper	490	ppm
Manganese	0.91	%
Molybdenum	326	ppm
Sodium	0.98	%
Nickel	1030	ppm
Selenium	23	ppm
Tungsten	60	ppm
Zinc	3010	ppm

pH-value (in aqueous solution): 6-8; Density: 800-1000 g/l.

We introduced a daily dosage of this product of  $2kg/100kW_{el}$ , meaning 20kg for 1 MW<sub>el</sub> for 3 months in order to see the results for a long

period and, of course, we monitored the results monthly like Table 4:

		Content of DM		
Element	Unit	April	May	June
Cobalt (Co)	mg/kg	0.94	1	1.3
Copper (Cu)	mg/kg	32	36	38
Iron (Fe)	mg/kg	1590	1700	2100
Manganese (Mg)	mg/kg	266	253	284
Molybdenum (Mo)	mg/kg	2.6	3.2	2.4
Nickel (Ni)	mg/kg	9.9	8.1	11.4
Sulphur (S)	mg/kg	5290	5040	4260
Selenium (Se)	mg/kg	0.24	0.31	0.36
Zinc (Zn)	mg/kg	231	171	166

Table 4. Evolution of the elements during the period April-June 2014

### CONCLUSIONS

After 3 months of dosing the trace elements powder, there was still a partial lack of cobalt but the other ones were in a medium range of the recommended values (in accordance with the laboratories recommended values). The limitation of cobalt inside the digester decreases the conversion of acetic and propionic acids into biogas. The recommended value of Cobalt was obtained after five months of feeding the powder <sup>[4]</sup>.

The improving of the trace elements concentration was also seen comparing the old feeding plan versus the new feeding plan: now the biogas production process is more stable and the daily amount feeded inside the digester is 52 tons per day. Also, we improved the methane concentration with 1%, from 52 % to 53 % according to the gas analyses from Table 5 <sup>[5]</sup>:

Table 5. Variation of the methane content between January and June

Month	Monthly average values of CH4 [%]
January	51.58
February	51.97
March	52.23
April	53.23
May	52.85
June	53.02

In this moment, the biogas plant runs with a daily dosage of powder of 10kg in order to supply continuously the lack of elements

contained in the maize silage and to have an efficient biogas production all over the year.

Feeding micronutrients and active ingredients blends may provide an optimum output of the methane production. They balance deficiencies as well as unfavorable ratios and availabilities of micro nutrients in the digesters of biogas plants. Thereby they support an ecological recycling management.

Like all biological processes, biogas plants are relating to Liebig's law, which means that due to the limitation of only one essential nutrient no full scale of yields can be obtained. An individually tailored trace element dosage thus provides the stabilization and optimization of the methane production by supporting the growth of the microorganisms being active in the degradation process as well as enables the production of necessary enzymes and coenzymes. A synchronization of single steps in the biogas production and a long-term increase of the digester performance are obtained by the application of trace elements.

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