WHITE PAPER

FOS/TAC Quotient for the optimization of methane production from biomass

When discussing renewable energies, it is mainly solar, water, and wind sources which are mentioned. Although all of these exhibit significant advantages compared to non-renewable energy, water and wind energy also have some disadvantages, like increasing the water temperature or generating electromagnetic radiation. However, biogas production is still neglected as a potential source of renewable energy. Over the last few years, it has developed significantly: from 2000 to 2015, biogas production in the European Union increased from 25 TWh to 182 TWh [1]. This huge growth in production was mainly achieved by construction of additional production sites. This white paper gives insight into why performing analytical monitoring of the biogas fermenter is of such enormous importance, and how the analysis is done in practice.

Metrohm

WHAT IS BIOGAS?

Biogas belongs to the category of renewable energy sources. It is defined as the production of methane from different organic matrices. These might include energy crops, agricultural residues, bio- and municipal waste, industrial (food and beverage) waste, as well as sewage [1].

All of these products are added to a fermenter, where enzymes split the compounds and eventually produce methane. The goal of every biogas manufacturing plant is to produce at least a share of 50% methane in the formed biogas. The main composition of biogas is listed in Table 1.

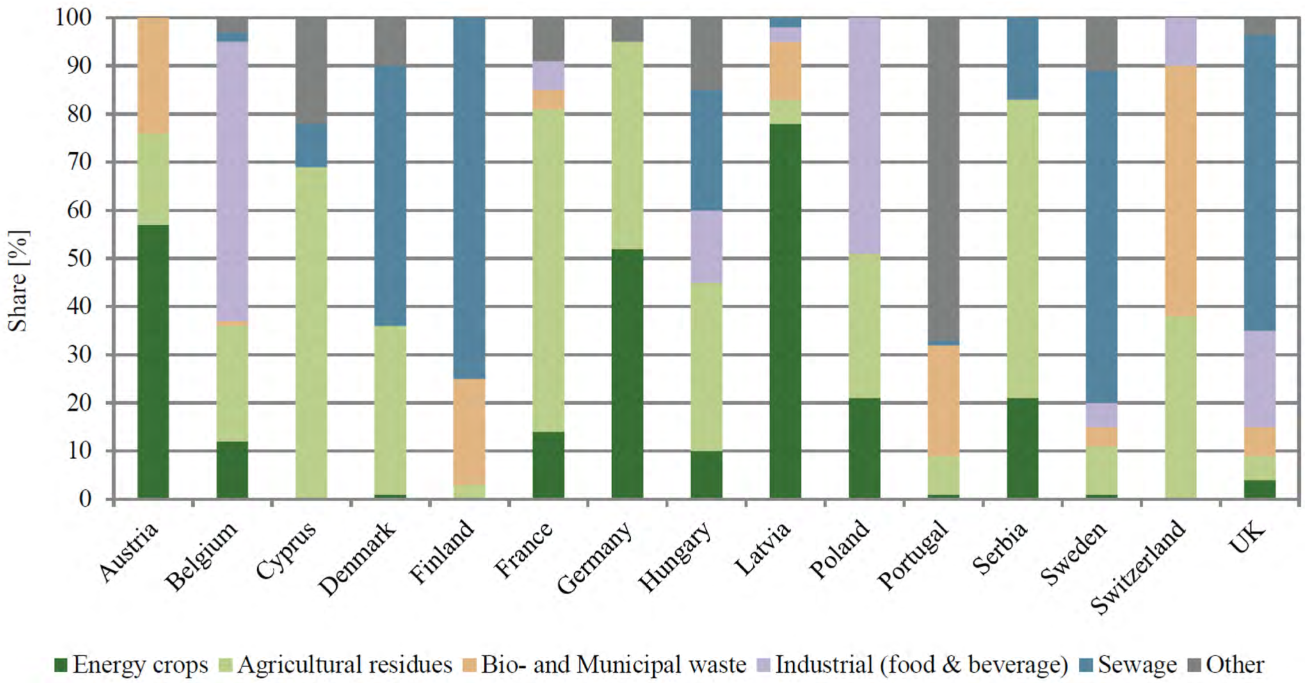


Figure 1: Chart showing the share of different organic matrices for the production of biogas [1].

Table 1: Composition of Biogas [2].

Component	Chemical formula	Percentage
– Methane	– CH_4	– 50–70%
– Carbon dioxide	– CO_2	– 25–50%
– Water	– H_2O	– 2–7%
– Dihydrogen sulfide	– H_2S	– < 2%
– Hydrogen	– H_2	– < 1%

HOW IS BIOGAS PRODUCED?

The aim of the biogas production is to produce methane with a volume concentration of at least 50%. The methane is produced under anaerobic (oxygen-free) conditions. Generally speaking, biogas production consists of four different steps:

1. HYDROLYSIS

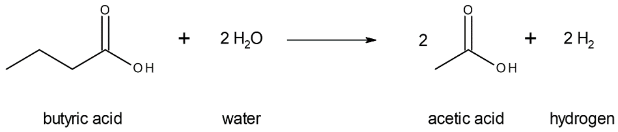
During this step, the macromolecules are broken down into smaller compounds by means of enzymatic activty. The enzymes are produced by hydrolytic bacteria, which are added to the biomass.

2. ACIDIFICATION

The bacteria take these smaller compounds up into the cell core, and degrade them into mainly propionic acid, butyric acid, valeric acid, and lactic acid. At this point, any remaining oxygen in the fermenter is consumed, and anaerobic conditions are therefore now present in the fermenter.

3. ACETIC ACID FORMATION

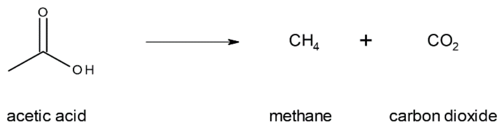
The molecules which were produced during the previous acidification process are now degraded to acetic acid, hydrogen, and carbon dioxide.



Equation 1: Chemical equation of the degradation process with butyic acid as example.

4. METHANE FORMATION

Methane is produced mainly from the anaerobic degradation of acetic acid by bacteria. Approximately 70% of methane is produced by the degradation of acetic acid, and the remaining 30% by methanation of carbon dioxide with hydrogen.



Equation 2: Methane formation from acetic acid.

$$\underset{\text{carbon dioxide}}{CO_2} + \underset{\text{hydrogen}}{4\,H_2} \longrightarrow \underset{\text{methane}}{CH_4} + \underset{\text{water}}{2\,H_2O}$$

Equation 3: Methanation process: formation of methane from carbon dioxide and hydrogen.

WHAT CAN NEGATIVELY INFLUENCE METHANE PRODUCTION?

Several factors can lead to process instability within the fermenter. Below is a list of some of these factors which cause imbalances [3]:

– UNSTABLE FEED SOURCE

Different types of feed contain various amounts of energy, resulting in a variance of methane yield production. If low-energy content feed is added to the reactor for a long period of time, the bacteria and enzymes could starve and become unable to produce any further methane.

– ORGANIC OVERLOAD

As soon as the organic matter feed exceeds the degradation capacity of the microorganisms, free fatty acids accumulate and lead to a change of pH. In an acidic environment, the microorganisms are not viable and the biogas production will decrease significantly.

– HYDRAULIC OVERLOAD

Hydraulic retention time corresponds to the time during which the feedstock remains in the biogas reactor. If this time is too short, the microorganisms cannot replicate, and their density in the fermenter reduces with time. As the amount of microorganisms in the fermenter is in direct proportion to the biogas production capability, this will also lead to a decrease in methane yield.

– TEMPERATURE CHANGES

Two different types of microorganisms are used during biogas production: mesophilic and the psychrophilic. The mesophilic microorganisms are more productive in warmer conditions (36–43°C), and the psychrophilic microorganisms are more productive in the cold (< 25°C). Normally a mixture of both types are used, and the optimal operating temperature is given by the mixture composition of these microorganisms.

– AMMONIA INHIBITION

Feed containing high amounts of nitrogen (e.g. high protein content) leads to the production of ammonia. Ammonia can freely pass through the cell membrane, and leads to an increase of the intracellular pH value. As microorganisms are sensitive to the pH, this leads to a decrease of the methane production yield.

Any of these factors can result in a destabilized fermenter, or in the worst-case scenario it could result in a total crash of the system. The enormous amount of work needed to re-establish the fermenter may endanger the profitability for an entire year.

While parameters such an ammonium nitrogen, pH value, or fermentation temperature give an impression of the current state of the fermenter, they cannot be used as an early indicator of an imbalance because it is already too late to avoid some damage. A different parameter is therefore needed which serves as an early indicator of an imbalance.

WHY IS THE DETERMINATION OF THE FOS/TAC VALUE ESSENTIAL?

The FOS/TAC value is such an early indicator. It determines the ratio of free organic acid (FOS) to total inorganic carbonate (TAC). The FOS value indicates an accumulation of volatile fatty acids, while the TAC value is a measure for the buffer capacity of the sample. An ideal ratio of an available source of carbon compared to the pH value is essential for healthy bacteria growth, and to obtain an optimal methane yield.

The FOS/TAC value is an empiric value historically used for estimating the conditions in the fermenter. By monitoring the FOS/TAC value, disturbances and perhaps a complete system shutdown can be observed early on, and preventive measures can be taken earlier overcome (further) negative impacts. This is absolutely necessary; otherwise a shutdown can lead to a drop in gas production for many weeks. The enormous amount of work required to recondition the fermenter may endanger the profitability for the whole year. With titration, the FOS/TAC value can be determined easily and cost-efficiently.

The obtained values from titration predicate the next measures for the biogas site:

Table 2: Relationship between the FOS/TAC value and the fermenter status, as well as the required measures to balance the fermenter [4]. The values are empirical ranges and can vary between different fermenters.

FOS/TAC Value	Meaning	Measures
> 0.6	Fermenter highly overfed	Do not feed
0.5–0.6	Fermenter overfed	Feed less
0.4–0.5	Fermenter highly loaded	Frequency of observation enhanced
0.3–0.4	Fermenter busy	Feeding is maintained
0.2–0.3	Fermenter hungry	Feeding is enhanced slowly
< 0.2	Fermenter very hungry	Feeding is enhanced quickly

DETERMINATION OF THE FOS/TAC VALUE – EASY AND COST-EFFICIENT

The FOS/TAC value can be determined easily and cost-efficiently with the new Eco Titrator from Metrohm. The sample is titrated with $c(H_2SO_4)$ = 0.05 mol/L until reaching a pH value of 2.5. The titrant consumption at pH 5 and pH 4.4 are determined. The FOS/TAC – quotient can be calculated afterwards with the following empirical formula:

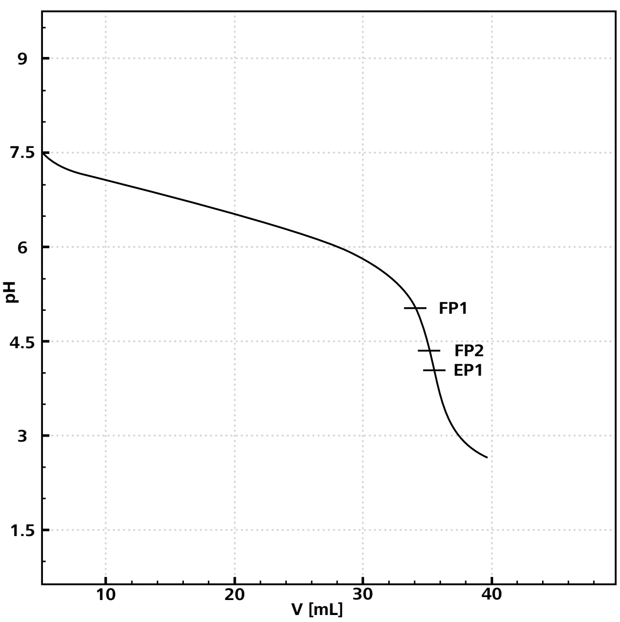
$$\text{FOS} = \frac{20 \cdot \left(\left(FP_2 - FP_1\right) \cdot 1.66 - 0.15\right) \cdot f_{H2SO4} \cdot 500}{\text{Sample Size}}$$

$$\text{TAC} = \frac{20 \cdot FP_1 \cdot f_{H2SO4} \cdot 250}{\text{Sample Size}}$$

$$\text{FOS/TAC-Quotient} = \frac{\text{FOS}}{\text{TAC}}$$

FOS:	free organic acid
20:	empirical factor
FP1:	fixed endpoint up to pH 5.0
FP2:	fixed endpoint up to pH 4.4
1.66:	free organic acid
0.15:	free organic acid
500:	free organic acid
f_{H2SO4}:	titer of $c(H_2SO_4)$ = 0.05 mol/L
250:	free organic acid

RESULTS OF FOS/TAC - DETERMINATION



Determination No.	FOS/TAC value
1	0.1061
2	0.1086
3	0.1034
4	0.1030
5	0.1047
Mean Value	0.1052
Absolute standard deviation	0.0023
Relative standard deviation	2.16%

Summary

The goal of the biogas production process is to obtain a yield of methane of at least 50%. The FOS/TAC value is an important characteristic to assess the status of the fermenter before costly problems arise. Depending on the FOS/TAC quotient, it can be determined whether a feeding is necessary or whether one will cause negative impacts on the fermenter. The new Eco Titrator from Metrohm allows the determination of this quotient in a fast, cost-efficient, and precise way.

References

[1] Scarlat, N.; Dallemand, J.-F.; and Fahl, F. Biogas: Developments and perspectives in Europe. *Renewable Energy* **2018**, *129*, 457–472. **doi:10.1016/j.renene.2018.03.006**

[2] *Gas in Zahlen 2018*; Verband der Schweizerischen Gasindustrie (VSB): Zürich, Switzerland, October, 2018 **https://gazenergie.ch/de/**

[3] Drosg, B. *Process monitoring in biogas plants*; IEA Bioenergy, December, 2013. **ISBN 978-1-910154-03-8**

[4] Mézes, L. et al. Novel approach of the basis of FOS/TAC method. Presented at International Symposium "Risk Factors for Environment and Food Safety" & "Natural Resources and Sustainable Development" & "50 Years of Agriculture Research in Oradea", Oradea, Romania, November 4–5, 2011; 802–807.

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