
FOS/TAC – Deduction, Methods, Application and Significance

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Zusammenfassung:

Ein relativ einfach zu bestimmender, aber durchaus aussagefähiger Parameter zur Beurteilung des Zustandes und der Entwicklung des anaeroben Abbauprozesses in einer Biogasanlage ist der sogenannte FOS/TAC Wert. Hier werden zwei Messgrößen und zwar der Gehalt an Flüchtigen Organischen Säuren (FOS) und das Puffervermögen (TAC) ins Verhältnis gesetzt. Beide Analysenwerte an sich geben schon wertvolle Informationen über den Zustand des anaeroben Prozesses. Aus dem Verhältnis der beiden Größen kann aber auch in gewissem Rahmen die Prozessstabilität der Anlage beurteilt werden und Entscheidungen für den Betrieb abgeleitet werden. Im vorliegenden Beitrag wird sowohl die historische Entwicklung dieser Analyseverfahren aufgezeigt, als auch Anwendbarkeit und Aussagekraft anhand von Betriebserfahrungen diskutiert.

Summary:

One parameter which can be determined quite easily, but which still yields meaningful information to evaluate the conditions and development of the anaerobic degradation process in a biogas plant is the so-called FOS/TAC value, which relates two measuring variables to each other: the contents of Volatile Organic Acids (FOS) and the buffer capacity (TAC). Each individual analysis value will yield valuable insights into the status of the anaerobic process. The relation of the two values, however, to some extent allows for the evaluation of the process stability of the plant and for decisions for the further operation. In this paper, both the historical development of this analysis method and its applicability and significance will be discussed on the basis of operation experiences.

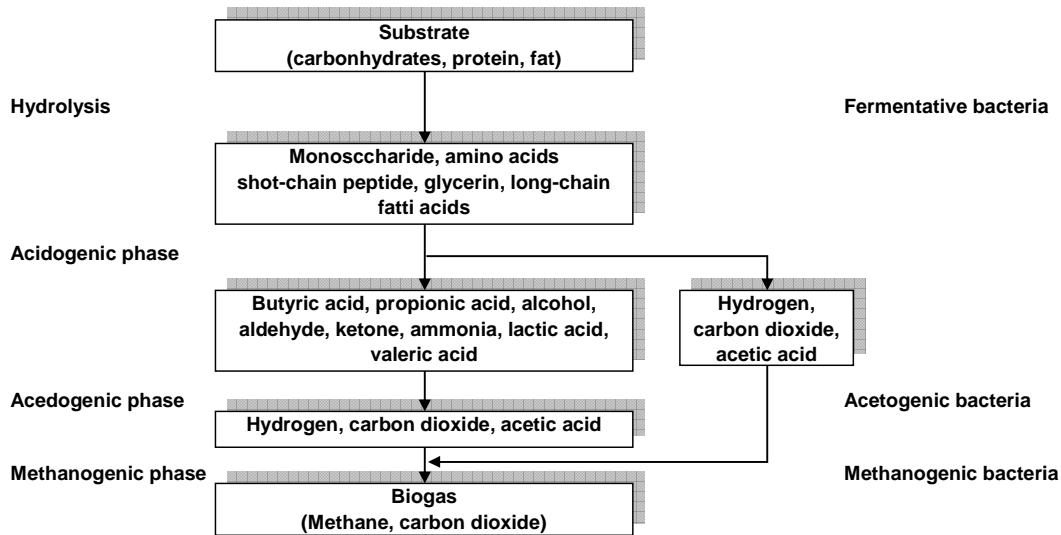
1 Introduction

The anaerobic degradation process, as it is schematically sketched in Figure 1, occurs in four stages and is subjected to a large number of influencing factors, the most important of which are: substrate composition, solids contents and volumetric load, biomass retention, temperature and pH-value, concentration of nutrients, inhibiting substances and trace elements, buffer capacity, and the concentration and range of organic acids. Additionally, there is a plethora of other factors which will have a more or less influential impact on the stability of the system.

Many of these influencing factors can be determined hardly or only with great efforts, and many of them only in a specially equipped analysis laboratory and at considerable costs. There are only a few informative parameters which can be determined on location in an

inexpensive and time-saving way. Apart from temperature and pH-value, two such parameters are the buffer capacity and the contents of volatile organic acids.

Figure 1: Anaerobic degradation in four stages [JUNGHANS, 1987]



2 Buffer Capacity and Organic Acids

In anaerobic systems, the pH-value can only be kept stable if there is a buffer system available (uptake of free protons (H^+ ions)). The buffer capacity is mostly rendered as carbonate buffer (lime reserve) in mg $CaCO_3/l$. Apart from the carbonate buffer system, however, there are other buffer systems, depending on the pH-value. For biogas plants, for instance, there is the nitrogen buffer system, in which ammonia serves as proton acceptor.

The organic acids play a crucial role in the anaerobic system, as the short-chain acetic acid (CH_3COOH) is – next to carbon dioxide (CO_2) and hydrogen (H) – the only source available for the production of Biogas (methane (CH_4) and CO_2). Apart from acetic acid, the system produces a large number of further organic acids in the acidogenic stage, of which only the short-chain and easily volatile acids like propionic acid (C_2H_5COOH), lactic acid (C_2H_5COOOH), butyric acid (C_3H_7COOH) and valeric acid (C_4H_9COOH) are important in this context. On their degradation path towards biogas, all these easily volatile acids must first be metabolised into acetic acid by the micro-organisms.

Table 1 shows that the organic acids which appear most frequently in these systems have their acid constant in a pH-value range between 5.0 and 4.4 and are displaced by the sulphuric acid with an acid constant of $pK_s -3.9$. Thus, it is possible to make qualitative statements on the contents of organic acids FOS, rendered as acetic acid equivalent.

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.

Table 1: Acid constants of selected volatile organic acids

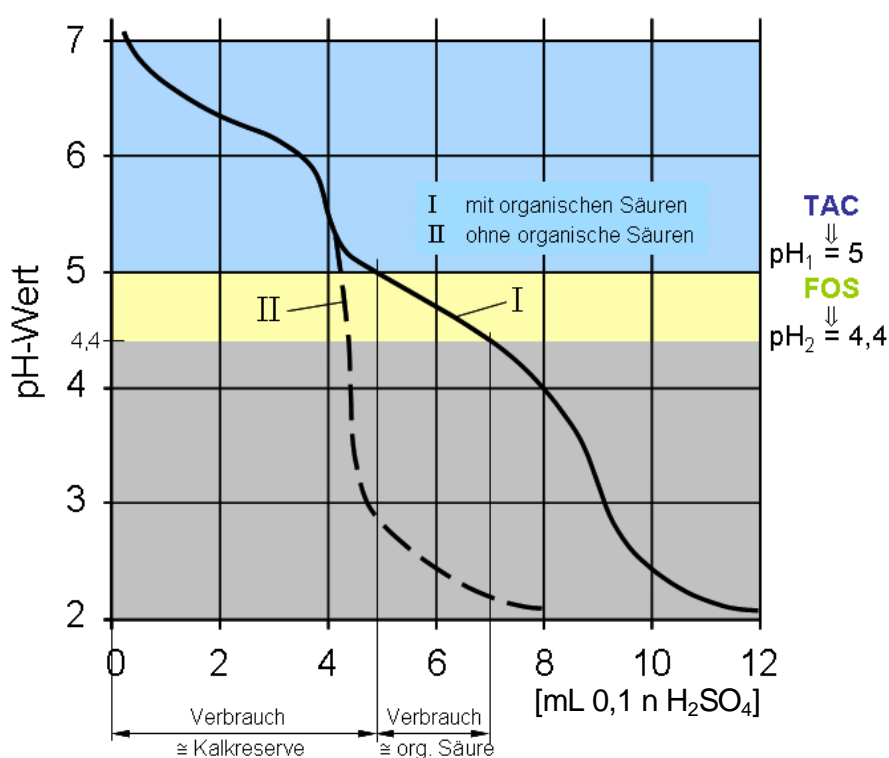
Name	Ion	pK _s
Carbonic acid	HCO ₃ ⁻	6.35
Acetic acid	CH ₃ COO ⁻	4.76
Propionic acid	C ₂ H ₅ COO ⁻	4.86
Valeric acid	C ₄ H ₉ COO ⁻	4.84
Butyric acid	C ₃ H ₇ COO ⁻	4.82

3 Development of the FOS/TAC

According to the hydro-analytical parameters acid and alkaline capacity and the analyses run by NORDMANN [NORDMANN, 1977], on wastewater treatment plants the contents of volatile organic acids and the lime reserve (buffer capacity) of sludge water from sludge digestion is determined through titration. The titration method which today is applied for the determination of FOS and TAC also in biogas plants was introduced by the Scot MCGHEE 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.

Figure 2 shows the titration procedure of H₂SO₄ in fermentation water within the limits chosen by MCGHEE. Curve I describes the development of a H₂SO₄ titration of a sample with organic acids; Curve II shows the development of a sample without organic acids.

Figure 2: Titration development in the FOS/TAC analysis [WEICHGREBE, 2007 extended according to NORDMANN, 1977]



The H₂SO₄ consumption up to pH-value 5 reflects the buffer capacity of the carbonate buffer system as lime reserve, which today is also referred to as TAC. Between pH-value 5 and pH-value 4.4, the protons are absorbed by the organic acids.

Table 2 shows further references and works, some of which were based on different ways of preliminary sample processing and on different titration end points, in order to increase the exactness of the method.

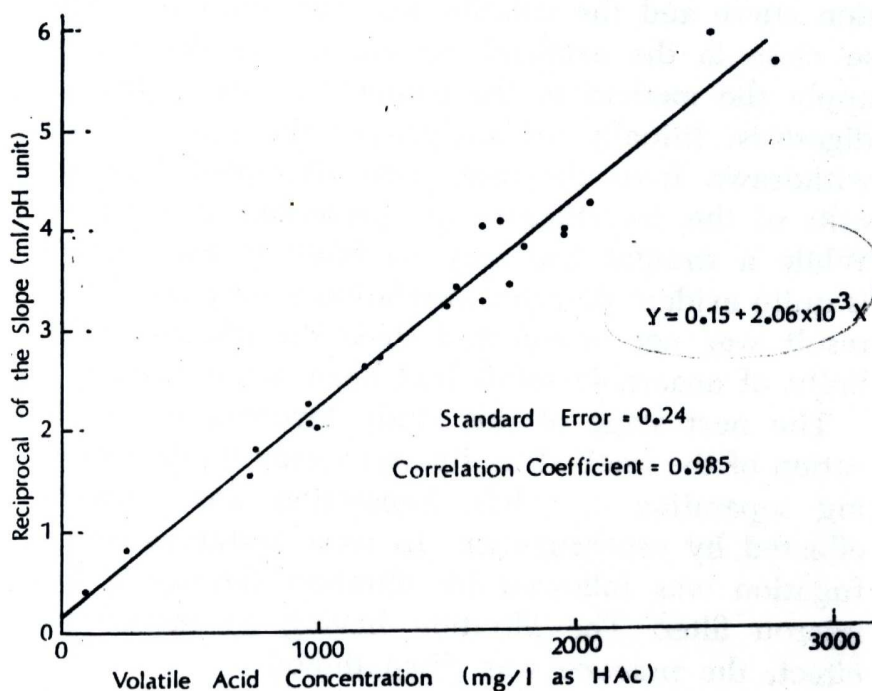
Table 2: History of titration tests to determine the volatile organic acids and the buffer capacity of fermentation water [WEICHGREBE 2007]

Authors	Year	Titration end points				Pre-Tr.	Medium
		pH ₁	pH ₂	pH ₃	pH ₄		
DiLallo/Albertson	1961	3.30	heating	4.00	7.00	centr.	ferm. water
McGhee	1968	5.00	4.40			FF	ferm. water
Nordmann	1977	5.00	4.40			FF	ferm. water
Jenkins	1983	5.75	4.30			n.a.	ferm. water
Kapp	1984	5.00	4.30	4.00		0.45µm	ferm. water
Anderson/Yang	1992	5.10	3.50			n.a.	ferm. water
Moosbrugger	1993	6.70	5.90	5.20	4.30	FF	ferm. water

Pre-Tr.= Preliminary treatment of the samples, centr.= centrifuged, 0.45 µm = filtered with 0.45µm, FF = folded filter

Figure 3 shows MCGHEE'S graphic evaluation of his titration tests with filtered sludge samples. The linear regression of the determined measuring points yielded a compensation function with a correlation coefficient of 0.985.

Figure 3: Relation of acid consumption and concentration of volatile organic acids in a filtered sludge sample, regression straight line according to MCGHEE [MCGHEE, 1968], (Original graphic from MCGHEE'S publication)



By conversion and simplification of this straight line equation

from $Y = 0.15 + 2.06 \times 10^{-3} \times X$ to (1)

to $X = ((B \times 1.66) - 0.15) \times 485.44$ or (2)

or $FOS \approx ((B \times 1.66) - 0.15) \times 500 [mg / lHAc]$ (3),

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

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.

$$TAC = A \times 250 [mgCaCO_3 / l] \quad (4)$$

With A as acid consumption of 0.1 n H₂SO₄ in [ml] for this pH-value range.

The original meaning of the abbreviation TAC could not be ascertained anymore. A German abbreviation like FOS is not plausible; the most fitting terms are *Total Alkalinity of Carbonates* or *Titre Alcalimétrique Complet*, but one has to consider that here the titration only to pH-value 4.4 and not to pH-value 4.3 like in the determination of the acid capacity (DIN 38409-H7).

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. Moreover, automatic titration methods are available on the market which calculates the FOS/TAC value according to this formula. Depending on the programming, deviations in the applied sample volume and the concentration of the titration acid must be considered by adaptation of the calculation formula.

4 Application of the FOS/TAC

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. One has to consider that because of the titration up to pH-value 5.0 the acid or buffer capacity is also only recorded up to pH-value 5.0, but not the entire acid capacity of the system. According to DIN 38 409-H7, the acid capacity with titration is titrated with 0.1 n HCL to pH-value 4.3.

Various analyses run by the Institute for Water Quality and Waste Management (ISAH) of Leibniz Universität Hannover on samples from biogas plants have confirmed the statement by MCGHEE that the preliminary treatment of the sample is crucial for the reliable determination of the FOS/TAC. MCGHEE could determine a linear connection between acid consumption and FOS only for the filtered sludge samples.

In the daily operation of a biogas plant, particularly one running with renewable energy resources, it will prove to be difficult to integrate an adequate preliminary processing of the samples. In the FOS/TAC determination, there have occurred massive differences in

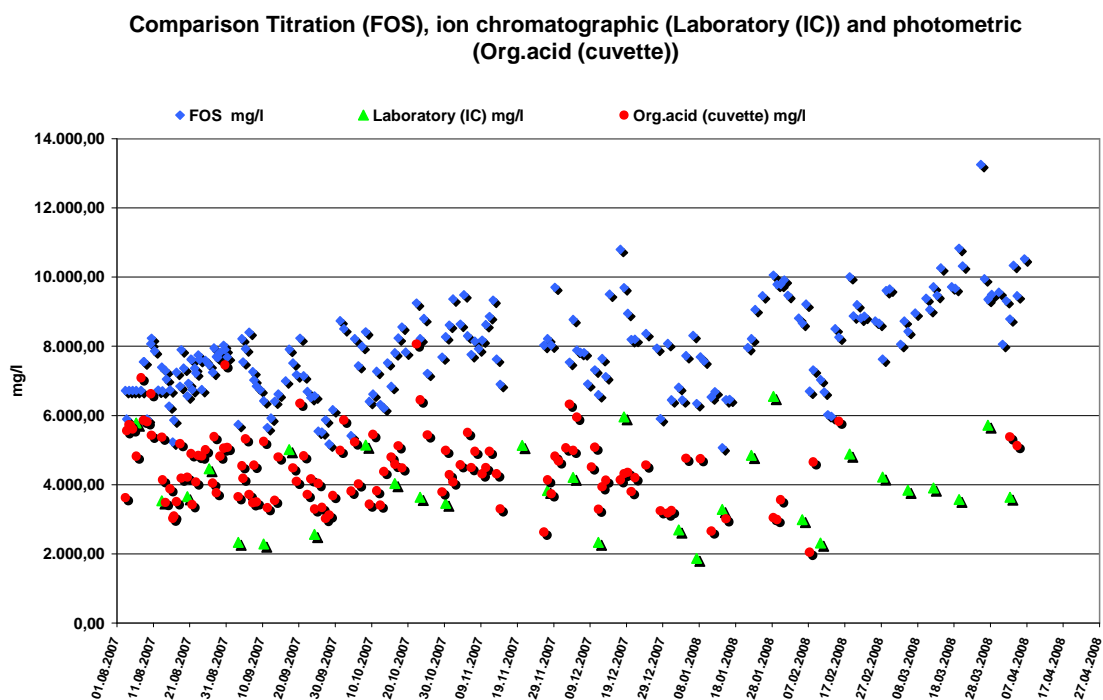
the acid consumption of differently pre-treated samples. Samples which were not filtered, but only sieved showed a considerably higher acid consumption than filtered (folded filter) or centrifuged samples. Moreover, the measuring of the FOS immediately after substrate input yielded clearly different results than samples taken prior to substrate input. A homogenisation with definite requirements on sampling, sample preparation, and titration would facilitate a considerably improved comparability of the analysed samples from different biogas plants. Or in other words: currently, any reliable comparison of FOS/TAC values of different biogas plants – determined with differing sample processing methods and differing sampling times – is not feasible.

A further potential source of errors is the manual titration by different persons, which can be eliminated through the application of modern titrators at the biogas plants. The inaccuracies inherent in manual titration, which to some extent are also due to the lack of reference samples for calibration and validation, are of quite high importance. Currently, the ISAH is busy developing suitable standards which fade out the plant-specific background matrix and thus facilitate more reliable information of this method both for FOS and TAC.

5 Meaning of the determined FOS/TAC values

As the titration method for the determination of the FOS/TAC allows for qualitative statements on the buffer capacity and on the organic solids, it should on biogas plants be applied daily and always with the same application procedure. A comparison with other methods for the determination of organic acids and a quantitative determination on this way could only be done under sufficient consideration of the edge conditions. Figure 4 shows our own experiences with various analysis methods.

Figure 4: Comparison of the FOS analysis results of different measuring methods



The comparability of the FOS/TAC values with other biogas plants must also be viewed critically. Such a comparison can only yield reliable results if the methods for sampling, sample preparation and titration are comparable. The most important and most valuable

information of the daily determination of the FOS/TAC values is the recognition of tendencies towards higher or lower FOS/TAC values, by which it is possible to notice overloads or underloads of the biogas plant much earlier than this will be indicated by changes of the pH-value. This is one reason why one should always go for the same sampling time after feeding. As general reference value for a stable process, a FOS/TAC ratio of 0.15 to 0.45 is assumed. Values below that could indicate a so-called alkalosis, or inadequate feeding, which will lead to rising pH-values and decreasing contents of the organic acids, which will then impair the hydrolysis and/or of the acidification. A high FOS/TAC value is often an indicator for a so-called acidosis, where an excessive accumulation of organic acids occurs, which can be caused by various phenomena.

Further causes of operation disturbances can be: shortage of trace elements, feeding of too much easily degradable input material (carbohydrates), too high volumetric load, continuously changing input material.

The daily analysis and recording of the determined values in such a way that they can be presented graphically is from our point of view mandatory for the safe and stable operation of biogas plants, as only the graphic rendition will let the operators know if the plant is still running within the normal deviation range or if there are significant tendencies which must be dealt with.

6 Reference Literature

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