Instructions to carry out the FOS/TAC analysis by titration

Date 01.02.2015

What is FOS/TAC?

The term FOS/TAC refers to the proportion between Flüchtigen Organischen Säuren (Oganic Volatile Acids) and the Total Alkalischen Carbonaten (Total Alkaline Carbonates). The determination of such proportion is carried out by titration, adding acid in a controlled way through a burette to a prepared substrate sample, to make then calculations with the help of an empiric formula. This process is very simple and easy to learn. An Excel calculation sheet is available, where some values have to be inserted to easy obtain the final calculation result.

Why to determine the FOS/TAC ratio?

The more organic acids will be contained in the fermenter (most important: acetic and propionic acid) the more the methane producing bacteria are going to be affected. Further more, this affection (inhabitation) is increased by an decrease in the pH value (extremely critical: pH<7, 4). Due that initially the acids will be buffered in the substrate (carbon buffer capacity), only pH measurement is not sufficient to determine a biological disequilibrium at time. The value of the FOS/TAC ratio in contrast considers such buffering effect.

The FOS/TAC titration presents an easy option to determine the proper feeding to a biogas plant, a periodical control helps to better operate your equipment.

For the titration there will be needed:

- For the first time: about one hour of time, with some practice, considerably less.
- A small amount of fresh substrate from the fermenter (see instructions for sampling)
- The FOS/TAC titration set from Fermenter-Doktor, unpacked and ready for its use.
- Water intake with a sink, if not available at least a bucket with some litres of fresh water.
- The FOS/TAC table: open the program on your computer, or a calculator and the printed table.
- Kitchen napkins (paper) to dry up the substrate sample, etc.
- Black marker, if available red and green additionally, for writing and labelling.
- Electrical intake to a maximal distance of 1.5 m for the magnetic stirrer (when not, use an extension)
- Around ½ m² easy to wash table as working space, preferably an illuminated one.
- A place to store the laboratory after use.

All the tools of laboratory equipment (excluding a pocket calculator) are included in the Titration Set!

Please read carefully the instructions before using the Titration Set to avoid operational errors and damage! pH-meters and maybe even the conductivity measuring stick must be calibrated before first use!

Protect yourself sufficiently! during titration you will be working with (in low concentrations) acid! (Suitable clothing, possibly goggles, use gloves, etc.)

Any questions? We're prepared to help you by phone or on site!

After reading these manual and operating instructions you normally will be prepared to operate the titration set by yourself. Short questions are answered by phone, of course, without extra charge!

If you have again more extensive questions about the operation, maintenance or use of your titration set, we also offer a telephonic advice to the usual Fermenter-Doktor consultation rates, prior request. In that case, our current prices for non-Fermenter-Doktor-members (unless they are already members of our counseling program, see price list), will be applied.
In 1 to 1.5 hours, you learn through our training many tricks of the titration and the interpretation of measurements relative to your individual plant situation, which also could be done by phone.

Procedure of FOS/TAC titration

(Please read carefully before you start!)

- NOTES for the general entry into service:
  BUFFER SOLUTION (pH4 and pH7) for calibrating the pH meter: please prepare 2-3 hours prior to first use, see user manual for the device.
  pH-METER: please calibrate before first use and continuously later on!
  ACID CONTAINER: Remove the cut cardboard pieces then unscrew the cap, then screw the drain tap fixed (located at the top / side of the box for shipping), then put aside, it appears the drain valve to the front. Now, fill the burette easily
  BURETTE: make sure to first close it completely, by fully opening the yellow plastic screw (turn it to the left) or press the emergency stop bar, then fill it with the 0,5 molar sulphuric acid (titration liquid). Press the plastic bottle softly until the burette is filled-up with acid comfortably until 0 ml on the scale; it adjusts itself automatically.
- Take your substrate sample from fermenter. Very important: Mix the whole fermenter thoroughly and fully before! Take the sample as possible with a pipe well far below potential layer of scum (general: Initially drain the pipe content!), possibly even out of the overflow, if it is just flushed with fresh substrate. Ore even better: Take your sample from the central substrate pump station if applicable (in that case make sure to pump long enough in and out to get fresh substrate from the appropriate fermenter!)
- For a first impression, measure the pH value in the fresh substrate and note it a side in the table. This is not the start-pH value but gives an initial idea of the pH of the fermenter. The pH value will be higher after the preparational work because of the CO_2-emissions while handling and stirring (gas emissions from substrate); 0,2-0,3 is normal.
- Percolate the substrate probe in the strainer included, so that only the fluid part be used, this makes easier the stirring and makes the pH reaction faster. When pressing the substrate use the rubber gloves included in the set, the handling helps you to get an idea of the substrate consistence, the solid residues in the percolator can be thrown away.
- Use the included electronic scales. Turn on the scale with out being charged, put a 400 ml glass on it (included), and then set it on zero (press TARA). Weigh exactly 50 g of the percolated substrate, in precision of 1 gram exactly.
- Weigh exactly 50 g of distilled water on the scales with one of the spray bottles (contained; more distilled water is available at the hardware store very cheep, about 2,-€ / 5l), 1l is for immediate start already included in the set
  TIP: Weigh the distilled water if necessary in an extra cup and give it to the substrate afterwards, this way there cannot be any mistakes!
- Put one of the small white magnetic devices into the weighted prepared substrate. Turn on the magnetic stirrer as intense as to obtain strong uniform mixing. Measure then the initial pH value of X (output value), and point in the table. In very dense substrates you regularly must move the electrode of the pH meter for additional stirring to obtain an exact value.

- Put the burette into a suitable position. Slowly add some ml of the 0.5 molar solution and observe the pH meter reach a value of 7. With the screw in front the burette drip rate can be regulated.
- TIPP: The burette has an "Emergency-Stop": Only slide down the yellow ring in front. You can replace it afterwards turning out the yellow screw in it completely
- If the fermenter sample starts to foam when you add the acid (sometimes starting from a pH value in between ph 6 to ph 5), add a drop of the ANTIFOAM LIQUID bottle. More of a drop usually is not necessary! Let it mix a moment and the foam will vanish. This is required for proper titration, avoiding a temporary absorption of the titration acid in the foam! The defoamer must be pH neutral and recharges can be ordered separately from Fermenter Doktor.
- Continue the titration to achieve a pH of exactly 5,0. When titrating empty the burette exactly to a value of 10 ml only and stop then! If you need more titration liquid please press the plastic bottle, fill up the burette again until zero and continue titrating. The amounts spilled over on top of the burette will run back into the bottle automatically.
- The total amount of acid that was required from the initial pH up to a value 5 should be noted in the table with an accuracy of .1 ml (= TAC). Don't forget the completely emptied amounts in the burette when a refill was required! The amounts required to reach a pH of 7 or 6 respectively could be useful for overall control of variations, but to calculate the FOS / TAC ratio these intermediate amounts are not required. Fill the burette to 0 ml again.
- Continue titrating to a final and exact pH 4,4. Insert the amount of acid into the table, with an accuracy of 0,1 ml, required to reach 4,4 starting from the pH of 5,0. (= FOS; only this amount, not from the very beginning of titration!).
- All in all please titrate continuously but not hectically. Make neither longer breaks nor pauses during titration, because in that case the substrate will buffer the acid already brought in, the pH will rise again and the final results will not be representative that way.
  Hint: Due to the buffer effects of the substrate it is almost not possible to achieve a stable ph of exactly 5,0 over a longer period. Thus you will have it on your finger tips in short time to know, when the appropriate moment is come to interrupt titration of the TAC because of only little changes remaining and to switch to the titration of the FOS. It's a matter of some experience only.
- While titrating be a little bit carefully when approaching the final pH 5 and the pH 4,4 respectively to allow the pH-meter to react properly, it always need some few seconds for reaction after introducing more titration acid into the substrate. The pH in both cases should become stable at least once for a short time, but then it will change again due to buffering.
- Hint: sink continually the ph meter electrode in a glass with water, so that the titration acid is properly distributed within the whole sample. Depending on the substrate consistence, it is possible that the stirring device could not properly mix. When the acids are not well distributed, the pH value suddenly may sink too fast and below the goal values as consequence and the titration must be done again.
- All the values indicated above must be filled into the table (see sample for more hardcopies attached). An electronic table can be sent by e Mail, which calculates automatically the values of FOS, TAC and FOS/TAC after inserting the required values properly. If you are interested in such a table, please send an Email to
  info@fermenter-doktor.com.
- After the titration, the substrate could be spilled back to nature. BE CAREFUL, before substrate disposal, it is necessary to "rescue" the magnetic bar of the mixing device. If the magnetic bar is lost, another one should be purchased (€ 2.50 plus shipping and handling).
- The sampling glass and other instruments should be washed out with water. The electrode of the pH meter must be washed out with distilled water at the end and then dried up carefully; the plastic covering with the KCl solution must be used for storage. The electrode cannot be kept dry, it will stop working properly. Place the pH meter in some available shelf. Read the manufacturer instructions (last page very important).

With some practice, the sampling and the FOS/TAC titration will take you around half an hour at maximum. This will very quickly turn out it's economic result because of better plant management backgrounds, first of all the feeding can be optimized.

Explanations of FOS/TAC titration and it's context

The less the need of adding acid to reach a pH value of 5, the substrates puffer capacity will be lower.

The less organic acids are present in the fermenter, the more acid will have to be added to reach a pH of 5,0 some times more than 20 ml, mostly when the initial pH is above 7,9. Also the greater the buffer capacity of the fermenter, the more acid will be needed to reach a pH of 5,0 (Carbonates and equilibrium between NH_4^+/NH_3^-).

A pH above 7,9 suggests a high NH_4-N concentration, which can be proved when measuring EC (electric conductivity, see below).

The more organic acids are accumulated in the fermenter, the more acid will be needed to pass from a pH value of 5,0 to 4,4, at same time, the buffer capacity usually decreases; it is meant the acid amount to reach a pH of 5,5. Likewise the FOS and TAC proportion will be smaller and the value of the FOS/TAC ratio will become bigger, closer to 1,0 ore even above.

Be very careful with the proper interpretation of the FOS/TAC: Regarding pH values of 7,9 and above (often generated by an increased amount of NH_4-N, significantly bigger than 2 g/l or 0,2 %), the organic acid amount of a supposed good can be very high, regardless a "good" FOS/TAC ratio of 0,5 and below. The organic acids are then well buffered. Thus, we must observe the development of the FOS and TAC values separately as time lines. An incremental increase of FOS in a constant ratio of FOS/TAC, must be taken into consideration and its reason must be figured out.

The required acid amount to reach a pH value of 7, particularly in high pH values, gives an idea of the buffer capacity of the ammonium.

It is known that the TAC values are to be found between 8,500 and 13,000, it is recommended by small or big values, to make an adjustment of the development with the process parameters.

The first periodic comparison values, allow to declare if the amount of organic acids in a substrate, raises, gets lower or stays the same. The value of FOS has similarities wit the HAc equivalence calculated in the laboratory. Through periodic analysis of the FOS/TAC changes, the feeding dosage can be regulated.

FOS/TAC calculation

Formula (to introduce in an EXCEL table):

$$\text{FOS/TAC} = \frac{\text{FOS } (((\text{amount of } H_2SO_4 \text{ from pH 5.0 to pH 4.4 x 1.66 / 2.5 x 10}) - 0.15) \times 500)}{\text{TAC} \qquad (\text{amount of } H_2SO_4 \text{ from pH X.X to pH 5.0 x 250 / 2.5 x 10})}$$

Formula explication:

- The factor of 1.66 (numerator) refers to the amount of substrate used by the Prof. Weiland (20g) and the molar mass of the sulphuric acid used in the titration (0,05 molar, 0.1 N).
- The factor of 0.15 (numerator) corrects the CO_2 contained in the sample.

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- The numbers (numerator) and 250 (denominator) are factors of the multiplication of the empiric formula.
- Because we will be working with sulphuric acid 0.5-molar (1 N) and 50 g of substrate, there are two red factors in the numerator and denominator, in comparison to the original formula of Prof. Weiland.

The normally calculated values will be smaller than 1. Values between .3 y .5 are considered as normal, and are the one that we want to obtain (orientation values). A wider interpretation of the calculated values helps to obtain the daily feeding ratio:

- > 0.6 OVERFED: decrease the feeding, maybe interrupt shortly
- 0.5-0.6 Overfeeding danger, feed less
- 0.3-0.5 Normal state: keep feeding rate
- 0.2-0.3 Hungry: raise feeding rate
- < 0.2 Very hungry: raise the feeding rate considerably

Warning: the optimum FOS/TAC of your biogas plant can only be found after periodic measurements. It depends on the used substrate, temperature, Nitrogen content, etc. The values mentioned give only an idea. Some biogas plants with FOS/TAC values over .5 can be stable operated, when this factor is intensively controlled. The causes must be controlled and observed, when a lower than .25 periodic value is presented, there is an alkali threat, which will cause the pH to raise. There should never be tolerated values around .5, there this could follow to problematic operation.

With the FOS/TAC proportion you have an excellent reference point to detect on time if your plant is being correctly operated. Its very important the early discovery of these values.

If you have questions over your FOS/TAC proportion values, give us a call: We're here to help you.

A small warning:

- Using the mentioned formula for the FOS/TAC calculation, there should be used only sulphuric acid, equivalent to 1 N. The use of acid of any other concentration is possible, but in the formula will have to be then included the correction values.
- For better results, the FOS/TAC value should be calculated daily, if not possibly, at least every 2 or 3 days. Is also of considerable importance that the titration is carried out always by the same person, only this way could be guaranteed a constant procedure. The bigger the charge per cubic meter and unit of time in the fermenter (bigger than 3.5 kg oTS/m^3 and day), the more important is the determination of this proportion because of the high instability of these systems.
- WARNING: the FOS/TAC proportion is not a replacement of the regular laboratory measurements. Laboratory tests to the substrate (every 4-6 weeks) of organic acids, and content of NH_4-N and organic matter, should be carried out. With these studies there can be obtained information about the proportions between the acids. The FOS/TAC proportion describes the daily changes of the contained acids in the fermenter in proportion with the (carbonates) buffer capacity of the fermenter.

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- The early correction of the amount fed to the fermenter thanks to the FOS/TAC proportion, helps you to save thousands of Euros in losses due to overfeeding, or for non-optimal gas production
- The pH meter calibrating solution can be stored in the refrigerator for 2-3 months.
- CLEAN WORK! The meter probe has to be cleaned periodically before storing. ! Wash out with water before changing the calibrating solution, as before titration!.
- When calibrating, be sure that all liquids have the same temperature that the substrate sample (around 20°C).
- The pH meter calibration has to be done once a week.
- The titrating acid has to be protected against light and should not be stored hot, if any property loss wants to be avoided.
- All the solutions and instrumentation can be order to Fermenter Doktor in the future.

Work with the salt meter stick (EC meter device).

EC represents the electric conductivity. The present salts raise the conductivity in liquids. The stick was considered in the daily substrate control laboratory equipment, this way is posible to dermine the conductivity of your biogas plant, one of the many control parameters.

Frequently in presence of great amounts of raw materials from the country side, and little dung addition, a part of the secondary fermenter from the storage tank will be reduced, raising the danger, independently of the substrate concentration, of reaching high concentrations of Ammonium-N, which could lead to serious problems in the gas production process. It is preferred the situations where only trash is fermentated. Between NH_4-N y NH_3 exists an equilibrium, which depends on the pH and the temperature. It is inhibitory for the bacteria the poisonous character NH_3.

It is worrying the results of laboratory analysis of the substrate that show a concentration of 0.25 % of NH_4-N (related to the fresh matter). Laboratory values rounding 3 g/l or 0,3 % NH_4-N are normally tolerable. Even with the high salt concentration, there are biogas plants that could be operated, when the bacteria have time to adjust them selves to these concentrations.

- It is necessary to read the stick salt meter instructions before the first use.
- The conductivity measurement device has to be calibrated at the beggining with one of the calibrating towels, then it can be used. Is the equipment is used periodically; it should be calibrated every 4 weeks, to obtain trustable measurements.
- Through the salt concentration, the conductivity will be measured; in order to measure, the device will have to be kept in the perfectly mixed substrate sample (without earlier preparations, without diluting). For a value to become stable, the analysis will have to be done for over a minute, then the shown value stops blinking and a value smaller than 19.99 is shown.
- A conductivity of 10-18 mS (mili Siemens) could be seen as inoffensive. In most cases, values under 25 mS are tolerable, if not inhibitions could start to show.
- As empiric rule it is taken that: 10 mS represent a content of NH_4-N of around 1 g/l or 0,1 %. There are also considerable differences. It is important to observe a tendency with a laboratory analysis to determine if the values are raising, getting lower or staying the same.
- It is possible, depending on the substances/materials used, that the measuring device does not show reasonable measurements. In this cause, measurements of 20 mS could be exceeded. As verification, proceed as here described:
- Weight 50 grams of substrate in one of the included glasses.
- Add 50 grams of distilled water and mix.
- Measure again the conductivity.

- For the determination of the conductivity in the original substrate, there should be doubled the shown value on the previous step, because this one was obtained in a diluted sample.
- This is the way that you should proceed to measure the conductivity when having high salt contents, for the optimum plant operation, it is recommended periodically values of around 20 mS, a reduction on the salt content makes the operation much easier.

Depending on the system and substrate, it is reasonable to compare periodically values like conductivity, pH and FOS/TAC.

For any question or doubt:

Please write your question by Email to info@fermenter-doktor.com
or contact us via Skype jmoerschner