University of Verona, Department of Biotechnology

Monitoring parameters in anaerobic digestion processes

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4. Evalutaion of the biogas potential (BMP) of a substrate

First of all, answer the question ….
Why monitoring ?!

(credits: prof Juan Lema)

…. to control the process !!!

(credits: prof Juan Lema)

Anaerobic digestion: a complex combination of biochemical and physical-chemical processes

"Primitive" monitoring

We can have a VERY basic monitoring, based on the determination of the typical engineering parameters like the organic loading rate (OLR, kgVS per m^3 of reactor per day) or the hydraulic retention time (HRT, days)…..

In this case, all we need to know is the volume of the reactor, the flowrate fed and the total and volatile solids concentration of the feed …..

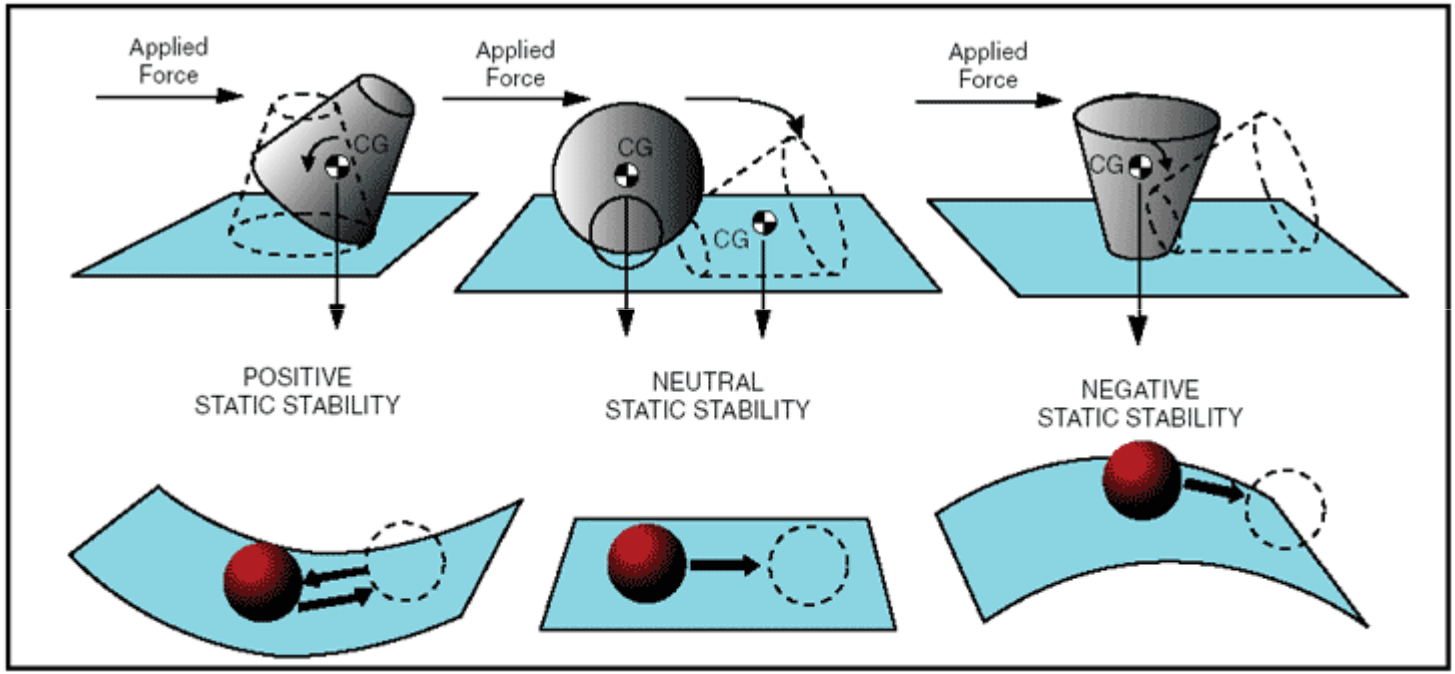
Uncreadibly, sometimes these are unknown …

However, to “drive” the process, beside engineering (operational) parameters, like temperature, hydraulic retention time, organic loading rate …. physical-chemical parameters need to be regularly monitored to check the state of the process (stability).

Among the most important we can remember here:

- ✓ pH
- ✓ alkalinity
- ✓ volatile fatty acids concentration and speciation
- ✓ biogas flowrate and composition
- ✓ ammonia concentration

These are also called “stability parameters” as they are helpful to define the “stable” operation of the anaerobic process ….



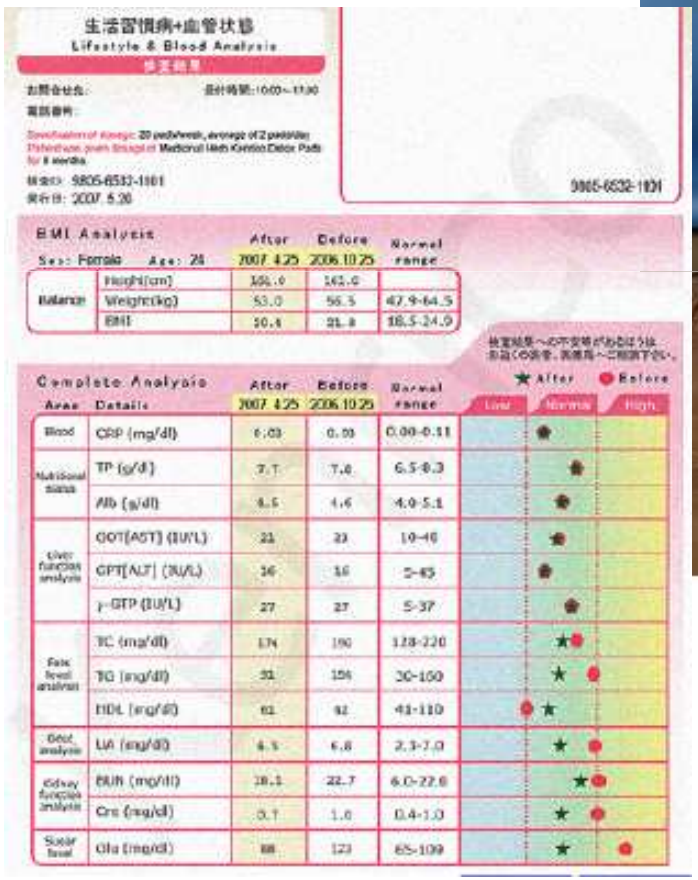
Which level of monitoring ?!

Keep it simple …
but do not exsaggerate ….

Simple monitoring (… but with some evident drawbakcs …)

(credits: prof Juan Lema)

Sophisticated monitoring (… but not too much …)


生活習慣病+血管状態
Lifestyle & Blood Analysis

BMI Analysis

		After 2007.4.25	Before 2006.10.25	Normal range
Balance	Height(cm)	165.0	165.0	
	Weight(kg)	53.0	56.5	47.9-64.5
	BMI	20.4	21.8	18.5-24.9

Complete Analysis

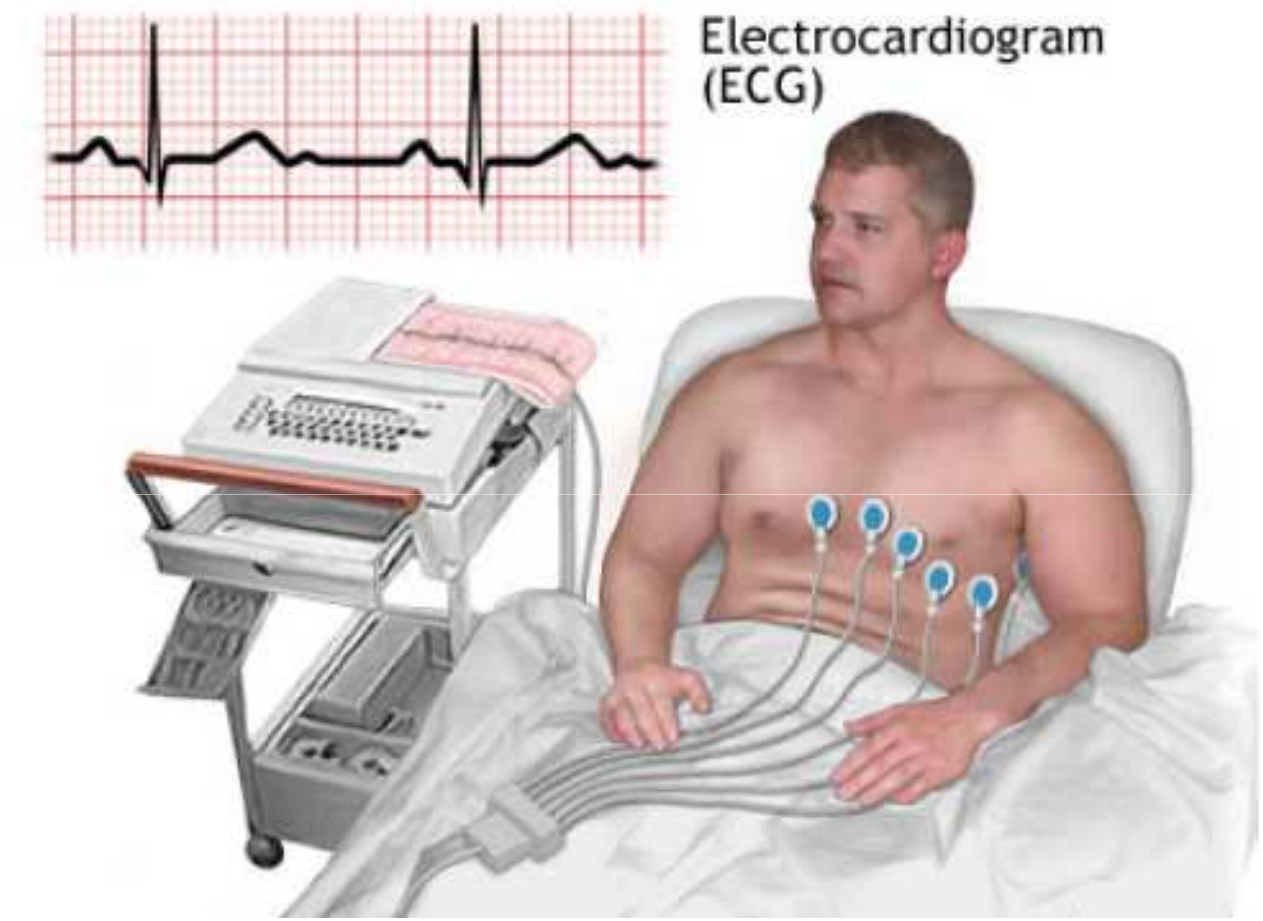
Area	Details	After 2007.4.25	Before 2006.10.25	Normal range
Blood	CRP (mg/dl)	0.03	0.09	0.00-0.11
Nutritional status	TP (g/dl)	7.7	7.8	6.5-8.3
	Alb (g/dl)	4.5	4.6	4.0-5.1
Liver function analysis	GOT(AST) (IU/L)	21	23	10-40
	GPT(ALT) (IU/L)	16	16	5-45
	γ-GTP (IU/L)	27	27	5-37
Fats level analysis	TC (mg/dl)	174	190	128-220
	TG (mg/dl)	91	156	30-150
	HDL (mg/dl)	61	62	41-110
Uric analysis	UA (mg/dl)	4.5	6.8	2.1-7.0
Kidney function analysis	BUN (mg/dl)	18.1	22.7	6.0-22.0
	Cre (mg/dl)	0.7	1.0	0.4-1.0
Sugar level	Glu (mg/dl)	88	123	65-109

(credits: prof Juan Lema)

Off – line monitoring

(credits: prof Juan Lema)

On – line monitoring



(credits: prof Juan Lema)

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"BASIC" MONITORING

- ✓ temperature
- ✓ pH

"MILD" MONITORING

- ✓ temperature,
- ✓ pH
- ✓ total and partial alkalinity

"HARD" MONITORING

- ✓ temperature
- ✓ pH
- ✓ total and partial alkalinity
- ✓ VFA conc and composition
- ✓ Biogas flowrate and composition
- ✓ Any other parameter……

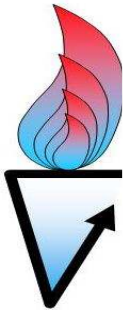
Monitoring of pH

pH is a measure of H^+ activity in an aqueous solution.

Because of its simplicity to be determined it is the most used parameter for AD monitoring: unfortunately, it is a "generic" parameter and almost useless in most of the case (see below) !

"Normal" pH values for AD processes follow in the range 6.5 – 7.5 but very different values can be found in stable AD processes perfectly working: this is because pH is the result of the presence several compounds in the bulk (ammonia, VFA, phosphates ….)

Lab pH-meters (off-line) or industrial on-line systems can be used for the purpose of pH measure



Please note that

In terms of routine monitoring, pH measurement cannot form the sole indication of imminent failure, because in medium or well-buffered solutions high VFA concentration would have to form in order to cause a detectable drop in pH, by which time failure would already occur.

Consequently, direct measurement of either (or both) VFA or total alkalinity concentration is necessary.

Monitoring of alkalinity

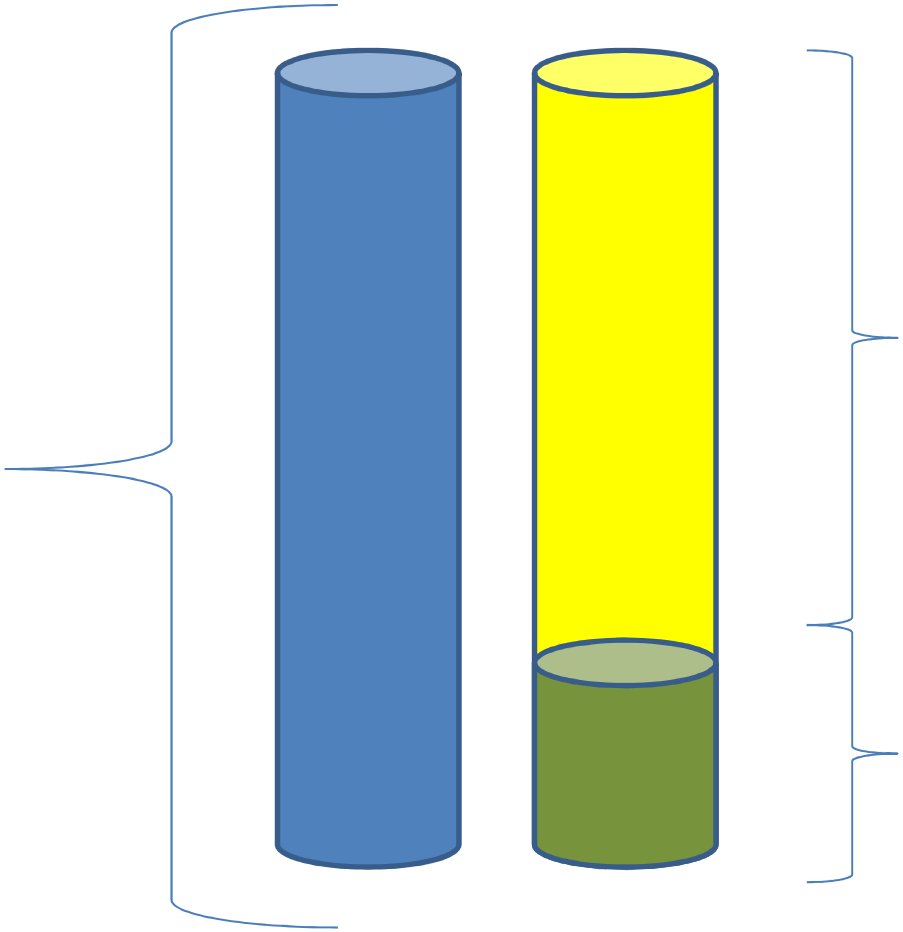
Alkalinity measures the ability of a solution to neutralize acids and can be expressed using several different units (typically calcium carbonate)

In AD processes it is strongly influenced by the presence of carbonate and bicarbonate (CO_2 dissolved in water), ammonia, phosphate, volatile fatty acids …. And is generally very high (some g/L as $CaCO_3$).

It is generally determined by tritation using 0.1 N HCl (or another strong acid) at two equivalent points:

pH 5.75 partial alkalinity (PA)
pH 4.3 or total alkalinity (TA)

The difference between TA and PA is the so called IA (intermediate alkalinity) and is related to VFA presence



Total Alkalinity (from pH around 7-8 down to pH 4.3)

Partial Alkalinity (pH 5.7), due to OH^-, NH_3 , HCO_3^- , $CO_3^=$

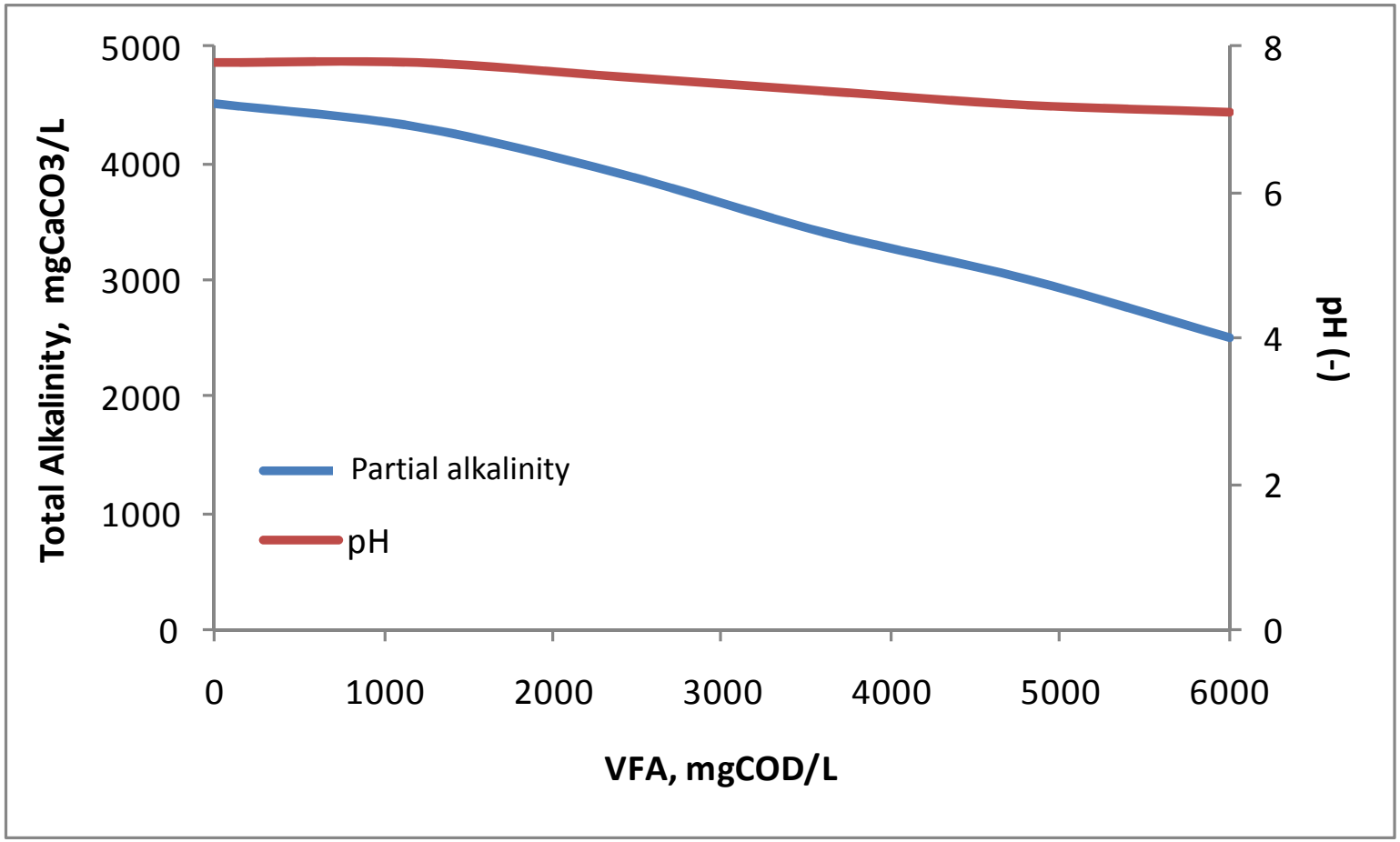
"Volatile acid" Alkalinity due to organic acids (from pH 5.7 to 4.3)

Partial to total alkalinity ratio (Ripley et al., 1986)

They suggested the tritation of the digestate to two final points: 5.75 and 4.3.
Then, the ratio (α) between the VFA alkalinity (determined as the difference between alkalinity at pH 4.5 and 5.75) and the partial alkalinity, determined at pH 5.75, is suggested to define the "state" of the anaerobic process.
In particular, they suggested that values < 0.3 indicate a good state of the anaerobic process:

$$\alpha = \frac{IA}{PA} < 0.3$$

Alkalinity determines the buffer capacity of the system and, differently from pH, is sensitive to process changes.



pH versus partial alkalinity for increasing VFA concentrations in the AD reactor

Clearly, different species in the bulk will contribute with a different "intensity" to the buffering capability of the system

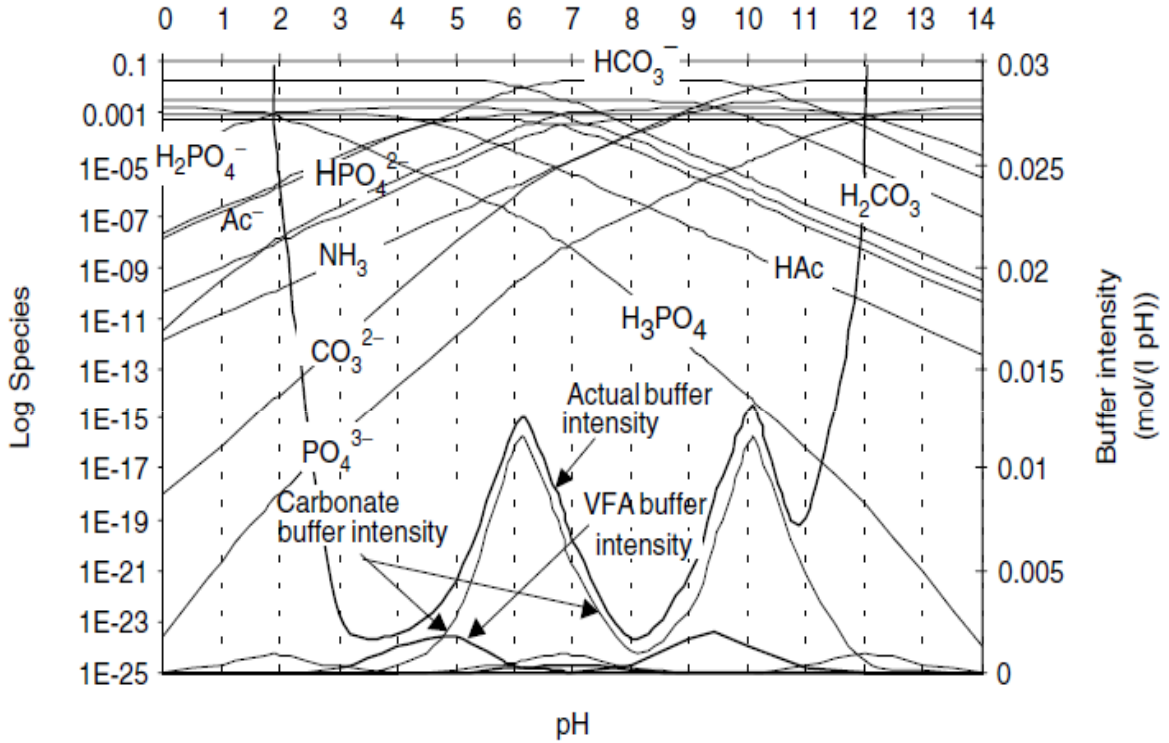


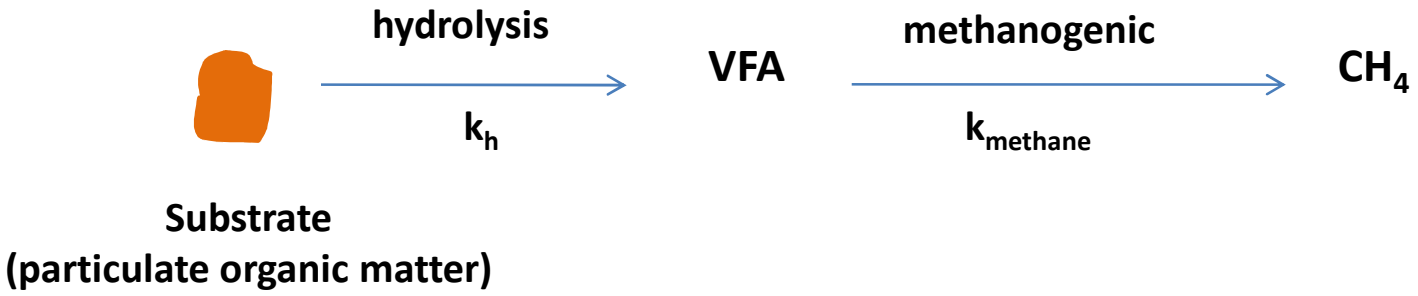
Figure 1. pH–log species and buffer intensity index diagrams in a typical anaerobic digestion sample ($C_T = 1000\,mg\,dm^{-3}$ as $CaCO_3$, VFA = $100\,mg\,dm^{-3}$ as HAc, total phosphate concentration (P_T) = $50\,mg\,dm^{-3}$ as P, total sulfide concentration (S_T) = $20\,mg\,dm^{-3}$ as S, and total aqueous ammonium concentration (N_T) = $50\,mg\,dm^{-3}$ as N, temperature = 22 °C, TDS = $3000\,mg\,dm^{-3}$). Actual buffer intensity is the sum of buffer intensity curves of all subsystems.

Lahav & Morgan, JCTB, 79(2004), 1331-1341

Monitoring of volatile fatty acids (VFA)

The fatty acids used for monitoring purposes are the so called short-chain volatile fatty acids (SC-VFA) with less than 6 atoms of carbon, from acetate (C2) to valerate (C5).

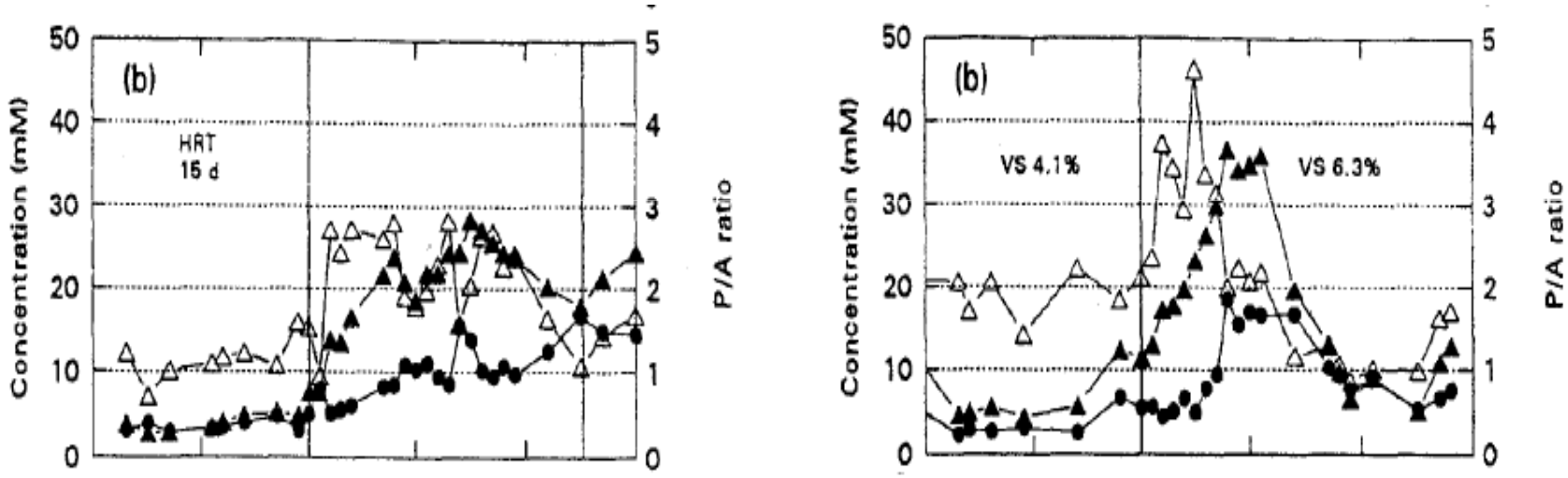
In a stable reactor, where the hydrolytic and methanogenic rates are balanced, with $k_{methane} \sim k_{hydrolysis}$ their presence will be constant, and normally at a very low level of concentration (however, AD reactors treating very biodegradable substrates can be an exception).



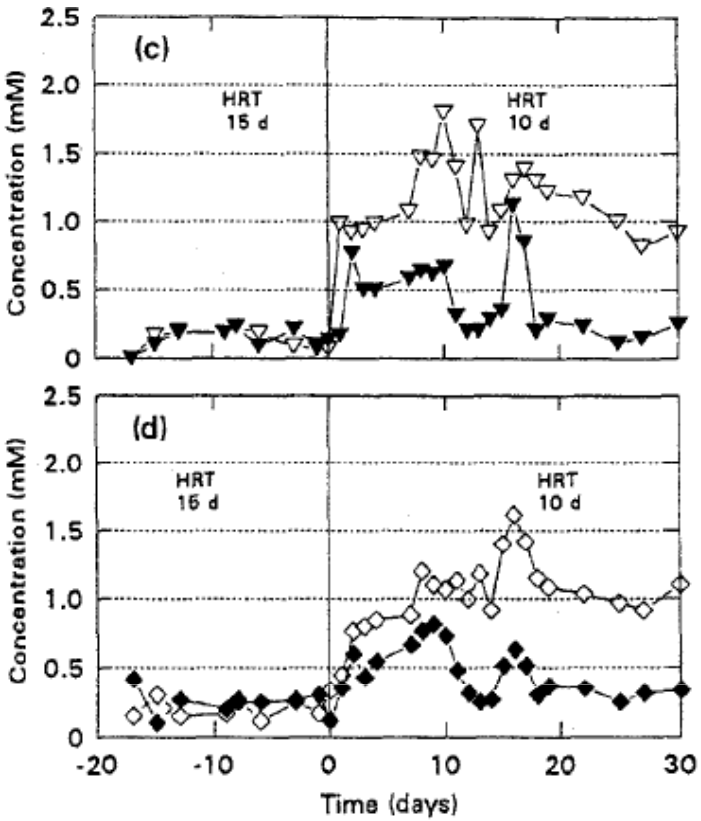
Current methods for VFA measurement include distillation, colorimetry, gas chromatography and various titration techniques.

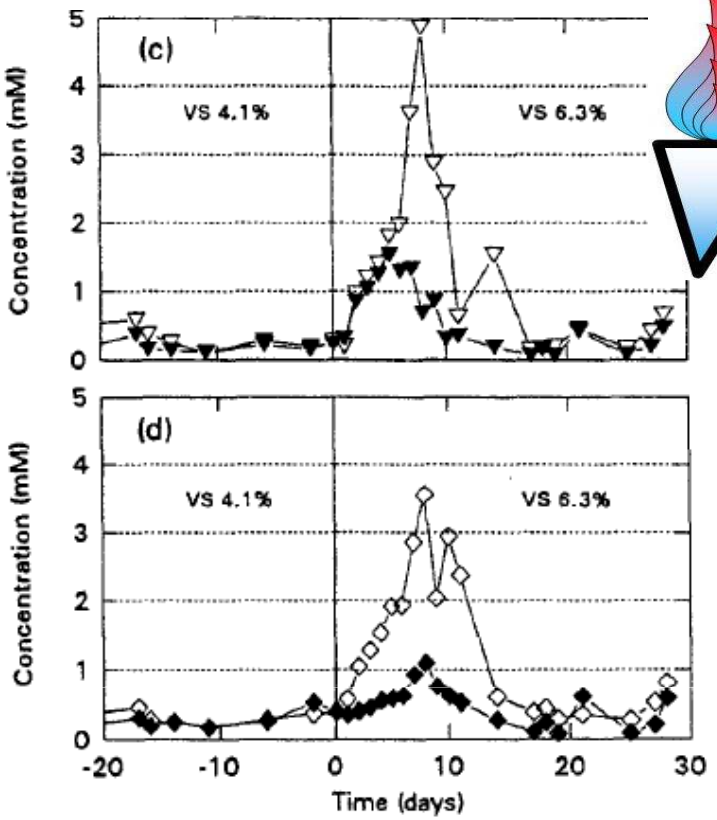
Despite titration techniques are simple and low in time and money consuming, only GC analysis allow for the definition of the different VFA species present in the reactor, and this info is particularly valuable ….

After a perturbation of a stable system (change in hydraulic retention time or organic loading) VFAs, all of them, tend to increase. Then, acetate, which is rapidly converted to CH_4 and CO_2 decrease, while propionate, butyrrate and valerate acids remain at considerably high levels for a longer time.



Changes in acetate (Δ) and propionate (✂) concentrations and P/A ratio (●) after a change in the HRT (left) and organic loading (right)
(from Ahring et al., Appl Microbiol Biotechnol 43(1995), 559)





Changes in isobutyrate (Δ) and butyrate (▪) and isovalerate (◊) and valerate (■) concentrations after a change in the HRT (left) and organic loading (right) (from Ahring et al., Appl Microbiol Biotechnol 43(1995), 559)

However, more properly, the three parameters pH, alkalinity and VFA should be considered as a whole ($H_2/CO_2/CH_4$ percentages in biogas complete the set of info).

In fact, under stable operating conditions, the H_2 and acetic acid formed by acidogenic and acetogenic bacterial activity are utilized immediately by the methanogens and converted to methane.

Consequently, the VFA concentration in properly running anaerobic digesters is typically fairly stable and (generally) low as *carbonate alkalinity* is not consumed in excess and the pH is stable.

Figure 1 shows the buffer capacity profile measured by the BCS during the experiment. As the overload proceeds, as shown figure 2, the main buffer in the system shifts from the bicarbonate (pKa ≈ 6.35) to the VFA (pKa ≈ 4.75) buffer plus small concentrations of the lactate buffer (pKa ≈ 3.86).

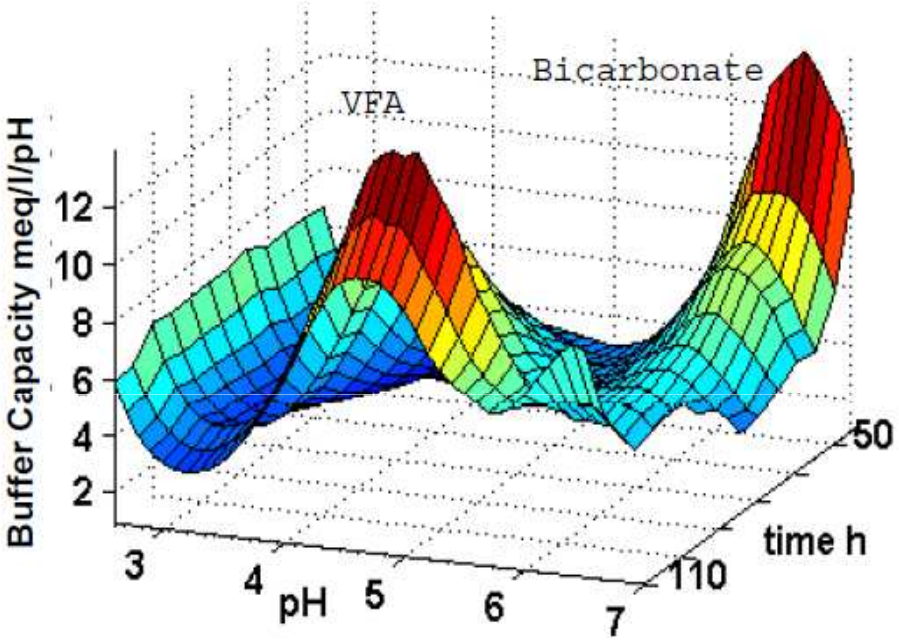


Figure 1: Buffers evolution from bicarbonate alkalinity to VFA during overload

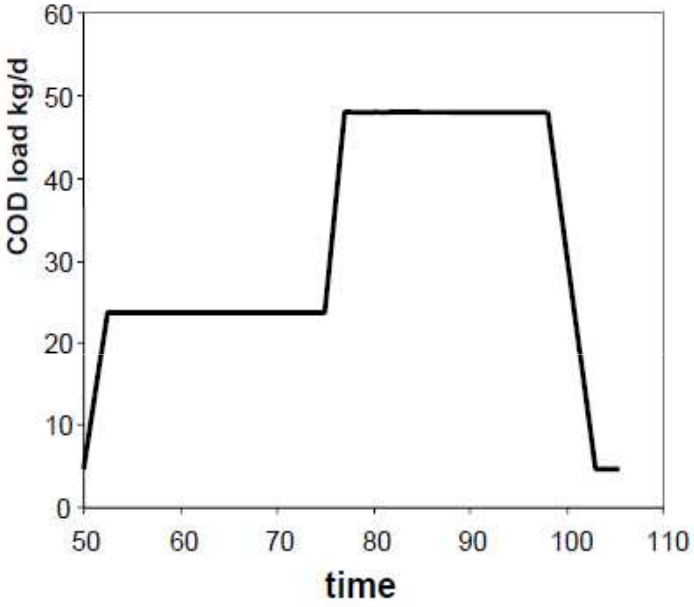


Figure 2: Organic overload to the reactor

Steyer & Vanrolleghem, ICA IWA Conference 2002

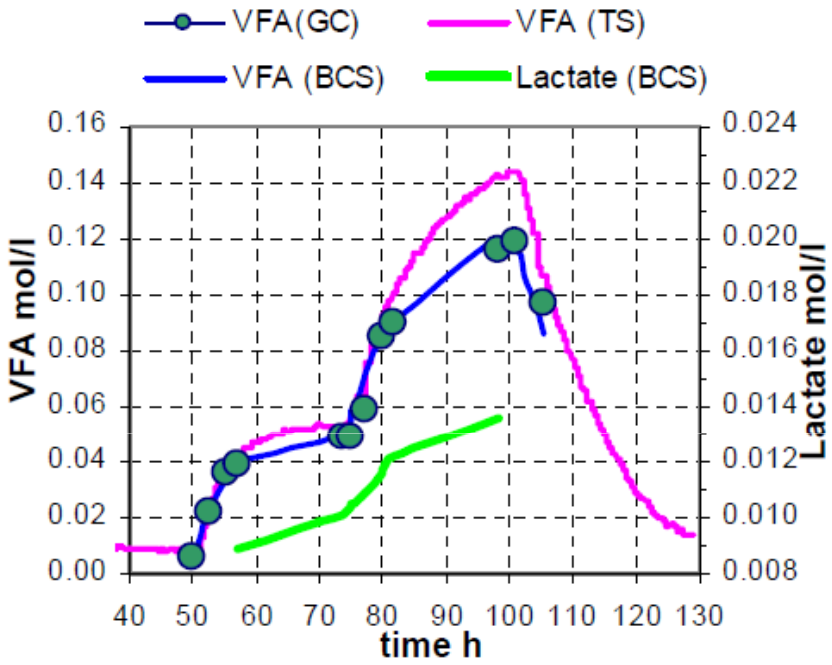


Figure 3: VFA and lactate measurement

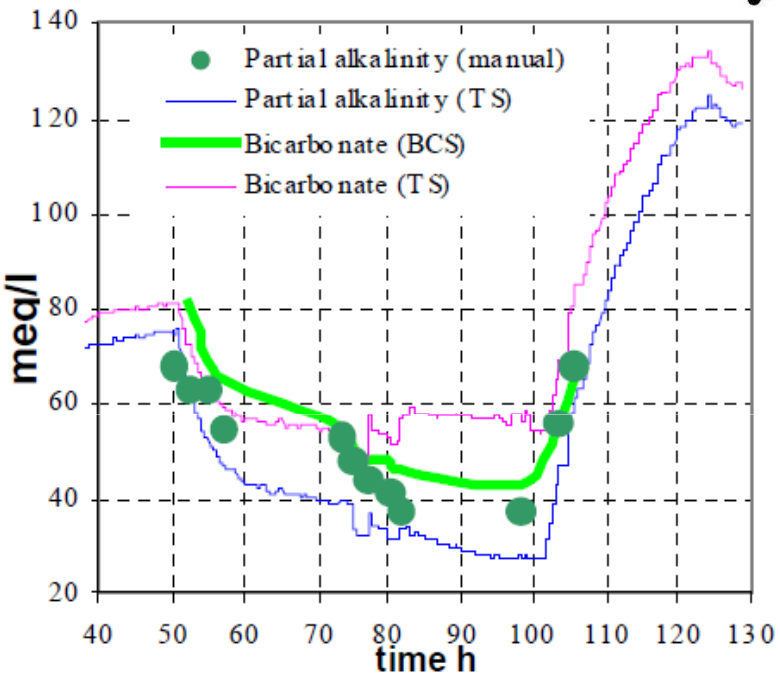


Figure 4: Bicarbonate and partial alkalinity measurement

Steyer & Vanrolleghem, ICA IWA Conference 2002

Monitoring of biogas flowrate and composition

Biogas flowrate and its composition in terms of methane, dioxide carbon and hydrogen is strongly dependent on the feeding conditions and the state of the reactor and are therefore fundamental parameters to be known.

It is clear that an increase in terms of H_2 and CO_2 presence in biogas I related to an over-loading situation.

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Determination of the Biochemical Methane Potential (BMP)

- AD is a proven technology which is gaining more and more appeal in recent years. Now, several “new” substrates are fed to reactors
- Because of the necessity of defining yields and economic balances, the assessment of the biomethane potential of a given substrate is very important
- Several standard methods have been proposed by different agencies during the last years. They generally focus on the biodegradability concept of single molecules rather than the biogas potential and some of them are really questionable
- From the scientific stand point, hundreds of papers have been publishing reporting different methods and using different units for the definition of the BMP…..

In 2007 the ABAI task group of the International Water Association proposed a protocol for the BMP determination (see Angelidaky et al. (2009), WST 59(5), 927

The objective of the protocol is to provide important experimental guidelines to carry out an accurate assessment of the anaerobic biodegradability of any compound or material to methane and carbon dioxide and define the ultimate methane production of a given substrate in terms of $m^3CH_4/kgVS$

Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays

I. Angelidaki, M. Alves, D. Bolzonella, L. Borzacconi, J. L. Campos, A. J. Guwy, S. Kalyuzhnyi, P. Jenicek and J. B. van Lier

ABSTRACT

The application of anaerobic digestion technology is growing worldwide because of its economic and environmental benefits. As a consequence, a number of studies and research activities dealing with the determination of the biogas potential of solid organic substrates have been carrying out in the recent years. Therefore, it is of particular importance to define a protocol for the determination of the ultimate methane potential for a given solid substrates. In fact, this parameter determines, to a certain extent, both design and economic details of a biogas plant. Furthermore, the definition of common units to be used in anaerobic assays is increasingly requested from the scientific and engineering community. This paper presents some guidelines for biomethane potential assays prepared by the Task Group for the Anaerobic Biodegradation, Activity and Inhibition Assays of the Anaerobic Digestion Specialist Group of the International Water Association. This is the first step for the definition of a standard protocol.

Key words | anaerobic digestion, batch assays, biomethane potential (BMP), energy crops, organic solid waste

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*TG-ABAI – Task Group for the Anaerobic Biodegradation, Activity and Inhibition of the Anaerobic Digestion Specialist Group of the International Water Association.

doi: 10.2166/wst.2009.040

What you need for a BMP trial at a given temperature is :

I. The substrate
II. An active and sufficient inoculum
III. A device for biogas measurement

Inoculum

- The inoculum should be "fresh", i.e. inoculum that is not stored for periods longer than a few days, originating from any type of active anaerobic reactor (e.g., sludge reactors, manure reactors or sludge bed reactors, such as UASB).

- The inoculum should have a "broad trophic" microbial composition in order to ensure that the anaerobic conversion of different substrates is not limited.

- Characteristics in terms of TS, TVS, COD and activity (on acetate) should be always stated

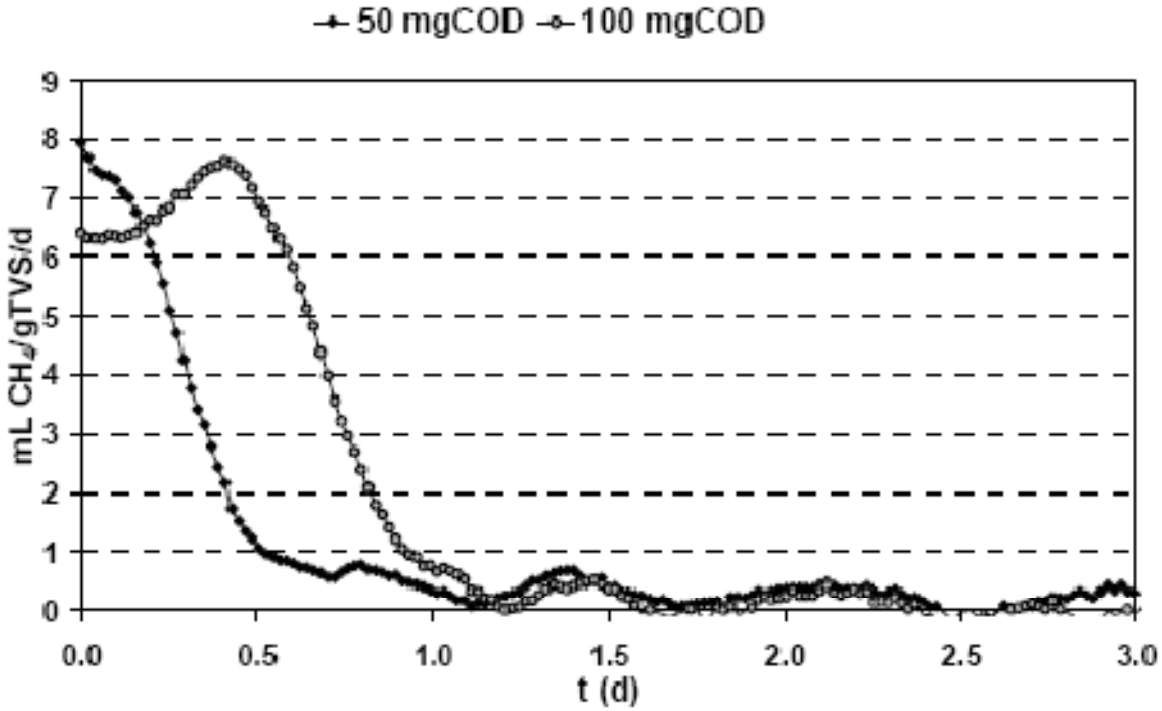
Inoculum pre-treatment (some suggestion …)

The inoculum should be “degassed” (i.e., pre-incubated) in order to deplete the residual biodegradable organic material (endogenous)

The inoculum should be a close representation of the one sampled from the reactor, and SHOULD NOT (as described on previous ISO 11734, ASTM E 2170 (2001)) be washed to remove residual substrate material and inorganic carbon compounds.

Activity of the inoculum

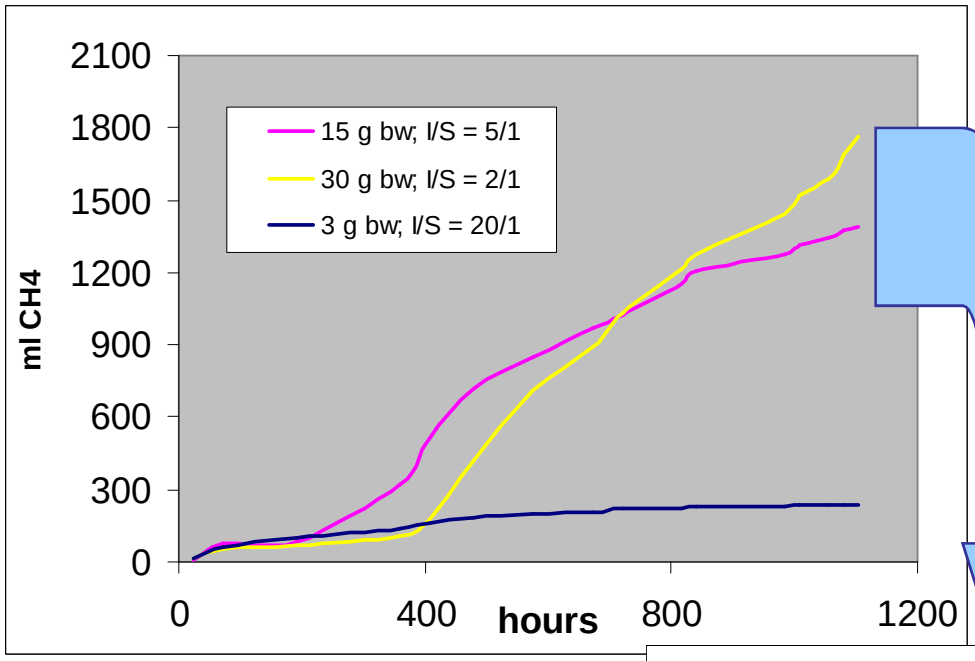
The quality of inoculum could be examined by performing activity tests on acetate and cellulose (or gelatine or both)

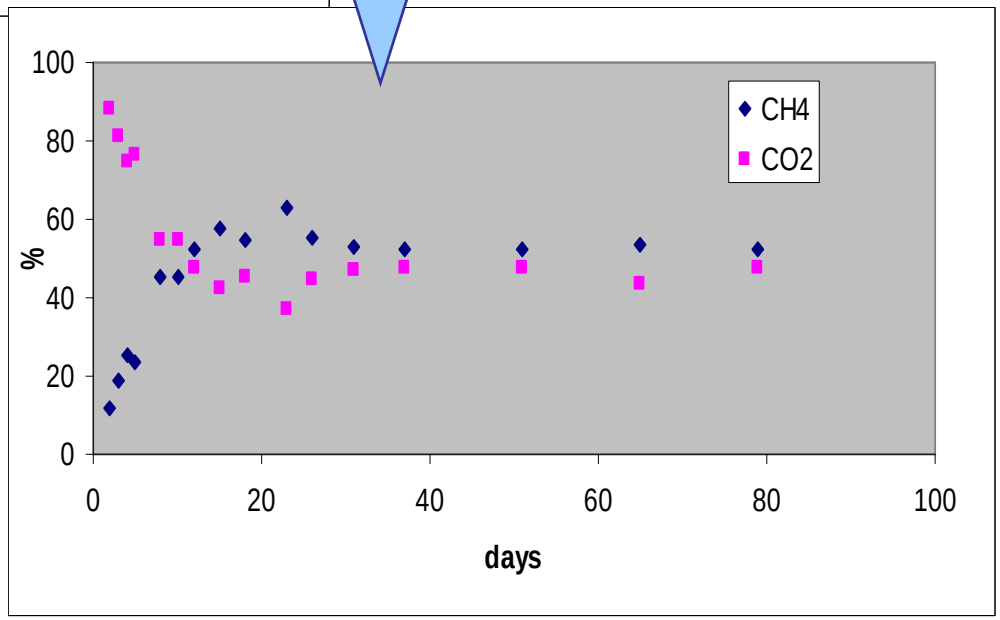


Specific Methanogenic Activity on acetate

- Typical SMA determined on acetate are in the range 30 – 40 $mlCH_4/gVSSd$ but can be as low as 10 $mlCH_4/gVSSd$; in last case the inoculum concentration in the test vessel should be very high (typically being 70% to 80% of the total liquid used in the test).

- High inoculum concentrations should always be preferred. This offers an excess of active biomass and buffer capacity, conditions similar to those of real anaerobic reactors (generally CSTR)

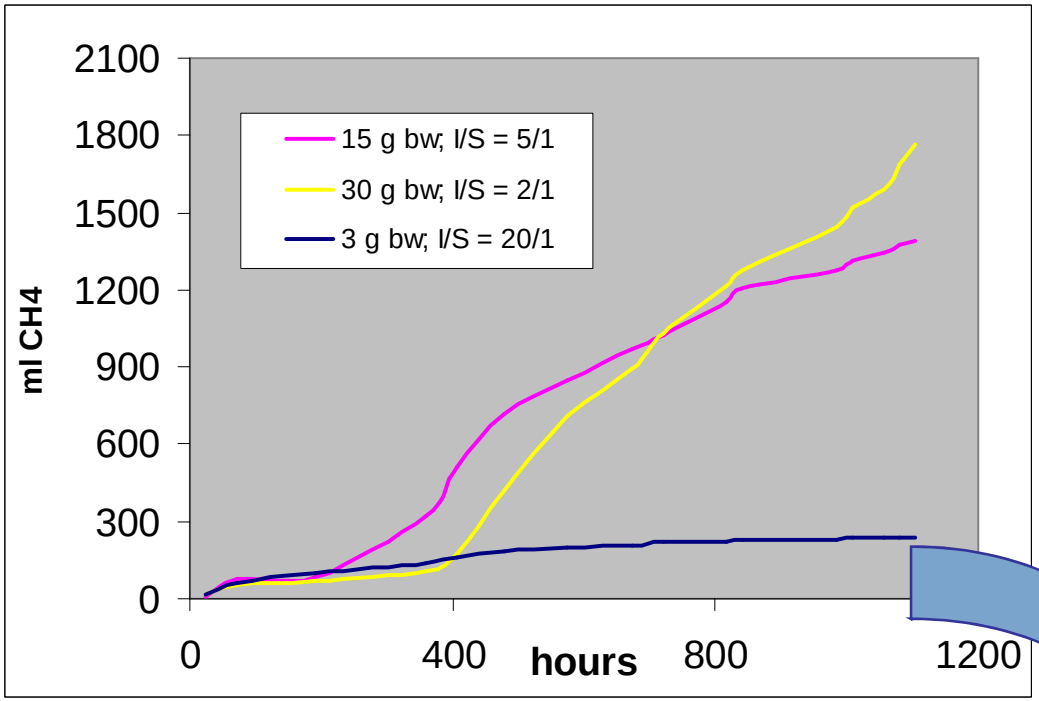


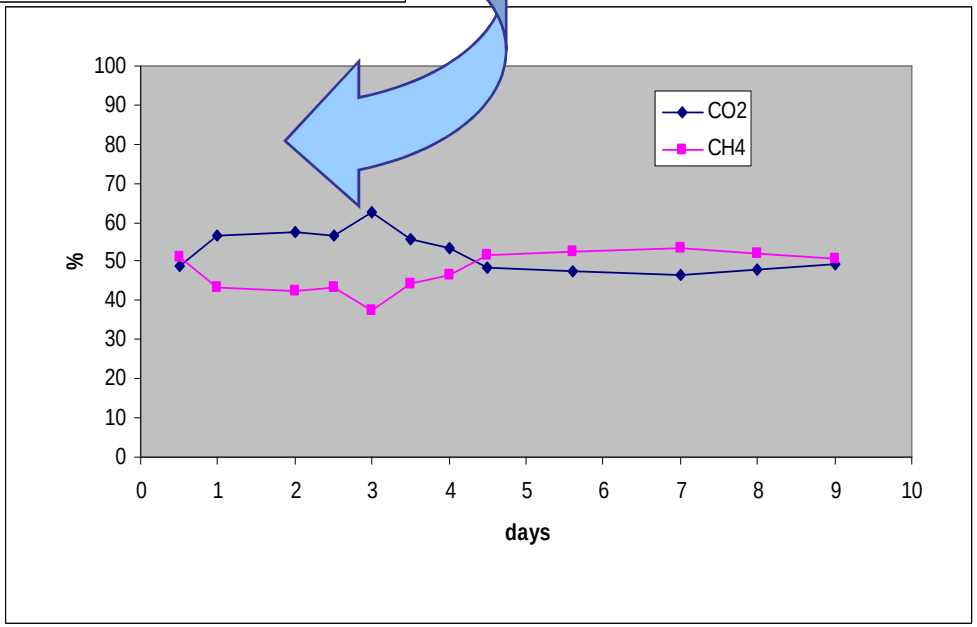


Too much substrate …

Initial flat curve and CO_2 evolution …

Acidogenic conditions !





Right proportion …

Good curve, useful also for kinetic tests and CH_4 evolution …

If the specific activity and hydrolysis constant are known (or at least estimated) the correct ratio can be eventually be determined according the mass balance for VS, which gives:

$$Vinoculum = \frac{X_{SS} V_{ww} k_h}{VSS_{inoculum} SMA_{inoculum}}$$

X_{SS} concentration of hydrolysable substrate (g/L), V_{ww} volume of waste(water) in the assay vessel (L), k_h first order hydrolysis constant (day^{-1}), $VSS_{inoculum}$ content of the inoculum (gVSS/L) and $SMA_{inoculum}$ specific methanogenic activity of the inoculum (g COD-CH_4/(gVSSday)).

Angelidaki and Sanders, 2004

Medium

Necessary nutrients/micronutrient/vitamins/buffers are generally required for optimal performance of anaerobic microorganisms

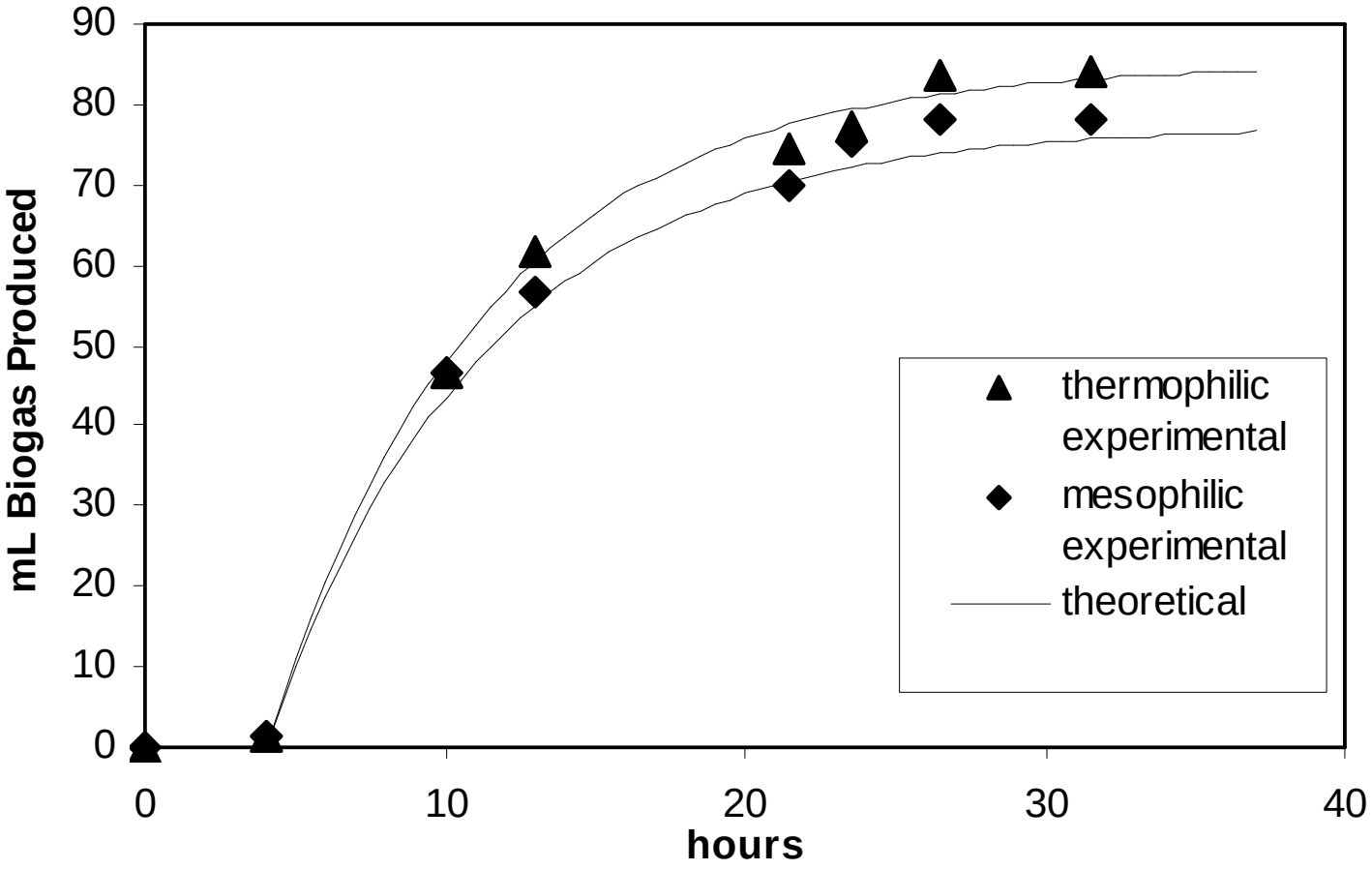
Table 4.2. Basic Anaerobic Medium (Angelidaki and Sanders 2004).

Description of Anaerobic Easic Medium
The basic medium is prepared from the following stock solutions, (chemicals given below are concentrations in g/l, in distilled water). (A) NH_4Cl, 100; $NaCl$, 10; $MgCl_2$ $6H_2O$, 10; $CaCl_2$ $2H_2O$, 5 (B) K_2HPO_4 $3H_2O$, 200 (C) resazurin 0.5 (D) trace-metal and selenite solution: $FeCl_2$ $4H_2O$, 2; H_3BO_3, 0.05; $ZnCl_2$, 0.05; $CuCl_2$ $2H_2O$, 0.038; $MnCl_2$ $4H_2O$, 0.05; $(NH_4)_6Mo_7O_{24}$ $4H_2O$, 0.05; $AlCl_3$, 0.05; $CoCl_2$ $6H_2O$, 0.05; $NiCl_2$ $6H_2O$, 0.092; ethylenediaminetetraacetate, 0.5; concentrated HCl, 1 ml; Na_2SeO_3 $5H_2O$, 0.1 (E) vitamin mixture (componets are given in mg/l): Biotin, 2; folic acid, 2; pyridoxine acid, 10; ridoflavin, 5; thiamine hydrochloride, 5; cyanocobalamine, 0.1; nicotinic acid, 5; P-aminobenzoic acid, 5; lipoic acid, 5; DL-pantothenic acid. To 974 ml of distilled water, the following stock solutions should be added (A), 10 ml; (B), 2 ml; (C), 1 ml; (D), 1 ml and (E), 1 ml. The mixture is gassed with 80% N_2 - 20% CO_2. Cysteine hydrochloride, 0.5 g and $NaHCO_3$, 2.6 g, are added and the medium is dispensed to serum vials and autoclaved if necessary. Before inoculation the vials are reduced with Na_2S $9H_2O$ to a final concentration of 0.025%.

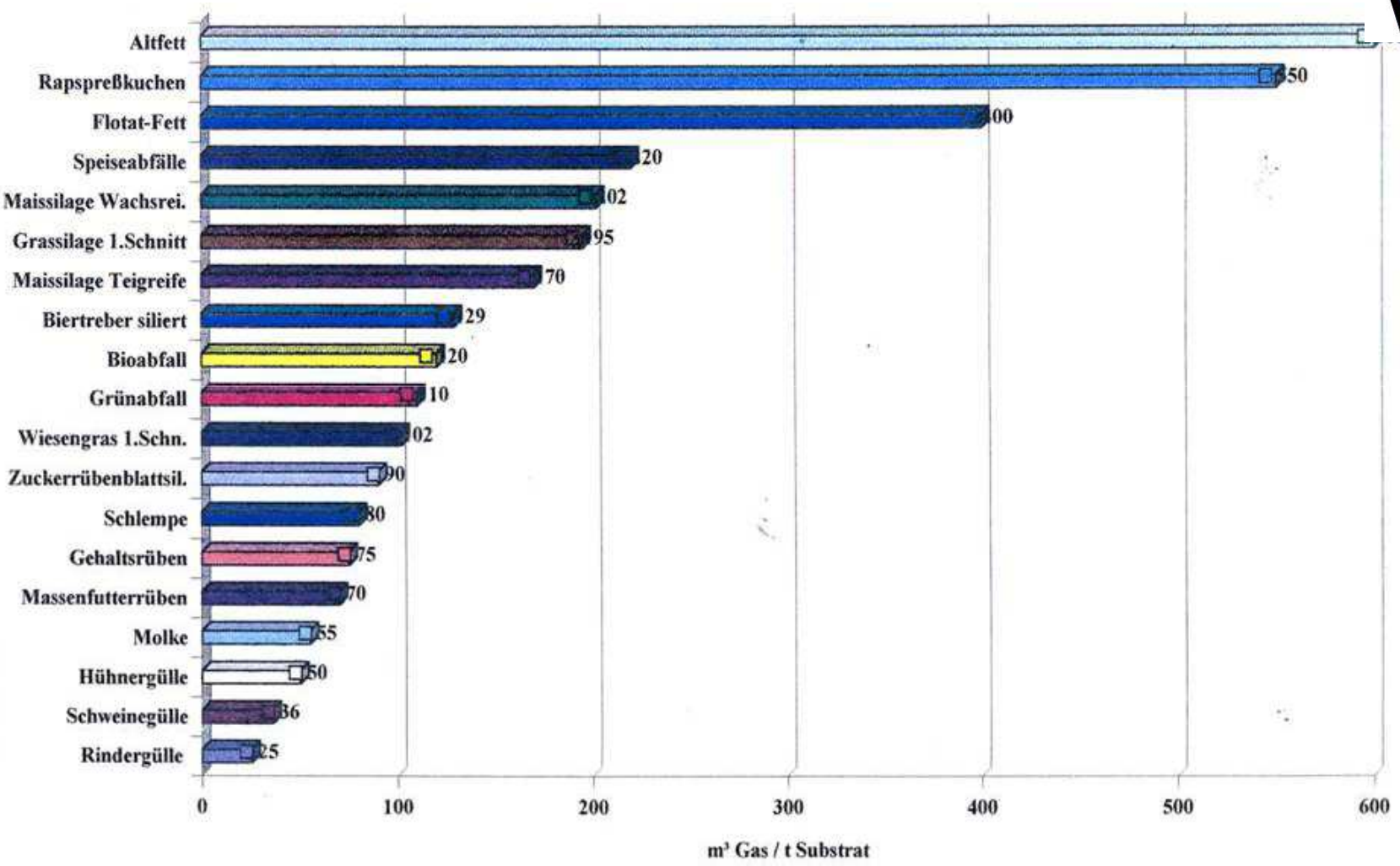
Data collection of produced biogas

Method	Comments
Volumetric	◆ Inaccuracy due to variations of atmospheric pressure ◆ Inaccuracy due to inorganic carbon in liquid phase ◆ Evaporation of water in displacement systems ◆ Simple and cheap
Manometric	◆ Manometric transducers limited range of accuracy ◆ Inaccuracy due to inorganic carbon in liquid phase
GC- TDC	◆ Special equipment ◆ Time and labour requiring ◆ Many simultaneous ◆ Direct measurement, precise
GC- FID	◆ Special equipment ◆ Fast ◆ Many simultaneous ◆ Direct measurement, precise

- The methane accumulated in the headspace of the closed vessel should be measured by gas chromatography (GC). For that, a sample volume of e.g. 100 µL should be collected with a gas-tight syringe and injected into the GC. Either a Thermal Conductivity Detector (TCD) or a Flame Ionization Detector (FID) can be used. The obtained peak area should be compared to that obtained by injecting the same volume of a standard gas mixture of the known composition.
- The volume of methane produced is obtained by multiplying the headspace volume by the % of CH_4 in the headspace as determined by GC analysis. For publication and comparison with other studies, the values are often calculated to STP conditions, i.e. converted to 0˚C and 1 atm.

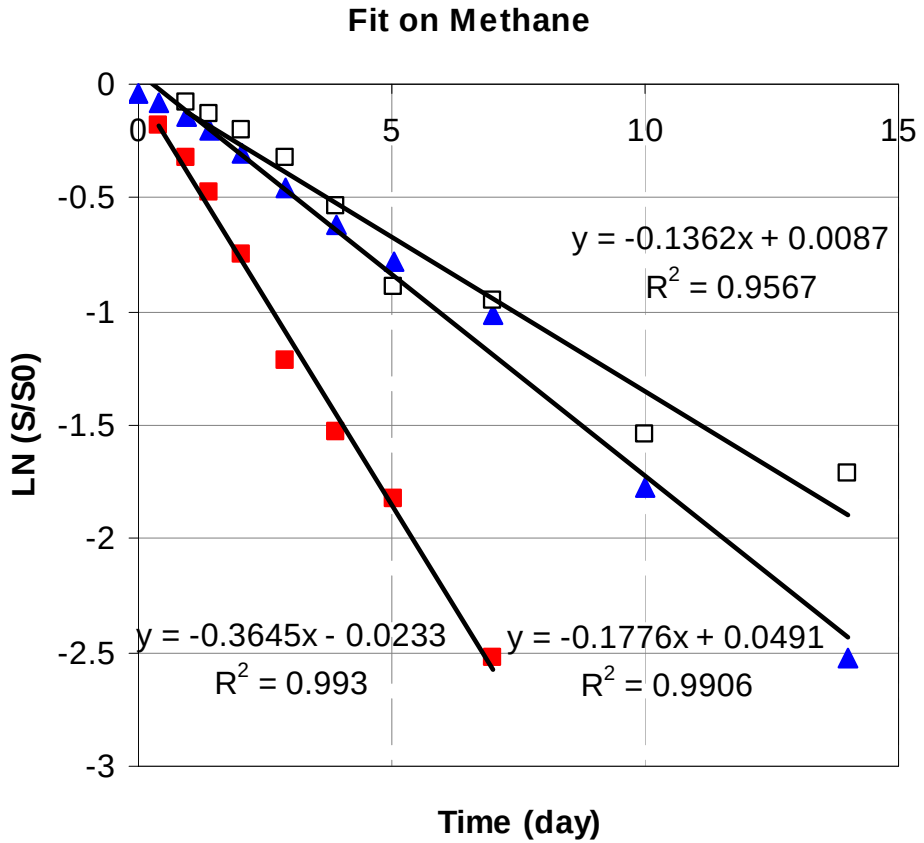

mL Biogas Produced
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
hours
thermophilic experimental
mesophilic experimental
theoretical

Biogas potential for different substrates



Determination of the hydrolysis constant (first order kinetic)

$$\frac{dS}{dt} = -k_h S \quad \Rightarrow \quad \ln \frac{B_\infty - B}{B_\infty} = -k_h t$$



As a first indication, the following range of values can be considered:

k_h > 0.3, very biodegradable substrates (e.g., food waste, material rich in carbohydrates ….)

k_h = 0.1, slowly biodegradable substrates (e.g., waste activated sludge)