Biogas Laboratory

沼气实验室

1st O&M Training 第一次运行维护培训

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Outline 概要

- Tasks of a laboratory 实验室的任务
  - Input control 进料控制
  - Process control 工艺控制
  - Effluent control 出料控制
  - Gas control 产气控制
- Equipment 设备
- Staff 人员
- Rooms 房间

Overall goals of laboratory activities
实验室活动的总体目标

Samples are analysed 分析样品以

- to guarantee high performance of the plants
保证沼气厂的高效运行
- to improve the methane yield per ton substrate
提高每吨发酵底物的甲烷产量
- to avoid ammonia or H_2S inhibition
避免氨或硫化氢的抑制作用
- to avoid acidfication 避免酸化
- *to fight micro nutrient deficits (you cannot do this on your plant)* 避免微量营养物质的缺失

Biggest biological problems for biogas plants
沼气厂最大的生物学问题

Fast inhibition + breakdown of a fermenter
Can be controlled on site
快速抑制+发酵系统运行崩溃是可以在现场控制的

- Acidification: too much input
- 酸化：进料量过大
- (toxic chemicals?)
- （有毒化学物质？）
- Toxification: too much NH_3, salts
- 细菌中毒：过高的NH_3浓度和含盐量

Slow inhibition
professional laboratory necessary
indicators can be found on site
慢性抑制需要专业的实验室，现场可以找到相应的指标

- „wrong acids“ in the fermenter (iso-acids)
- 发酵罐内产生“错误的有机酸”
- Deficiency of trace elements
- 缺乏微量元素
- Toxification: other toxic chemicals
- 细菌中毒：其他有毒化学物质

Laboratory – tasks 实验室的任务

- To control input material进料控制
- To control the daily performance of the AD plant 沼气厂生产效率控制
- To control the effluent 出料控制
- To control the gas 产气控制

Input control 进料控制

- To check on suitability of the material for a biogas plant: 检查物料是否适合沼气厂
  - dry matter content 干物质含量
  - organic dry matter content / COD 有机干物质含量/COD
  - pH
  - Salt 含盐量
  - biogas yield of the material and potential inhibition of the biogas process 物料的产沼潜力和潜在的抑制因素
  - nitrogen and ammonium 氮和铵
  - inorganic buffer 无机缓冲能力
  - volatile fatty acids 挥发性脂肪酸
  - Pollutants 杂质

Input control 进料控制

- New substrates should be checked 新的底物需要先经过检测
- If source of the material is the same (e.g. the same animal husbandry) then control analysis are recommended once a year 如果物料来源是单一的（如相同的畜禽养殖），那么进料分析控制频率建议为一年一次
- Some material changes in quality according to seasons (e.g. household biowaste) 部分物料性质随季节而变化（如有机生活垃圾）

Process control 工艺控制

- To keep the biogas process stable 保持沼气厂工艺运行稳定
- To avoid breakdown of the biogas process 避免沼气工艺系统崩溃
- To optimize the biogas process 优化沼气厂工艺

Process control 工艺控制

- Parameter: 参数
  - dry matter content 干物质含量
  - organic dry matter content / chemical oxygen demand 有机干物质含量/化学需氧量
  - pH
  - Salt 含盐量
  - biogas yield of the material and potential inhibition of the biogas process 物料产沼潜力和潜在的抑制因素
  - nitrogen and ammonium 氮和氨
  - inorganic buffer 无机缓冲能力
  - volatile fatty acids 挥发性脂肪酸
  - trace elements 微量元素

Effluent control 出料控制

- To calculate the efficiency of the biogas plant 计算沼气厂的效率
- To control the fertilizer value of the effluent 控制出料的肥效
  - dry matter content 干物质含量
  - organic dry matter content / chemical oxygen demand 有机干物质含量/化学需氧量
  - pH
  - Salt 含盐量
  - biogas yield of the material and potential inhibition of the biogas process 物料产沼潜力和潜在的抑制因素
  - nitrogen and ammonium 氮和氨
  - inorganic buffer 无机缓冲能力
  - volatile fatty acids 挥发性脂肪酸
  - Pollutants 杂质

Gas control 产气控制

- CH_4 control to get information on the biogas process 甲烷浓度控制以获取发酵工艺运行情况
- H_2S control to avoid problems at the CHP
  H_2S 浓度控制以避免热电联产系统出现问题
- Gas quality gives information on the biological status of the biogas process and on the suitability of the gas for its use 沼气质量能提供发酵工艺运行状况信息，并确定是否适宜其用途。

Parameter 参数

	Input material 进料	Process control 工艺控制	Effluent control 出料控制
dry matter 干物质	x	x	X
organic dry matter 有机干物质	x	x	X
chemical oxygen demand 化学需氧量	x	x	X
pH	x	x	X
Salt 含盐量	x	x	X
Biogas yield 产沼能力	x		
nitrogen and ammonium 氮和氨	x	x	X
inorganic buffer 无机缓冲能力	x	X	
volatile fatty acids 挥发性脂肪酸	x	X	
trace elements 微量元素	X	X	
Pollutants 杂质	x		x

Parameter 参数

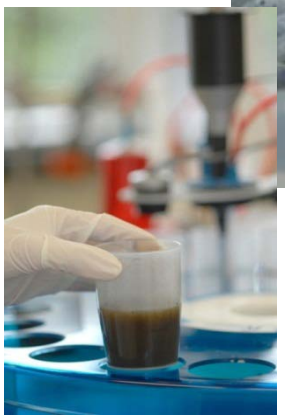
	Devices 测试设备
Temperature 温度	Thermometer 温度计
dry matter 干物质含量	Oven (up to 105 °C) 恒温箱（可达到105 °C）
organic dry matter 有机干物质含量	Muff le oven (up to 550°C) 马弗炉 （可达550°C）
chemical oxygen demand 化学需氧量	Digestion and titration unit 消化及滴定设备
pH	pH meter pH计
Salt 含盐量	EC meter 电导率仪
Biogas yield 沼气产量	Fermenter, volumeter, gas analyser 发酵罐、容积计、气体分析仪
nitrogen and ammonium 氮和氨	Kjeldahl, BiogasPro 凯氏定氮仪、BiogasPro
inorganic buffer 无机缓冲能力	Titration, BiogasPro 滴定仪、BiogasPro
volatile fatty acids 挥发性脂肪酸	Titration, gas chromatography or high pressue liquid chromatography 滴定仪、气相色谱仪或者高压液相色谱仪
trace elements 微量元素	Atomic adsorption spectrometer (AAS) or ICP 原子吸收光谱（AAS）或者电感耦合等离子（ICP）
Pollutants 杂质	AAS/ICP

Parameter 参数

	Professional lab 专业实验室	Well equiped lab 较完善实验室	Basic lab 一般实验室
Temperature 温度	x	x	x
dry matter 干物质	x	x	
organic dry matter 有机干物质	x	x	
chemical oxygen demand 化学需氧量	x	x	
pH	x	x	x
Salt 含盐量	x	x	x
biogas yield 沼气产气率	x	x	
nitrogen and ammonium 氮和氨	x	x	(x)
inorganic buffer 无机缓冲能力	x	x	x
volatile fatty acids 挥发性脂肪酸	X (single component, sum) （单一成分、总计）	X (single component, sum) （单一成分、总计）	X (sum) （总计）
trace elements 微量元素	x		
Pollutants 杂质	x		
continuous flow reactors 连续流反应器	x		
biogas quality 沼气成分	X	X	x

Preparation 准备

- Sieving 筛选
- Homogenizing 混合均匀
- Milling 研磨



Pictures by bonalytic

Basic analysis – substrate 基本分析—底物
(as well: parameter for a training)（以及：培训用的参数）

- pH pH值
- EC 电导率
- Dry matter 干物质
- Organic dry matter
  有机干物质
- Chemical oxygen demand
  化学需氧量
- Alcalinity and voltile fatty acids
  碱度和挥发性脂肪酸
- Ammonium 铵

Pictures by bonalytic

Advanced analysis – substrate 高级分析—底物

- GC (Gas Chromatography) or HPLC (High Pressur Liquid Chromatography): single component analysis
  气象色谱仪或高压液相色谱仪：单一组分分析
- ICP (inductively coupled plasma): trace elements
  电感耦合等离子体：微量元素

Pictures by bonalytic

Biogas analysis 沼气分析

- H_2S and explosion limit detectors 硫化氢和爆炸极限探测器
- Biogas quality 沼气质量
- Batch fermenter 序批式发酵罐
- Continuous fermenter 连续式发酵罐

Pictures by bonalytic

Determination of Biogas Yields
沼气产量测定

Substrates are analysed using 底物用以下方法进行分析

- Batch tests 序批式测试
  - to determine the biogas potential 确定产沼潜力

- Continuous fermenter 连续式发酵罐
  - to study influence of hydraulic residence time and organic loading rate 研究水力停留时间和有机负载率的影响
  - to overcome biological problems in the fermenter such as acidification, micro nutrient deficits, high NH_3 concentration, the effect of antibiotics
    克服发酵罐中生物学问题，例如：酸化，微量营养物质不足，氨浓度过高，抗生素影响

Skilled Staff for the Laboratory 实验室技术员

- The basic analysis and basic biogas tests can be performed by one skilled person (experienced BSc or MSc **or very experienced technician).**
  基本分析和沼气基本测试由一名熟练操作员完成（有经验的学士或硕士）

- For advanced analysis a second staff is necessary (experienced BSc. or MSc.). 深入分析需要另外一个人员（有经验的学士或硕士）

- Example: a well running biogas laboratory in Germany may handle more than 100 samples per day with 6-10 persons.
  例如：在德国一个运作良好的沼气实验室有6-10名员工，每天处理100多个样品。

- This could be a size for a well running Provincial/National laboratory, too
  运作良好的省级/国家实验室也应该具有同样规模。

Rooms for a full service laboratory
提供全面服务的实验室

- Sample Arrival, packing 样品到达，包装
- Storage 储存
- Preparation 准备
- Basic analysis 基本分析
- Advanced analysis 高级分析
- Sum: around 60-100 m²

  总计：约60-100平米

Picture: http://www.laborbausysteme.de/bilder-laborbau/galerie-schule/DSCF5349_1-klein.jpg

Necessary rooms 必要的房间

	Professional laboratory 专业实验室	Well equiped laboratory 设备较全实验室	Basic laboratory 基础配置实验室
Sample arrival, packing 样品到达，包装	X		
Storage 储存	X		
Preparation 准备	X	X	
Basic analysis 基本分析	X	X	X
Advanced analysis 高级分析	X	X	
Biogas test room 沼气测试室	x	x	

Basic laboratory 基础实验室

- Temperature 温度
- pH, EC pH值，电导率
- inorganic buffer 无机碱度
- sum of volatile fatty acids 挥发性脂肪酸
- Ammonium 铵
- biogas quality (minimum: CH_4, H_2S; installed in the gas pipeline to the gas user) 沼气质量（最少：CH_4，H_2S；安装在沼气用户的管道上）

VERY IMPORTANT: Sampling
非常重要的环节：采样

Prior to sampling 采样之前

- Beware of dangers on a biogas plant 了解沼气厂的危险
  - Danger of explosion 爆炸的危险
  - Danger of H_2S H_2S的危险
- A representative sample of the fermenter or of the substrate is necessary! 需要有代表性的发酵罐内样品或者底物样品
- For fermenter samples: If there is a sampling valve: flush it first and discard the first material (20 Liters) 对于发酵罐内样品：如果有采样阀：先冲洗并排掉开始的部分（20L）
- If no sampling valve: perhaps sampling is possible out of the effluent (again discard the first 20 Liters) 如果没有采样阀，可能要从出口采样（同样排掉开始的部分20L）

Sampling valve 采样阀

Temperature 温度

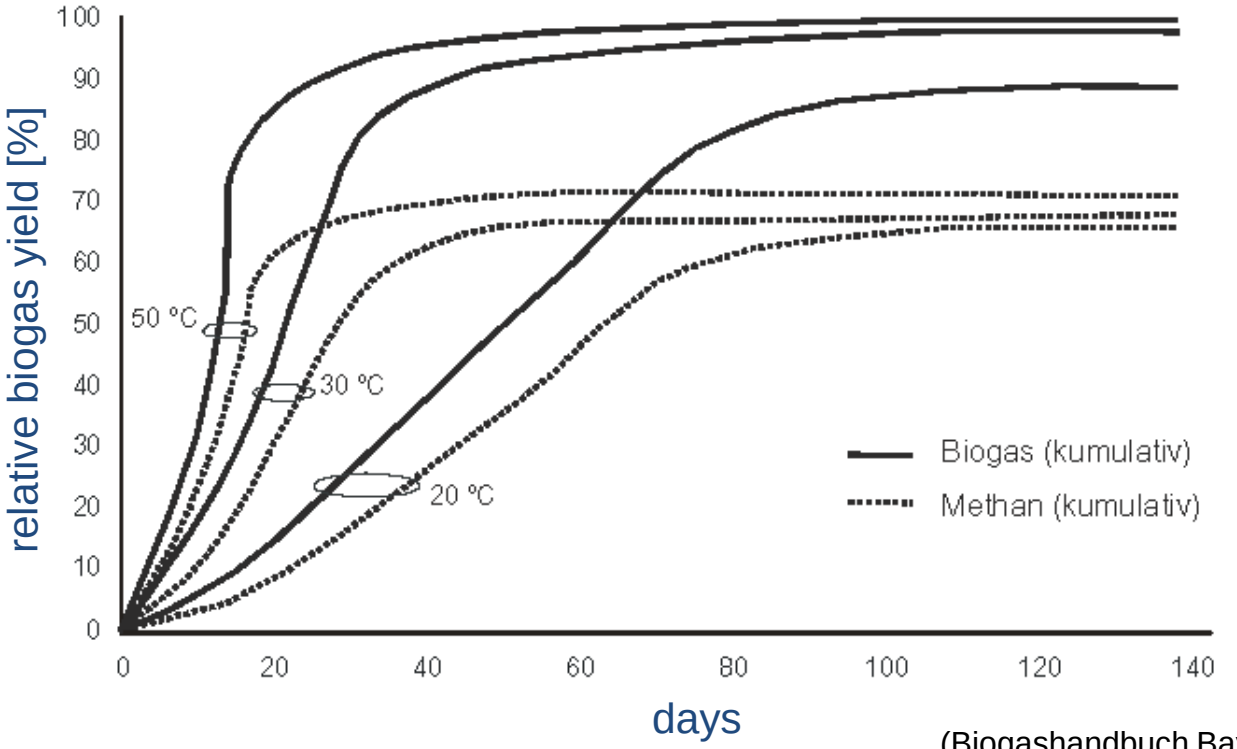
Why? 为什么？

- Temperature should be kept stable, best around 39°C 温度必须保持稳定，最好在39°C左右
- Otherwise the biogas yield is lower 否则沼气产量会较低

Examples – Temperature variability

示例 – 温度变化

- The lower the temperature, the lower the biogas yield and the lower the degradation rate of COD or the organic dry matter. 温度越低，沼气产量越低，COD和有机干物质的降解率也越低。



(Biogashandbuch Bayern, 2004)

pH

- Why? too low and too high pH inhibit the biogas process 为什么？pH太低或者太高都会抑制产沼进程
- pH meter pH计
- In the fermenter: pH of > 7 and < 8.4 is advised 建议反应罐内pH值在7到8.4之间

pictures: www.conrad.de www.wtw.de

What is pH 7.5? pH值为7.5表示什么？

- These are表示 0.000000032 g Protons/Liter! 克质子/升
  0.0000001 g Protons/Liter may be too low already and CH4-production is reduced.
  克质子/升可能已经太低，产沼能力被降低
- These are表示 0.0001 g Protons/m³质子/方
- These are表示 0.1 g Protons/1000 m³质子/1000方

pH

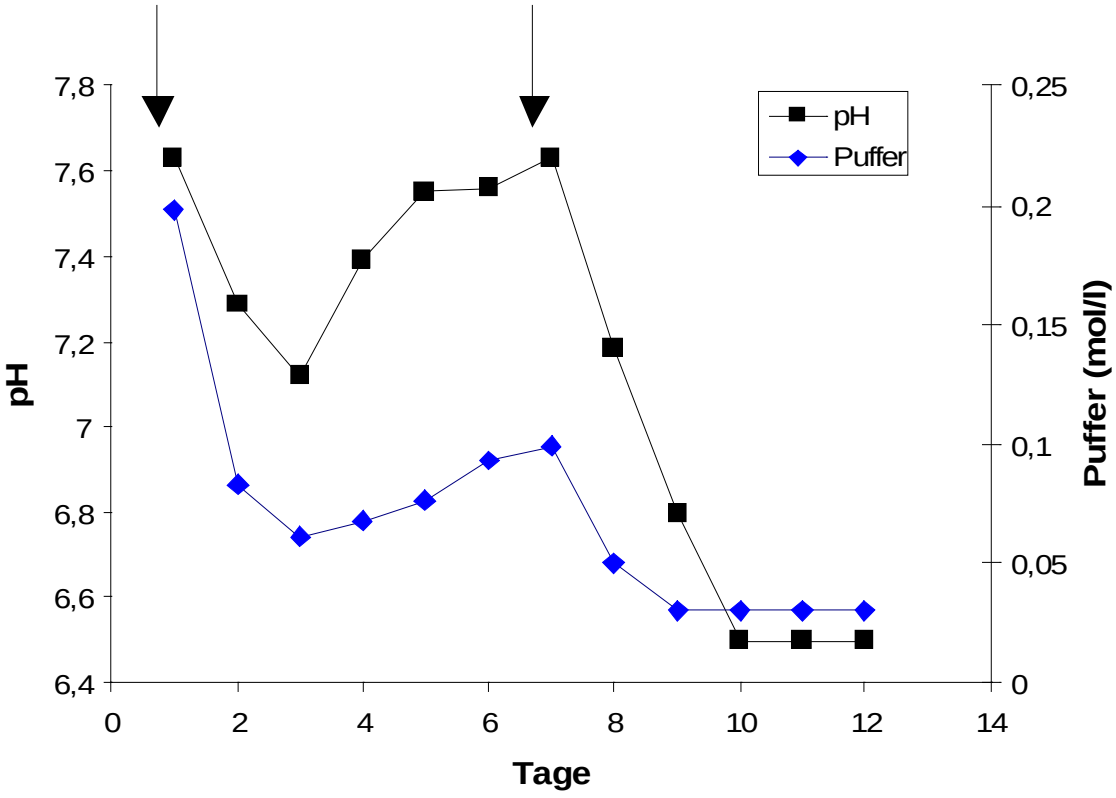
- A pH-meter looks like an every day tool, BUT it is a precision instrument and it requires maintenance.
  pH计看起来像日常工具，但它是精确仪表，需要维护
- This means: 包括：
  1. Calibration 校准
  2. Store the tip of the electrode correctly (3 M KCl)

     正确储存电极的探针(3 M KCl)

pictures: www.palintest.com, www.tunze.com

pH is not a suitable indicator – Example
pH值不是一个合适的指标 – 示例

- In the substrate: hydrogen carbonate buffers (TIC), organic acids (VFA).底物内含有碳酸氢根碱度(TIC)和挥发性脂肪酸(VFA)。
- pH may recover, but the status of the fermenter is labile and may yield to a final breakdown.
  pH值可能会恢复，但发酵罐内状况不稳定，有可能导致最终崩溃



Why analyse Total Inorganic Carbon (TIC, „buffer“) and Volatile Fatty Acids (VFA)?

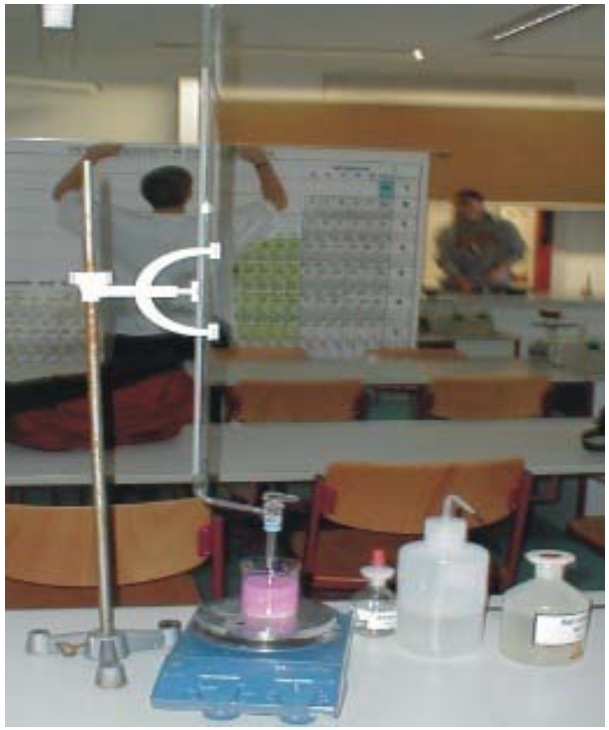
为什么分析总无机碳(TIC,“缓冲能力”)和挥发性脂肪酸(VFA)?

- TIC: shows the amount of buffer in the fermenter TIC：指示了发酵罐内的缓冲能力
- VFA: shows the acid formation
  VFA：指示了酸的形成
- Both parameter give information on acidification 两个指标提供了酸化的信息
- If the biogas plant acidifies, then the biogas process stops. 如果沼气厂发生酸化，产沼过程会停止

(TIC): Manual titration TIC：手动滴定

- Titration with acid to pH 5 用酸滴定使pH值下降到5 (Problems: foaming, maybe treatment prior to titration in form of sieving) （问题：泡沫，可能在滴定前需要过滤）

$$TIC = \frac{20\ ml}{V} * M_{TIC} * 250$$



TIC: Total inorganic Carbonate (mg/kg) or „buffer“
TIC: 总无机碳（mg/kg）或者“缓冲能力”
V: sample volume (mL)
V: 样品体积（mL）
M_{TIC}: amount of 0.05 M sulfuric acid in mL
M_{TIC}: 0.05 M 硫酸的量（mL）

picture: http://www.msd-media.de/autsch/Facharbeit_Versuchsaufbau.htm

(TIC): Automatic titration TIC：自动滴定

picture: www.hach-lange.de

(TIC): Volumetric Determination TIC:体积法

- Addition of a reactant (Main component is mineralic acid)
  加入反应剂（主要成分是无机酸）
- Acid removes buffer in form of CO_2
  酸能以CO_2的形式去除碱度
- Volume of removed CO_2 is recorded
  测量去除的CO_2 的量

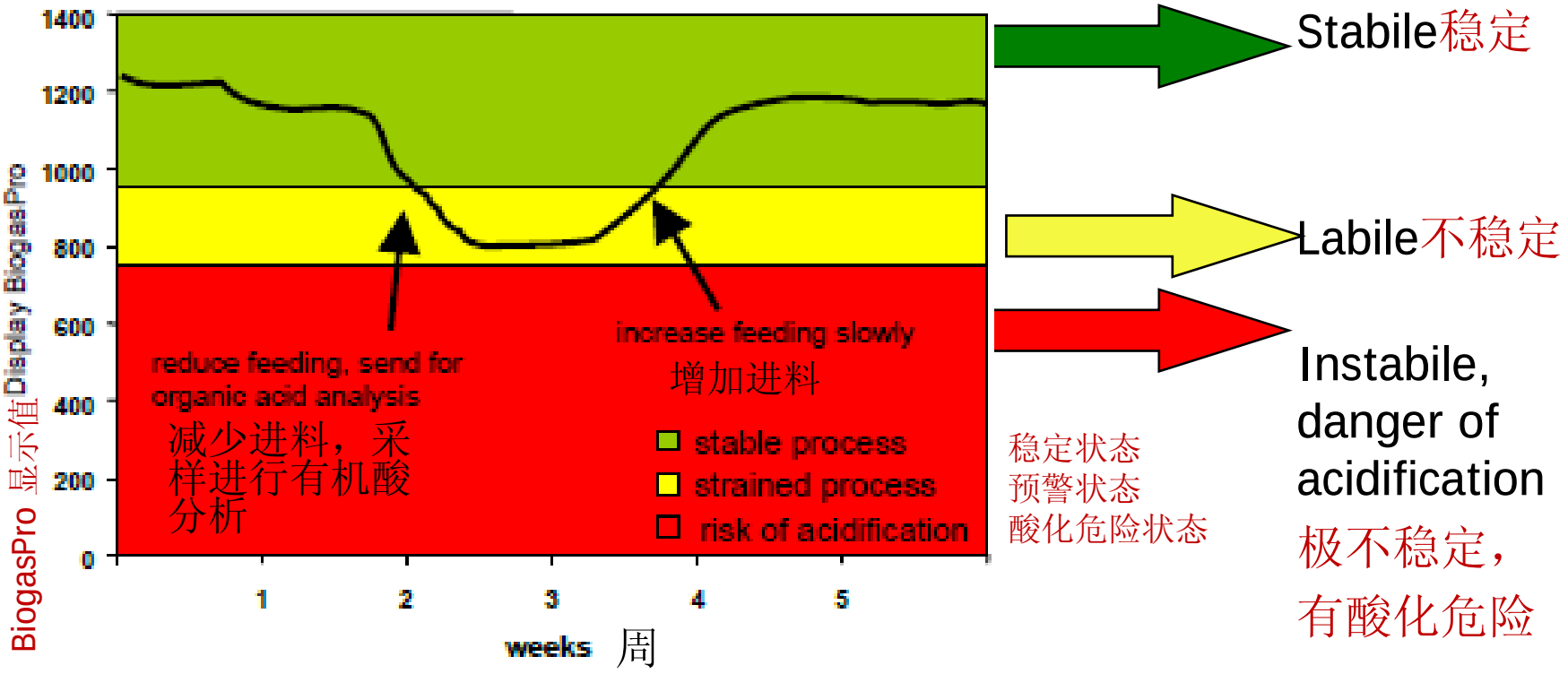
picture: www.biogaspro.de

You can use the TIC determination as a monitoring tool ...but every plant is different!

可以采用TIC值作为监测工具，但每个沼气厂都不同

Simplified example (non-transferable):

简化示例（不适用于其他案例）



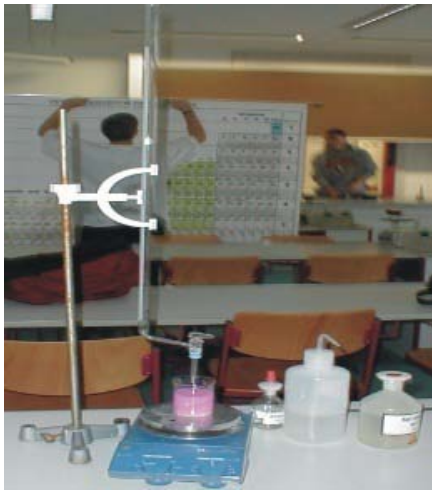
Volatile Fatty Acids (VFA)
挥发性脂肪酸（VFA）

- This is a sum parameter. It does not inform you which acids are there. It informs you, there are acids. It requires titration and can be done at a biogas plant.
  这是统计参数，并不表明有哪些酸而只是表明酸的存在。需要滴定测量，可以在沼气厂内进行。
- A single component analysis of the fatty acids has more information, because of the ratio of acetic and propionic acid and the concentration of iso-acids. But this requires more laboratory equipment.
  对脂肪酸单一成分的分析能得到更多信息，比如乙酸和丙酸比例，以及异形脂肪酸浓度。但是需要更多的实验室设备。

VFA: Manual titration 挥发性脂肪酸：手动滴定

- Titration from pH 5 to 4.4 将pH值从5滴定到4.4

$$VFA = (\frac{20\ ml}{V} * M_{FVA} * 1.66 - 0.15) * 500$$



VFA: Volatile Fatty Acids (mg/kg)

V: sample volume (mL)

M_{VFA} amount of 0.05 M sulfuric acid mL from pH 5 to pH 4,4

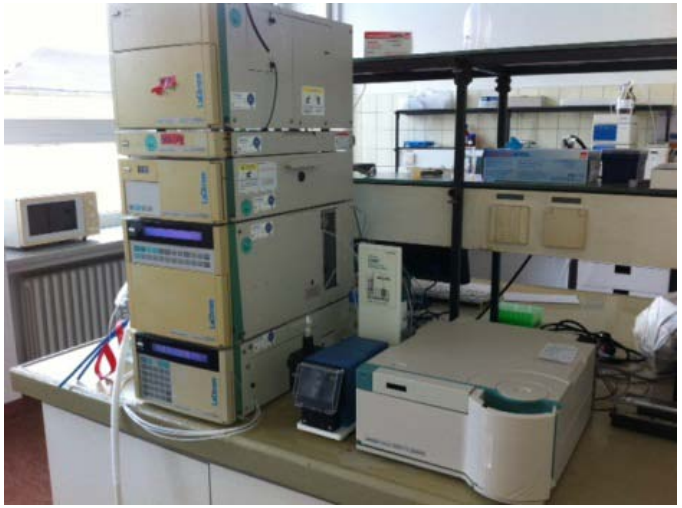
VFA: 挥发性脂肪酸(mg/kg)

V：样品体积(mL)

M_{VFA}：将pH值从5滴定到4.4消耗的0.05 M 硫酸的量

VFA: with chromatography
挥发性脂肪酸：色谱法

- Only in very well equiped or professional laboratories 只有在配置非常高或者专业实验室内才可进行



VFA/TIC ratio
VFA/TIC 比例

- The VFA/TIC ratio shows the effect of acidification clearer as compared to TIC or VFA alone. 与单独分析TIC或者VFA相比，VFA/TIC比例更清楚的显示了酸化的效果
- Example: 示例

	TIC	VFA	VFA/TIC
Sample 1 样品 1	6000	1000	0.17
Sample 2 样品 2	4000	2000	0.5

Electric conductivity 电导率

- Why? EC gives hints on the salt content.
  为什么？电导率提供含盐量信息
- If the salt content is too high, the biogas process may stop 如果含盐量过高，产沼过程可能会停止
- Analysis with a EC-meter 采用电导率仪进行分析

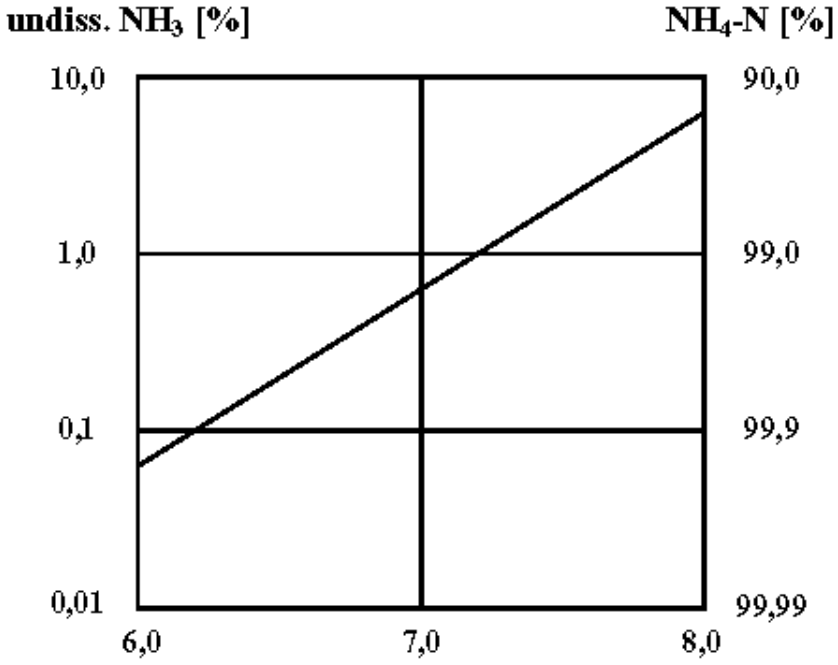
Ammonium 铵

- Why? Ammonium is in equilibrium with Ammonia. This depends on the pH.为什么？根据酸碱度，铵与氨保持平衡。
- Ammonia may inhibit the biogas process 氨可能抑制产沼过程
- Analysis via Kjeldahl, cuvettes or volumetric reaction 通过凯氏测氮法，比色法或者体积法测定

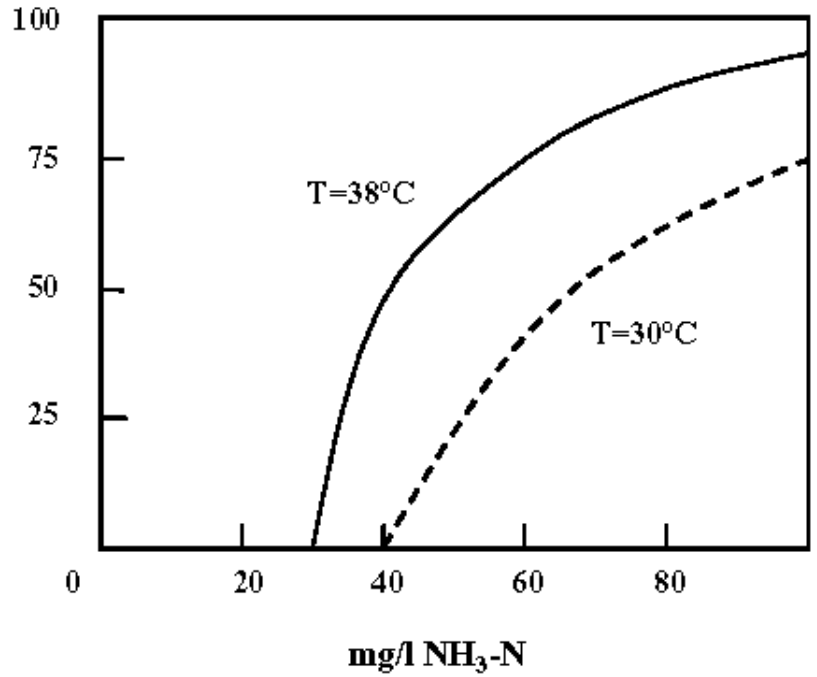
NH_4 is not a problem but NH_3

NH_4 不是问题，但NH_3 是

- Equilibrium of NH_3/NH_4
  NH_3/NH_4的平衡



Inhibition of
CH_4-production by NH_3
NH_3对CH_4产量的抑制



(Biogashandbuch Bayern, 2004)

How to perform onsite control?

怎样进行现场控制

- Record gas production and quality (daily)
  记录沼气产量和质量（每天）
- Record input (m^3 or t , daily)
  记录进料量（m^3或吨，每天）
- Analyse Total Inorganic Carbon (two times a week or more frequent when input changes) 分析总无机碳（每周两次，当进料变化时增加分析频率）
- Analyse pH (once a week) 分析pH值（每周一次）
- Analyse VFA (once a week) 分析VFA（每周一次）
- Analyse Ammonium and calculate NH_3 (every two weeks)分析铵并计算NH_3（每两周一次）
  - $[NH_3\text{-}N] = 10^{pH\text{-}pKa} * [TAN] / (1+10^{pH\text{-}pKa})$ (pKa=9.25)

Definition of a stable process in a biogas plant fed with energy crops

采用能量作物为底物的沼气厂稳定运行状态定义

please note: there are many exceptions! 注意：有许多例外情况!

Parameter 参数	Range 范围
pH	7.2 – 8,After sampling pH increases 采样后pH值增加
EC	20 – 30 mS/cm
NH_4	1.5 – 3 g/L
DM	< 10%
oDM	< 8%
VFA	< 3 g/L (higher values are possible可能有更高的值出现)
Acetic/Propionic acid	2:1
Propionic acid	< 0.8 g/L
Iso - acids	< 0.05 g/L
TIC	8 – 20 g/L
CH_4	> 50%

External help 外部帮助

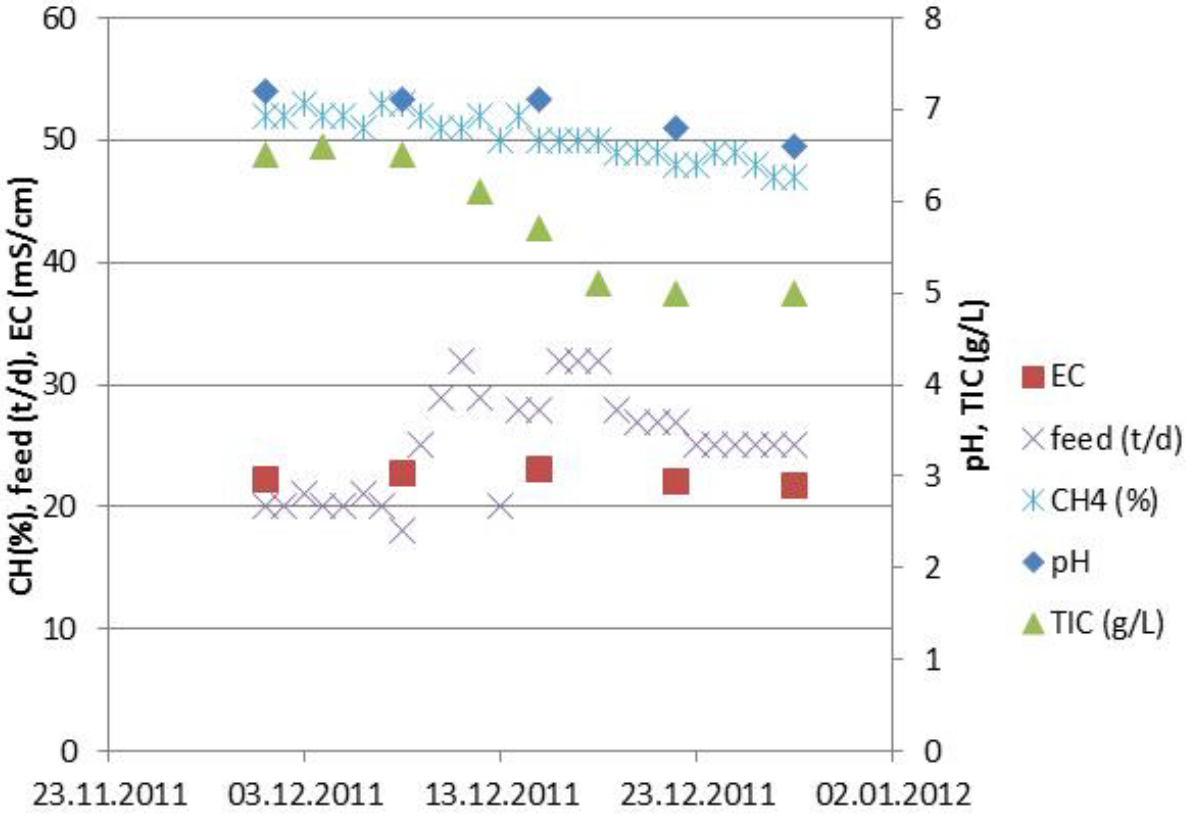
Find an external experienced laboratory that can analyse for you: 寻找一个外部的有经验的实验室可以帮助你分析

- Single component VFA (e.g. acetic and propionic acid) 单一成分VFA（如乙酸和丙酸）。
- Trace elements (e.g. Ni, Cu etc.) 微量元素（如镍、铜等）。
- Biogas yields from new substrates 新底物的产沼能力。
- Try to find the lab before you have problems! 在发现问题之前先找到这样的实验室！

The biogas process is a steady state system

产沼过程是一个稳定状态系统

- Arrange your data in time series 将数据按照时间顺序排列
- Don´t focus on absolute values but on changes 不要关注于绝对值而应注意其变化



TIC drops: actions 总无机碳下降：对策

(attention: pH may still be ok 注意：pH值可能还正常)

- When TIC drops > 15% reduce feeding
  当总无机碳降幅大于15%，减少进料量
- When TIC drops > 30% stop feeding until TIC recovers 当总无机碳降幅大于30%，停止进料直到碱度恢复
- You may use a buffer stabilizer, to increase TIC immediately. Good products are for example $NaHCO_3$, Na_2CO_3 可以采用缓冲稳定药剂来迅速增加总无机碳，比如$NaHCO_3$和Na_2CO_3

NH_3 is too high: actions
NH_3过高：对策

- If NH_3-concentration correlates with a decrease of biogas production, then reduce feeding with N-rich material or add N-low feedstock

  如果氨浓度增加对应有沼气产量降低，则减少含氮量高的物料或者增加含氮量高的物料

Biogas decreases at high TIC: action
总无机碳高时沼气产量下降：对策

- If biogas production decreases at constant loading rate and constant or slightly increasing TIC, pH and constant NH_3 then check for a single component analysis of fatty acids (no emergency) 如果在进料负荷不变，总无机碳和pH值不变或者略增，氨浓度不变的条件下沼气产量减少，可以测试单一成分脂肪酸（非紧急情况）
- If propionic acid is high and iso-acids are detected, then reduce feeding for some time and recheck of single component analysis. 如果丙酸浓度过高并检出异形脂肪酸，则减少进料量一段时间再重新进行单一成分分析

Propionic or iso acids are high: actions
丙酸或者异形酸浓度过高：对策

- If propionic acid is high and iso-acids are still high/detected, then add micronutrients or additional pig/cow manure when you run your plant on biowaste. If you run your plant on animal manure, you may add some biowaste. BE CAREFUL WITH ACIDIFICATION!
  如果丙酸浓度过高且异形酸仍可以检出或含量高，则需在以生物垃圾为主的沼气厂里添加微量营养物或者猪/牛粪便，而在以动物粪便为主的沼气厂内添加生物垃圾。**注意避免酸化**

EC increases because of new substrate and biogas production decreases
由于新底物导致电导率增加和沼气产量下降

- Action 对策:
  - Stop feeding the material with high EC 停止添加电导率高的物料
  - dilute the fermenter content with material with low EC 采用电导率低的物料稀释发酵罐内底物
  - Not so good: Dilute with water (be careful of potential temperature drop) 不建议采用水稀释（注意避免温度下降）
- EC can influence biogas production 电导率可能影响沼气产量
- EC should be checked in new substrates before using it in the fermenter 新底物加入发酵罐前需先测定其电导率
- Every fermenter reacts different on EC increase (tresholds are hard to give) 每个发酵罐对电导率增加反应不一（很难提供一个阀值）

Thank you 谢谢！